U.S. BIODIESEL OVERVIEW

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Abstract

Biodiesel is the mono alkyl esters of long chain fatty acids derived from renewable lipid sources. Through research and market development efforts led by the National Biodiesel Board, government agencies, academia, and private industry, biodiesel is moving toward commercialization as regulations take effect in specific diesel markets and as biodiesel becomes recognized as a practical, low-cost alternative fuel option. Environmentally, biodiesel is biodegradable, non-toxic, and reduces most regulated engine exhaust emissions. Operationally, it performs very similar to petroleum based diesel (petrodiesel) in terms of power, torque, and fuel economy. Biodiesel also offers improved lubricity characteristics compared to petrodiesel. Economically, production and use of biodiesel will enhance both rural and urban economic development. Also, biodiesel blends can be utilized in vehicle fleets without modifying engines or infrastructure and competes favorably with other alternative fuels on a life cycle cost basis. Market development activities have been, and will continue to be, targeted toward specific market segments where the attributes of biodiesel justify the price of a premium fuel. More biodiesel production will come on-line as markets are established.

Biodiesel is not a new fuel to North America. In fact, activities with biodiesel as the mono alkyl esters of long chain fatty acids date back to the late 70's and early 80's. As a result of the OPEC crisis, a significant amount of research was conducted by various universities and government agencies. In many cases, however, the research was completed with biodiesel purities which would not meet the existing quality specifications. Regardless, the general conclusion at that time was that biodiesel was a technically acceptable substitute, replacement, or blending stock for conventional petroleum diesel, but that its costs were prohibitive compared to petroleum based diesel fuel. The recent passage of the Clean Air Act Amendments of 1990 and the Energy Policy Act of 1992, reflecting the overall sentiment of the public to reduce air pollution and protect the environment as well as reduce our dependence on foreign oil sources has spurred the recent activities to commercialize biodiesel in North America.

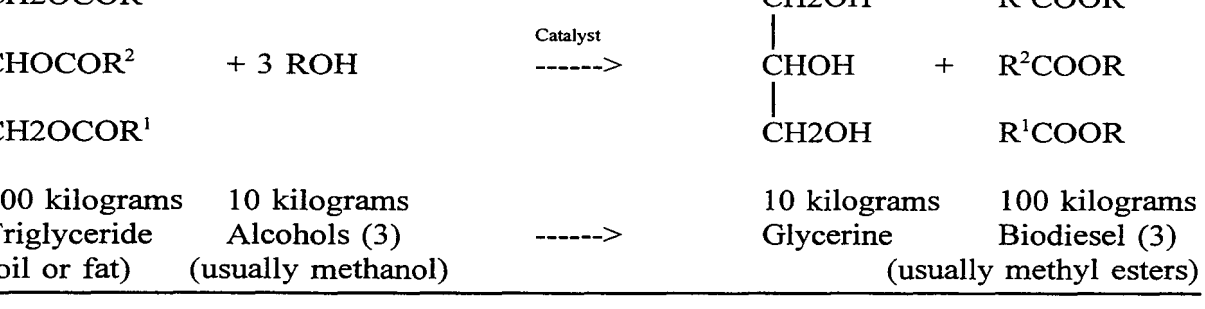
In 1992, the National SoyDiesel Development Board (NSDB) was formed by soybean farmers, funded through the United Soybean Board with national soybean checkoff funds, as the lead organization in the United States conducting research and market development activities with biodiesel. With guidance through a board of soybean farmer directors, the National SoyDiesel Development Board set off initially to prove the technical feasibility and quantify the attributes of biodiesel, as well as to gain overall familiarity of biodiesel in the United States. The NSDB changed its name to the National Biodiesel Board (NBB) in September, 1994. The rational for this change was the realization that in order for the biodiesel industry to develop, additional feedstocks besides soybean oil would play a role and it was in the industry's best interest to consolidate and coordinate research and promotional efforts.

Definition of Biodiesel

Biodiesel is defined as the mono alkyl esters of long chain fatty acids derived from renewable lipid sources. Biodiesel, as defined, is widely recognized in the alternative fuels industry as well as by the Department of Energy (DOE), the Environmental Protection Agency (EPA) and the American Society of Testing and Materials (ASTM). This definition has been the topic of some discussion, however, as other materials (tree oil derivatives, other woody products, or even biological slurries) have sometimes been referred to as "biodiesel." Although these other materials are biological in nature, and are a substitute for diesel fuel worthy of additional research and attention, they are not deemed biodiesel as accepted by the NBB, DOE, ASTM, or diesel engine manufacturers.

Biodiesel is typically produced through the reaction of a vegetable oil or animal fat with methanol in the presence of a catalyst to yield glycerine and methyl esters. The reaction is depicted in figure 1. Virtually all of the biodiesel used and produced in the U.S. to date has been made by this process, however, one additional process of importance is the direct reaction of a fatty acid with methanol, also in the presence of a catalyst, to produce a methyl ester in water.

Figure 1. Trans-esterification process.



note: R^1, R^2, and R^3 are the fatty acid chains associated with the oil or fat

Biodiesel Specification

Biodiesel is an alternative fuel which can be used in neat form, or blended with petroleum diesel for use in compression ignition (diesel) engines. Its physical and chemical properties as it relates to operation of diesel engines are similar to petroleum based diesel fuel. These properties are described in Table 1.

Table 1. Biodiesel Specifications

Property	ASTM	Value	Unit
Specific Gravity	D1298	0.86-0.90	g/g H_2O
Gross Heating Value	D2382	11.4 min	kW-hr/kg
Cloud Point	D2500	+3 max.	°C
Pour Point	D97	-3 max.	°C
Flash Point (Open Cup)	D92	149 min.	°C
Viscosity @ 40°C	D445	4.00-5.50	Cst
Sulfur	D129	0.02 max.	%
Carbon Residue	D524	0.1 max.	%
Cetane Number	D613	48 min.	
Ash	D482	0.02 max.	%
Neutralization	D4739	1 max.	mg OH/g
Methanol	*G.C.	0.2 max.	%
Free Glycerine	*G.C.	0.03 max.	%
Total Glycerine	*G.C.	0.2 max.	%
Oil Ester	*G.C.	97.5 min.	%

Of special interest is the high cetane nature of biodiesel and the absence of sulfur or aromatics. Also noteworthy is the increased lubricity of biodiesel which will be discussed later in this paper. These physical and chemical properties make biodiesel a premium grade diesel fuel substitute. In fact, at the most recent ASTM meeting, diesel OEM's stated their desire to investigate changes to existing petrodiesel specifications to increase cetane standards to 50 as well as to investigate the addition of a lubricity specification for diesel fuel.

Driving Forces for Biodiesel and Biodiesel Blends

Environmental concerns and energy security issues have prompted legislation and regulatory actions spurring demand for alternative fuels such as biodiesel. Specifically, the U.S. Congress and many states have passed several legislative actions that address both environmental and energy security concerns. The Clean Air Act Amendments of 1990 were enacted to address environmental concerns. Specific regulatory programs that have been finalized as a result of the Clean Air Act Amendments address the emissions output of urban buses, exhaust emissions of new marine engines, exhaust emissions of new off-road engines, and others. These regulations have created the demand for cleaner burning fuels. Attention to the U.S. balance of trade and economic situation has also highlighted the interest in domestically produced, renewable fuels that can build markets for agricultural products.

Three years ago, Congress enacted the Comprehensive Energy Policy Act of 1992 (EPACT). The intent of this statute is to strengthen the nation's energy security by displacing imported petroleum through the promotion of alternative fuels and alternative fueled vehicles. To help accomplish this goal, EPACT requires that by the year 2000, 75% of all affected vehicle purchases for state fleets and 90% of all affected vehicle purchases for private alternative fuel provider (mostly utilities) fleets must be alternative fueled vehicles. In addition, regulations have been finalized that also affect federal fleets and DOE has the authority to regulate other fleets in the future in order to meet the established petroleum displacement goals.

However, the greatest driving force for the use of biodiesel and biodiesel blends is the need to have a fuel that fulfills all of the environmental and energy security needs previously mentioned which does not sacrifice operating performance. One of the largest roadblocks to the use of alternative fuels is the change of performance noticed by users. Biodiesel has many positive attributes associated with its use, but by far the most noted attribute highlighted by fleet managers is the similar operating performance to conventional diesel fuel and the lack of changes required in facilities and maintenance procedures.

Research Highlights and Biodiesel Attributes

Research efforts have been completed in coordination with government agencies, universities, as well as local and state agencies. To date, significant information has been learned of biodiesel and its attributes. Some of the highlights are as follows:

- The Institute for Local Self-Reliance conducted an energy balance assessment which quantified the positive energy balance of biodiesel as between three and four to one.

- Booz-Allen & Hamilton conducted an economic analysis comparing biodiesel with other alternative fuels on a total cost basis and showed that biodiesel was the least cost alternative fuel available presently on the market.

- A significant amount of emissions testing has been conducted on 20% biodiesel blends that have shown a dramatic reduction of visible smoke and solid carbon particulates, as well as reductions in carbon monoxide and hydrocarbons. NOx emissions have been mixed, with some showing reductions, some showing increases and some remaining the same depending on the engine configuration, engine timing and the test cycle being used.

- The cetane benefits from biodiesel have been quantified showing the cetane number of neat (100%) biodiesel generally between 48 and 60. It has also been demonstrated that the use of the cetane index is not appropriate for biodiesel.

- The cold flow properties of biodiesel have been quantified. A 20% blend of biodiesel increases the temperature at which the blend will gell by 1 to 3 degrees Celsius over the values of the neat petrodiesel.

- The lubricity of neat biodiesel and biodiesel blends has been quantified. Neat biodiesel has a BOCLE number of 6100 grams, and when blended with petrodiesel at a 20% blend raised the BOCLE number from 4200 to 5200 grams.

Release Attributes

Biodiesel is biodegradable and non-toxic. These characteristics make it a valuable fuel, particularly in environmentally sensitive areas. It is believed that biodiesel blends will improve the biodegradability and toxicity of petrodiesel. The effect on biodegradability when biodiesel is blended with petrodiesel in varying percentages is currently being studied.

Operating Performance

The operating performance and characteristics of biodiesel are similar to that of conventional diesel fuel. Research results indicate that power, torque, and fuel economy with B20 are comparable to petrodiesel. In addition, tests have demonstrated that

the lubricity characteristics of biodiesel are superior to that of conventional diesel fuel. There are, however, two precautions to consider when utilizing biodiesel, or high percent biodiesel blends. Biodiesel is a natural solvent and will soften and degrade certain types of elastomers and natural rubber compounds. Precautions are needed to ensure that the existing fueling system, primarily fuel hoses and fuel pump seals, does not contain elastomer compounds incompatible with biodiesel. If they do, replacement with biodiesel compatible elastomers is recommended. Fortunately, due to the introduction of low sulfur in 1993, virtually all the diesel OEM's have gone to a fluorocarbon (Viton) type seal that is biodiesel resistant. Over the past three years, however, there have been no reported elastomer problems with 20% blends of biodiesel with petrodiesel, even with older engines.

The second area for caution is related to the cold flow properties of biodiesel. A 20% blend of biodiesel will increase the cold flow properties (cold filter plugging point, cloud point, pour point) of petrodiesel approximately 1 to 3 degrees Celsius. Thus far, no precautions have been needed for fueling with 20% blends, however, operation of neat (100%) biodiesel in cold weather will experience gelling faster than petrodiesel. The solutions for this potential issue are much the same as that with low-sulfur diesel (i.e., blending with No. 1 diesel, utilization of fuel heaters and storage of the vehicle in or near a building). Biodiesel appears to be unaffected by conventional pour point depressants.

Macroeconomics

An important factor that is not usually considered when calculating the costs and benefits of industrial feedstock materials is the macroeconomics effects associated with domestically produced, renewable energy sources. Benefits of a biodiesel industry in the U.S. would include value added to the feedstock (oilseeds, fats, or yellow grease), an increased number of jobs, an increased tax base from plant operations and income taxes, and investments in plant and equipment.

Van Dyne (1995) estimates that 98 jobs (temporary and/or permanent) would be created for every million gallons of biodiesel used in the domestic U.S. In addition net increased income would increase $3.2 million and total net industry output would increase by $9.6 million for every million gallons of biodiesel used.

A sustained biodiesel market would also provide direct benefits to the agricultural sector. According to economic modeling conducted by the Food and Agriculture Policy Research Institute (FAPRI), 70 million gallons of annual demand could add up to $0.18 per bushel increase to the price of soybeans alone. Achievement of 34 million gallons of annual demand could increase revenues to soybean farmers between $125 to $225 million (based on 1994 soybean production of 2.5 billion bushels and increased prices of $0.05 to $0.09 per bushel).

Market Focus

The NBB has identified several market opportunities where the attributes of biodiesel appear to justify the additional cost per gallon. During the next three years, biodiesel industry efforts will most likely be concentrated in four markets: urban transit, government/regulated fleets, marine, and underground mining. The NBB will also continue to investigate other unanticipated marketing niches for biodiesel/biodiesel blends. As new high potential niches are identified, NBB will work to provide an indepth assessment of each market.

Urban Mass Transits

This market was established as a priority because it was the first major diesel market segment regulated as a result of the Clean Air Act Amendment of 1990. Approximately 80 percent of the nation's 58,000 mass transit buses are subject to this rule which aims to reduce particulate exhaust beginning in 1995. Information collected during assessment of the urban bus market indicated that EPA regulations would create a marketing opportunity for biodiesel blends. Economic work completed by Booz-Allen & Hamilton, under contract with NBB, supported the conclusion that biodiesel blends (B20) were competitive with other alternative fuels that transits may consider. Research work was conducted, and is being finalized, to verify that emissions reductions could be achieved and engine performance was similar to diesel.

Because biodiesel is the only alternative fuel that can be tested prior to conversion, the NBB completed a series of short-term demonstrations with transit operators throughout the nation. The NBB also completed surveys with transit property officials about their intentions to use biodiesel. Approximately 20 percent said they consider biodiesel the top alternative fuel choice and approximately 50 percent were impressed with the prospects for biodiesel. The American Public Transit Association (APTA) estimated the urban bus market annually consumes approximately 575 million gallons of petrodiesel.

Regulated Fleets

The U.S. Department of Energy was authorized to implement the provisions of EPACT and on February 28, 1995 proposed the Alternative Fuel Transportation Program regulations. As proposed, state fleets and private alternative fuel providers will be required to begin purchasing specific percentages of alternative fuel vehicles in model year 1996 (beginning September, 1995). In addition to this federal regulation, many states have implemented or will implement similar legislation.

Although biodiesel was not mentioned by name as an alternative fuel in the proposed regulations, DOE has confirmed that biodiesel is an alternative fuel. The biodiesel industry is working with the American Soybean Association (ASA), other national associations, state soybean associations, oilseed crushers, cooperatives, electric utilities, and others to ensure that biodiesel blends are recognized by DOE as an alternative fuel under these regulations.

Successful revisions in DOE's regulation could increase the use of biodiesel in affected fleets. Previous economic work through NBB has demonstrated that biodiesel blends, specifically B20, are competitive with other alternative fuels on a full fuel life cycle basis.

Marine Market

The recreational segment of the marine market appears to offer the most potential for "neat" biodiesel sales. Two other segments which may be targeted include the U.S. Coast Guard and research vessels operating in domestic waters. An estimated 16,212,000 recreational vessels operate in and around the U.S., with a significant portion operating in California, Florida, Michigan, and Minnesota. Approximately one million diesel powered boats consume on average 95 million gallons of diesel fuel annually. The other two segments highlighted have less than 3,000 vessels operating in U.S. waters, but do consume large amounts of diesel fuel.

Various reasons exist for boaters to use an alternative fuel such as biodiesel. Regulatory drivers for the marine market include the Clean Air Act Amendments and the Clean Water Act. Although the exhaust emission requirements outlined by the EPA for marine engines will most likely not result in large increased use of alternative fuels, risk associated with fuel spills and the resulting liability may prove to be a driving force for the use of biodiesel. Current research indicates that biodiesel is non-toxic and biodegradable. In addition, many boaters have indicated that lack of smoke and the dramatic change in exhaust odor are reasons why boaters will consider switching to biodiesel or biodiesel blends.

Underground Mining

There are currently 252 metal and non-metal underground mines operating in the U.S., in addition to 183 underground coal mines which use diesel engines. On an annual basis, these mines consume over 200 million gallons of diesel fuel. There is increasing interest in using diesel equipment in mines because of cost considerations. Diesel-powered equipment is potentially less expensive to operate compared to other transportation systems and can increase productivity. Safety is also an issue. Mine operators are interested in replacing electric trolleys used to transport miners with diesel-powered equipment because workers have expressed concern of electrocution by power lines and mine explosions caused by electrical sparks. For these reasons, the number of diesel units being used in mines is gradually increasing.

Because biodiesel has a higher flash point than diesel and since it lowers emissions of particulates, CO, oxides of sulfur, and potentially other air toxics, it could reduce the cost of providing adequate ventilation in mines and improve the performance of dry emissions systems by increasing the interval between cleaning particulate traps.

Future Biodiesel Research

Future research activities with biodiesel will include further quantification of the benefits of biodiesel, including quantification of other air toxics (i.e., PAH's) as well as a full complete life cycle analysis, confirmation and negotiation of an SAE or ASTM specification with fuel suppliers, and users, distributors and OEM's; further quantification of the emissions and durability of benefits of biodiesel both in bench scale and real life usage in additional markets; and further research on the cost effectiveness of biodiesel (lower blend levels, less expensive feedstocks, niche markets of high value).

Selected References

Arthur D. Little. 1995. Biodiesel Marine Market Pre-evaluation -- Draft Final Report. Prepared for the National Biodiesel Board. March 31, 1995.

FAPRI. 1994. Increased Soybean Oil Demand - Its Effects on the Soybean and Corn Industries. University of Missouri-Columbia. April, 1994.

Fleishman-Hillard Research. 1994. Biodiesel Awareness and Attitudes by Transit System Managers. Prepared for the National Biodiesel Board. September, 1994.

Howell, Steve. 1994. Lubricity of Biodiesel Fuel- Update #3. July 21, 1994.

Institute for Local Self-Reliance. 1994. How Much Energy Does It Take to Make a Gallon of Soydiesel? Prepared for the National SoyDiesel Development Board. January, 1994.

Midwest Biofuels. 1994. Biodiesel Cetane Number Engine Testing Comparison to Calculated Cetane Index Number. Prepared for the National SoyDiesel Development Board.

Van Dyne, Donald L. 1995. Estimated Impacts of Biodiesel Production for Use in the Kansas City Metropolitan Area. Presented at the Food for the 21st Seminar Series; Food, Feeds & Products Cluster on April 25, 1995.

THE BIODIESEL RESEARCH PROGRAMME OF NEW ZEALAND

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Abstract

Research into using triglyceride fuels in compression ignition engines began in New Zealand in the 1970's. The objective was to identify, produce and evaluate a fuel from vegetable oils or animal fats which could be used to power the existing engine fleet without modification. From a variety of fuels screened, methyl rapeseed oil esters and methyl tallow esters appeared most promising due to their fuel characteristics and their potential availability of supply, tallow being a low value by-product from the export meat industry equivalent to 10% of the national diesel fuel demand.

Short term bench tests and long term road tests of engine performance were conducted for a range of vehicles using neat esters and also blended with diesel. The high cetane value of tallow esters (> 70) was noteworthy. No technical problems were observed even after extended oil change tests or on turbo-charged engines. Engine wear, after over 200 hours of normal road use, was less than in companion vehicles running on diesel alone.

Economic analysis of a range of process plant sizes, from 4000 l/year on-farm, to 25,000 m^3/year for a regional plant, showed economies of scale. By-product credits for glycerol and rapeseed meal were included in both commercial and national economic analyses. For tallow esters a single plant of 25,000 m^3/year was preferred to match the national supply of tallow. This would enable a blend of 10% esters/90% diesel to be produced to the current national fuel standard specifications.

The programme was concluded in 1989 after having shown triglyceride fuels were technically feasible but not economically competitive. High production costs for rapeseed resulted in esters being double the wholesale diesel price. For tallow esters to be competitive crude oil would need to rise to US$27/barrel.

The New Zealand government is currently evaluating means of reducing the national CO_2 levels including that produced by the transport sector. The biodiesel programme may therefore be re-visited.

Introduction

New Zealand's primary industries, which account for over 60% of annual export earnings, depend on diesel fuel for operating tractors, trucks and heavy machinery. Whereas a major proportion of gasoline has been substituted with synthetic petrol, compressed natural gas (cng) and liquid petroleum gas (lpg), all the diesel is still refined from imported crude oil. A research programme was instigated in the mid 1970's to evaluate diesel fuel alternatives. At the time this was deemed to be strategic research in order to maintain the balance of products from the oil refinery and to combat the anticipated continued rise in the price of crude oil.

Much of the work reported here was contracted by the Liquid Fuels Trust Board, which was funded by a $US0.002 levy on every litre of gasoline or diesel sold. It was disbanded in 1987 following the continued low price of crude oil.

A series of oil crop production trials were undertaken to assess the yields and costs for various regions of New Zealand (see for example Sims 1979(a) and 1979(b)) since vegetable oil crops were not commonly grown. This work was followed by an overview study to ascertain the availability, yields and costs of supply of natural oils and fats (Sims et al, 1982). It was apparent that oilseed rape was the preferred vegetable oil crop due to its yield potential throughout the length of New Zealand; the ability to use conventional cultivation and harvesting equipment; its high protein meal by-products; and the suitability of the chemical and physical properties of the oil when used as a fuel. In addition, inedible tallow; a by-product from the meat industry, was selected for further evaluation, the export volumes being in excess of 10% of the national diesel demand on an energy basis. Research on the use of cng, lpg and alcohol fuels as diesel substitutes was also conducted but the problems of low energy density, high production costs, and expensive engine modifications were limitations to their uptake.

The overall aim of the New Zealand research programme on triglyceride fuels was to develop a fuel which would be technically feasible to produce, could be distributed nationwide, would have a high strategic value, would produce no environmental pollution, would be competitively priced, and would be suitable for use in the existing engine fleet without modifications being required. This paper outlines the programme and highlights the major findings which could be of value to current programmes being undertaken elsewhere. In addition the environmental benefits resulting from any biofuel when used as a substitute for fossil fuels is considered, the feedstock needing to be produced on a sustainable basis.

Raw vegetable oils

The use of untreated home-grown rapeseed oil as a tractor fuel by a number of New Zealand farmers in 1982 created national interest but, as predicted, eventually led to engine operating problems. Some power loss became evident, fuel pumps seized, carbon build-up appeared on injectors resulting in poor atomisation, and dilution of the lubricating oils occurred leading to polymerisation and then, suddenly under specific conditions, the oil turned into a gel leading to disastrous results. Problems also appeared during storage of the oil after only a few weeks following extraction. These factors served to confirm that although it was relatively easy to grow the rapeseed crop, extract the oil and put it in the fuel tanks, continuation of a proper scientific evaluation was justified. Blending the oil with diesel could serve to reduce the problems listed,

particularly those resulting from high viscosity, but it would not eliminate them. It was therefore strongly recommended to farmers not to use vegetable oil based fuels in compression ignition engines, particularly those with low compression ratios, rotary fuel pumps, worn injectors, direct injection, and those likely to operate under light duty cycles or cold conditions. Furthermore for any engine using such fuels daily checking of lubricating oil for thickening and regular cleaning of injector nozzles was strongly advised. (Liquid Fuels Trust Board, 1982).

The solution to many of the problems experienced by these early rapeseed oil users appeared to be solvable by converting the triglyceride oils to esters by trans-esterification, a well understood process with glycerol as the resultant by-product.

Triglyceride oil esters

Resource assessment

The resource assessment was an important early component of the programme. The availability of suitable land for growing oilseed rape crops was evaluated and the returns to the farmer, based on assumed seed yields of up to 3 t/ha (but typically 1.6-1.8 t/ha) and 45% oil content, were compared with other farm enterprises. The volumes and quality of tallow produced at many meat works and transported to several ports for export were also evaluated.

The oil/fat qualities in terms of engine fuel specifications were measured. These included properties such as free fatty acid content, iodine value, viscosity, energy value, degree of chemical saturation as well as variations between batches and from different extraction plants. For tallow esters, details were reported elsewhere (Sims et al, 1987). The existing infrastructure for processing and transporting the oils/fats was also examined.

Existing markets

The values of the edible and inedible oil/fat supplies for export or for the domestic market were determined from market research. Future trends were considered but, as with most commodities, it proved difficult to assess them with any reliable degree of accuracy. For example in the decade since this market assessment was undertaken, the sheep meat and wool price has fluctuated widely such that the New Zealand flock number reduced to close to 50 million and is only slowly increasing again back to its peak of 65 million. The markets for the by-products, glycerol and protein meal were also examined as it was realised their future value could offset production and processing costs in part and this could affect the economic viability of the enterprise.

Process and scale

Selection of the most appropriate process and design of plant was undertaken by chemical engineers. A base catalysis process using methanol and sodium methoxide as catalyst was selected for New Zealand, the methanol currently being produced from the natural gas resource for export. The choice was partly dependent on the availability of chemicals and the scale of operation. Assessments were undertaken for rapeseed oil when extracted by a single grower on-farm, by small co-operatives of a few farmers, by larger co-operatives, and at a regional plant (with annual production of 4,000, 36,000, 190,000 and 2,750,000 litres respectively). Tallow ester plants of 4,200 m^3/year and

25,000 m^3/year capacities were also evaluated. The smaller plants were more expensive to operate (Sims et al, 1982) and the by-product values were more difficult to capture. Commercial costs of oil production, extraction and inter-esterification were all significantly less at the larger scale.

Product specifications

The goal was to produce a fuel blend which would be totally within current diesel fuel specifications in all respects. Hence no engine modifications would be necessary and no changes in storage or handling regulations would be required. The intention was to later relax these standards to make production more economic under less stringent processing conditions but only after considerable experience had been gained. This cautious approach was to provide early confidence in the fuel by consumers having a choice between diesel and biodiesel.

To meet these stringent conditions a test blend of tallow esters was restricted to 10% methyl tallow ester/90% diesel, although engine performance testing was also carried out on 20% ester blends and 100% esters. If a 10% blend was introduced nationally to replace diesel, the total volume of tallow available would be utilised. At higher blends cold temperature limitations of separation of the esters (at below 3° C) could become evident. Blends with greater volumes of rapeseed esters could remain within current fuel specifications since rapeseed oil esters have higher degrees of saturation and higher melting points. There is also the potential to produce sufficient volumes assuming land is available.

A summary of the stringent fuel specifications set for the tallow esters is given in table 1.

Table 1

Summary of Tallow Ester Fuel Specifications used during Production of the Test Fuels

Fuel component	Level	Reason
Free fatty acids	< 0.1%	Attacks metal
Water	< 0.5%	Storage deterioration
Methanol residue	< 0.05%	Fire/explosion
Catalyst residues	< 0.5 ppm	Wear in engine
Monoglycerides	< 0.05%	Filter blockage
Iodine value	42-52	Solubility/oil degradation/melting point
Insolubles	4 micron filter	Fuel system blockage

Fuel blend property evaluation

A wide range of standard fuel tests (ASTM) were undertaken for a range of esters and blends. The major concern was the phase separation under cold conditions when higher blend levels of methyl tallow esters were produced. This was thought to result from

supercooling of the esters as ambient temperatures dropped. At warmer temperatures homogeneous mixes occurred at all blend levels.

A high cetane value of over 70 was measured by Perkins Engines (UK) for methyl tallow esters when evaluating these fuels under contract to the Liquid Fuels Trust Board. It is not clear what produced this extremely good combustion property and further evaluation is required. As a result of this characteristic, tallow esters could be used as an additive to upgrade poorer quality diesel produced cheaply from a wider-cut middle distillate. This would help improve the product balance at the oil refinery.

Storage evaluation

The stability of vegetable oils and tallow after prolonged storage is questionable mainly due to biological degradation by bacteria, yeasts and other organisms particularly under warm conditions. A field trial of tallow esters stored in 200 litre drums for fourteen months showed no thermal, oxidative or biological degradation. A more thorough evaluation of storage potential conducted in Germany (Widman, 1989) confirmed that oils/fats in the form of esters can be stored successfully for at least two years.

Engine performance tests

A series of screening trials were initially conducted on a wide range of oils, esters and blends (Sims, 1985). No major limitations became apparent in these short term tests other than when using raw tallow which as might be expected, solidified in the fuel system on cooling of the engine after shut down!

A series of engine bench tests using tallow ester fuels and blends were undertaken by Perkins Engines (UK). Compared with diesel it was noted that combustion improved, emissions were reduced, and that even under worst case operating conditions, lubricating oil dilution was not a limiting factor.

Demonstration vehicle fleet trials

A fleet of 42 vehicles was selected to represent open road use (long and short haul distances), urban transport, agricultural vehicles and marine engines (table 2).

Table 2

Trial Vehicle Fleet Operating in Farm, Road, and Marine Environments on a Fuel Blend of 10% Methyl Tallow Esters and 90% Diesel

Operator	Location	Type of operation	Vehicles in trial	Companion vehicles (diesel)
Glentanner Station	Tekapo, South Island	Hill farming	1	-
Telford Training Institute	Balclutha, South Island	General farming	1	-
Massey University	Palmerston North	General farming Utility delivery Truck, road	2 1 1	1 contractor 1 contractor -
Winstones Concrete Ltd	Seaview	Road delivery	1	1 - same company
BP Ltd	Seaview	Road tankers	11	-
Eastbourne Borough Council	Wellington	Bus	20	3 Newlands Bus Co
Titan Cranes	Seaview	Mobile crane hire	2	1 - same company
Blue Fin Launch Services	Paremata	Charter launch	2	

Over 300,000 litres of 10% ester blended fuel were consumed during the trials. No technical problems became apparent even under extreme operating conditions. Operators reported visible reductions in smoke emissions and reduced engine noise. This served to confirm the laboratory bench tests and showed that operators would probably notice little difference between using diesel or ester/diesel blends should the latter be introduced as a commercial fuel at the 10% blend level.

More detailed evaluations were conducted on four vehicles at Massey University.

1 A John Deere 3140 tractor was run on a tallow ester/diesel blend for over 500 hours and closely monitored before a turbo-charger was retrofitted (Sims et al, 1990a). Temperatures were recorded throughout the engine's lubricating oil circuit and lubricating oil samples were taken at frequent intervals. The tests included immediate engine shutdown from full power to gauge maximum oil

gallery soak temperatures in the turbo-charger housing. The objective was to investigate the baking propensity of the lubricating oil if diluted with unburnt ester contaminants. No problems became evident.

2 A 15 tonne Ford N 1317 truck with Hino EH700 engine was run under normal road conditions for double the recommended period between lubricating oil changes on the 10% ester/diesel blend. After 12,000 kms no significant lubricating oil dilution was observed. The viscosity and total base numbers reduced with travel distance and the total acid number rose slightly before stabilising after 2000 km, but no significant oil deterioration occurred (Sims et al, 1990b).

3 A Ford 6610 tractor and a Ford Courier utility with a 2 litre Mazda engine, both fuelled by 10% esters/diesel, were compared with diesel-fuelled companion vehicles of similar work loads and age after over 300 hours of running. Monitoring of the lubricating oils was undertaken. A slight ester dilution was noted in the tractor but oil dispercancy tests remained satisfactory for both vehicles. The diesel-powered utility gave a rise in lubricating oil viscosity and acid number coupled with a drop in base number towards the end of one oil change period showing oil failure was imminent. This did not occur with the ester/diesel vehicle. On completion of the trials, engine strip downs showed the wear and cleanliness of the test fuel engines to be superior to those running on diesel fuel alone. Full details were reported in Sins et al, (1990b)

Economic Analysis

National economic analyses were undertaken for rapeseed ester production which included feedstock costs, transport costs, and opportunity costs together with by-product credits in addition to the normal commercial costs. The unit cost of rapeseed oil ester fuel production for a large central processing plant was less than half the cost of a small scale on-farm process but was still well over double the wholesale diesel fuel price. This was confirmed under USA and European conditions (Reed, 1993).

Actual costs depended on oil yield per hectare, opportunity cost of land for other enterprises, the assumed relative export value of vegetable oils, and world prices for protein meal, glycerol and methanol. In countries where there is surplus production of vegetable oils; average yields are expected to increase; there is strong competition from elsewhere for oil export products; and there is little competition for land to grow food crops; then the socio-economic factors of producing biodiesel should also be considered. In addition the environmental benefits from avoidance of burning fossil fuels should be included in any comparative calculations. The use of biofuels will help to mitigate carbon dioxide outputs so that if economic instruments such as carbon taxes are imposed to reduce fossil fuel use, biodiesel may well become a more economic proposition than at present.

A similar national economic analysis was also undertaken for tallow esters. As in the rapeseed oil analysis, transfer payments such as interest were ignored since they do not represent real resource costs. Being a by-product of the meat industry rather than having to be specifically produced for fuel as is rapeseed oil, more favourable economics resulted. A concept study determined that a single processing plant adjacent to the existing oil refinery was the best option, the tallow being back-loaded from meat processing plants and ports after delivery of fuel to the region by the existing fleet of

coastal and road tankers. Such a concept study involving feedstock collection, oil processing, product distribution and quality control should be an essential part of any national study of alternative fuels.

A further disadvantage of small scale installations would be the variation in fuel quality which is bound to result from varying standards of feedstock and processing which could lead to a miscellany of engine operating problems.

The base cost assumptions of US$250/t to purchase tallow, US$0.10/t/km to transport it, US$85/t to process and blend the esters, and US$1200/t for the glycerol by-product credits, the crude oil price would have to reach and maintain US$27/bbl to provide a 10% real rate of return after tax. The by-product value is critical such that a lower glycerol price resulting from saturation of the market would increase the ester costs.

Market constraints

Several constraints were identified which will require careful assessment before implementation of biodiesel fuels could successfully occur.

(a) Engine manufacturers will need to meet their usual warranties. In Austria where esters have recently been manufactured and made commercially available several tractor manufacturers have agreed to maintain warranties within certain restrictions (Worgetter, 1993).

(b) Distributors and consumers will need to be convinced that the ester fuel supplies will remain secure and readily available. This is another justification to use modest blends with diesel initially then once proven, increase the ester proportion if appropriate.

(c) If the ester is to be blended with diesel, the refinery company must be agreeable or regulations put in place to enforce it. The petroleum suppliers will also need to be in agreement.

An extensive proving programme may also be needed over and above the demonstration fleet trials. This would be unlikely to be supported until the use of biodiesel is imminent and is planned to continue for a long term.

Financial incentives by way of carbon emission levies, taxation benefits or capital grants may be required if a government wishes to seriously encourage the use of biofuels. As the environmental concerns from using fossil fuels increase; their price rises; long term security of supply becomes questionable; and land use diversification from food and fibre crops to energy crops become feasible, then such incentives could well be warranted.

Conclusions

Technically the use of triglyceride fuels in the form of neat esters or blended with diesel for use in compression ignition engines is well understood.

Economically it is not a commercially viable proposition compared with current diesel prices in most OECD countries. To become commercial some form of government

incentive is needed, or the environmental costs of using fossil fuels must be included, or the crude oil price must rise substantially, or the costs of producing and processing the biodiesel need to decline by increasing crop yields or developing cheaper process systems.

Research on biodiesel should be continued and international collaboration encouraged to develop it as a competitive fuel.

Acknowledgements

The New Zealand Liquid Fuels Trust Board funded the research programme. Massey University Council are thanked for approving my attendance at this conference.

References

Liquid Fuels Trust Board (1982). The use of rapeseed oil as a diesel fuel. Report LF 5007 - advisory leaflet for users. Ministry of Commerce, Wellington, New Zealand.

Reed, T.B. (1993). An overview of the current status of biodiesel. Proc. 1st Biomass Conference of the Americas. Vol. II, 797-814. Burlington.

Sims, R.E.H. (1979a). Comparative methods of harvesting oilseed rape. N.Z. Journal of Experimental Agriculture 7, 79-83.

Sims, R.E.H. (1979b). Drying cycles and optimum harvest stage of oil seed rape. N.Z. Journal of Experimental Agriculture 7, 85-9.

Sims, R.E.H., Evers, M., Garland, B.R., Gendall, P.J., Johnson, C.B. Meister, A.D., Newton S.D., Williamson, K.I. and Withers, N.J. (1982). Yields, costs and availabililty of natural oils/fats as diesel fuel substitutes. Liquid Fuels Trust Board Project Report. LF 2021, 273 pp. (Available from Publications, Ministry of Commerce, Private Bag, Wellington, New Zealand).

Sims, R.E.H. (1985). Tallow esters as an alternative diesel fuel. Transactions, American Society of Agricultural Engineers. 28(3), 716-721.

Sims, R.E.H., Ritchie, W.R. and Thompson, M.C. (1987). Power from oil plants, systems and costs. Proc. of International Solar Energy Society conference "Advances in Solar-Energy Technology". Bloss, W.H. and Pfisterer, F. (eds). pp 2188-2195 Hamburg. (Pergamon).

Sims, R.E.H. (1990). Tallow esters and vegetable oils as alternative diesel fuels - Solar and Wind Technology (Pergamon) 7(1), 31-36.

Sims, R.E.H., Ritchie, W.R., and Chadwick, A.J. (1990a). Turbocharging of an agricultural tractor engine. Journal of Agricultural Engineering Research. 47, 177-186.

Sims, R.E.H., Ritchie, W.R. and Thompson, M.C. (1990b). Tallow esters and vegetable oil esters. Proc. 1st World Renewable Energy Congress. Vol 3 pp 2128-2141. Reading (Pergamon).

Widman, B.A. (1989). Fundamental research to develop a standard for fuel quality of rapeseed oils and esters. Proc. 5th European Biomass Conference pp 9-13. Lisbon (Elsevier).

Worgetter, M. (1993). Biodiesel in Austria. Proc. of seminar on "Vegetable Oils as Transport Fuels". International Energy Agency Bioenergy Agreement Tasks VIII and X. pp 45-50. Pisa.

A SUMMARY OF THE UNIVERSITY OF IDAHO CONFERENCE COMMERCIALIZATION OF BIODIESEL -- ESTABLISHMENT OF ENGINE WARRANTIES

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Abstract

The University of Idaho, Department of Agricultural Engineering with assistance from The National Center for Advanced Transportation, The PNW and Alaska Regional Bioenergy Program, The Idaho Department of Water Resources Energy Division and the ASAE T-11, Energy Committee sponsored an invited, focused workshop on Commercialization of Biodiesel, Establishment of Engine Warranties. Participants were invited from all segments of the Biodiesel industry but engine manufacturer's and users were particularly targeted. Representatives from Detroit Diesel, Navistar, Cummins, Mercedes Benz, the National Biodiesel Board, the Austrian Biodiesel Industry, Link Transportation, Spokane Transit plus other interested research workers and individuals participated in the conference. The conference had two goals 1) development of a brief statement on the current status of the effect of Biodiesel on Engine Warranties 2) development of a strategic plan for making Biodiesel a recognized fuel acceptable by engine manufacturers for use in their engines. This paper will summarize the presentations of the conference, will discuss the draft statement on where we are today on warranty for use of Biodiesel and the issues related to warranty which the engine manufacturer's and users developed as part of the conference.

A complete proceedings of the warranty conference is available from the National Center for Advanced Transportation Technology at the University of Idaho.

Introduction

Biodiesel -- methyl or ethyl esters of animal or vegetable oils -- has received worldwide attention as a possible substitute for petroleum diesel fuels. As Biodiesel moves from research and demonstration to serious utilization there are many issues to be resolved. One of these issues is acceptance by manufacturers of diesel engines and in particular how use of these fuels would affect the manufacturer's engine warranty.

The workshop was organized to bring together Biodiesel users, research workers, representatives of the National Biodiesel Board and other interested parties to explore the current status of Biodiesel, its effect on engine warranties and what issues remain to be resolved before Biodiesel can be thought of as a legitimate fuel for diesel engines. The workshop format included brief "state-of-the-art" presentations by researchers, NBB, DOE and Biodiesel users, followed by group sessions which developed a statement of where we are now with engine warranties and a statement of issues that need to be resolved to bring Biodiesel under full warranty coverage equivalent to diesel.

The University of Idaho, Department of Agricultural Engineering; the National Center for Advanced Transportation Technology (NCATT), the Pacific Northwest and Alaska Regional Bioenergy Program, The Idaho Department of Water Resources, Energy Division and the ASAE T-11 Energy Committee were the principal underwriters for this workshop. The planning committee included Craig Chase (a consultant to DOE), Jim Butler (consultant to NBB), Steve Howell (Director of Research at NBB), and Dave Woodall (Associate Dean, College of Engineering, University of Idaho).

NCATT

The National Center for Advanced Transportation Technology (NCATT) was founded in 1991 through an act of Congress. It received funding to construct a new engineering and physics building and a mandate to develop a transportation center with a focus on the needs and agenda of industry. During the past two years, it has organized its efforts around five technology working groups, including hybrid electric vehicles, advanced materials and manufacturing, power electronics, traffic control systems, and alternative fuels. While the center is still relatively new, its work during the past two years has generated about $1.5 million in external research funding involving nearly 100 University of Idaho faculty and students. The work at the center is guided by three primary customers: private industry and governmental agencies with a direct stake in our nation's transportation system, engineering students, and faculty at the University of Idaho.

Program

Welcome and Introductions

Charles L. Peterson, Agricultural Engineering Department, University of Idaho
Dave Woodall, College of Engineering, University of Idaho
Mike Kyte, National Center for Advanced Transportation Technology, University of Idaho

Biodiesel Research
Jim Butler, P.E. -- Moderator
Earle E. Gavett, National Biodiesel Board
Mehboob Sumar, Ortech

Bill Marshall, National Institute for Petroleum and Energy Research
Mark Russell, University of Missouri
Charles L. Peterson, University of Idaho
Werner Korbitz, Korbitz Consulting, Austria

Transit System and Other Use of Biodiesel
Craig Chase -- Moderator
Dick Yost, Spokane Transit
Todd Daniel, Link Transit
Howard Haines, Montana Department of Natural Resources

Luncheon Speakers
Jeffrey James, U.S. Department of Energy
Jerry Allsup, U.S. Department of Energy

Engine Warranty Policy
Steve Howell -- Moderator
Rodica Baranescu, Navistar, Engine Manufacturers Association
Karl Koontz, Cummins Engine Co., Inc.
Ansgar Shafer, Mercedes Benz
Lester Walker, Detroit Diesel
Madan R. Goyal, Deere Power Systems Group (written only)

Industry and Biodiesel
George Durany, J.R. Simplot Co.

Group Sessions: Questions and Answers.

Introductory Remarks

This was a focused workshop on commercialization of Biodiesel and the establishment of engine warranties. There are many Biodiesel issues that are important, but this conference was to focus on engine warranties.

During a trip some time ago in Europe several pieces of advertising literature were found which recognized Biodiesel as an engine fuel. A Mercedes Benz "Unimog" advertisement says, "Attention: New Information for Agriculture! I have RME in my tank. It can be used in diesel engines. It can be mixed with diesel. There's no effect on the engine. There's no effect on the engine warranty." In Europe there are other manufacturers who do warrant engines, and state so in their advertising literature. Deutz Fahr, for example, in an advertisement says "Environmentally Friendly, Energy Sparing with Deutz Fahr Tractors," referring to use of rape methyl ester. An advertisement from an Agricultural show in Frankfurt for Deutz Fahr tractors says "RME Usable" directly under the Deutz Fahr tractor model listing on the display. There are many other manufacturers that warrant their engines operating on Biodiesel in Austria.

This conference focused on the issue of establishment of engine warranties in the United States. The issues are where we are currently and what we have to do. There were two goals for the final product from this meeting. First, a brief statement on the status of Biodiesel today with respect to engine warranties. In many of the publications from the University of Idaho notices are included stating that this is a research report and that we are not advocating use of Biodiesel in personal vehicles. We would like to rewrite that statement. When Biodiesel is used in a vehicle we want the owner to know what effect that will have on their

engine warranty. Second, to develop a strategic plan for what needs to be done to establish full warranty of engines fuelled with Biodiesel. The goal is for Biodiesel, as a recognized fuel, to be accepted by the engine manufacturers, removing the concern for engine warranty. At this meeting were engine manufacturers, Biodiesel producers, and research teams. They all need to be part of the strategic plan. The goal was to develop the plan while they were together.

Biodiesel Research

For lack of space the Biodiesel Research results will not be included in any depth. Most of the research has been or will be presented elsewhere. Biodiesel is used to describe esters of lipids from a variety of feedstocks.

Specific Conclusions noted during the Conference from a variety of feedstocks:

Biodiesel has been found to be an acceptable substitute for diesel fuel, performing normally in unmodified diesel engines.

Recipes for producing Biodiesel have been developed and used to produce demonstration quantities of fuel.

Biodiesel is safer because the flashpoint is over 56 C (100 F) degreeshigher than that of diesel.

Engine durability tests of up to 1000 hours have generally shown Biodiesel to be equivalent to diesel fuel.

Biodegradability of Biodiesel was higher than the biodegradability of reference dextrose and much higher than diesel fuel.

Toxicity of Biodiesel was at least 15 times less than diesel and probably even much lower.

Smoke, as measured by an opacity meter, has generally been found to be 33% to 65% lower than from diesel fuels.

Emissions test have shown a reduction in HC and CO_2 and an increase in CO_2 . Results for PM and NOx are mixed. Much more work on emissions with Biodiesel is required.

Transit System and Other Use of Biodiesel

Spokane Transit, Dick Yost

Spokane Transit has a bus fleet of 144 heavy duty coaches that are operated in the city of Spokane and surrounding area. The main base is in the downtown area where approximately 124 busses are stored. A satellite facility is in the Spokane valley. The facility in the valley is where the year-long test on biofuel was conducted. The test was divided into two six-month segments: the first six months the coaches used a 70% blend of #1 diesel with a 30% soy-based oil. For the second six-month period the fuel was changed to an 80% #1 fuel with a 20% soy-oil. The engines in the coaches designated for the test are all Detroit diesels with

several different engine types: six V-71's; six V-92's; six L-71's. The coaches are from various years ranging from 1974 to 1992.

The test was conducted from October, 1993 to October, 1994. Particulate levels were tested with a Bosch smoke analyzer, which is what the State of Washington uses for testing particulate matter. Oil analysis tests were taken at different times during the test. Three months into the test the injectors were removed from two coaches, both an electronic injector and a mechanical injector, which were sent to Salt Lake City, Utah by Spokane Detroit. No problems were found with any injectors at any point in the test. There also were no mechanical problems. The results from the test were really very positive. They reported a clean burning fuel. The particulate level decreased about 12% and they had an average of about 0.2 kilometer/liter (0.5 miles per gallon) better fuel mileage with the biofuel than with the straight diesel.

During the first six months, the soybean association provided the fuel; during the second six months they purchased the fuel. They were hoping from a maintenance standpoint to continue with the fuel, but the cost was too high. The cost was about $0.76 per liter ($2.89 a gallon) for the soy fuel and $0.19 per liter ($.73 per gallon) for diesel. The increase in the annual fuel cost was 59%. Even with the advantages of Biodiesel they are not able to justify the extra cost to the Board of Directors.

Link Transit Biodiesel Demonstration Project, Todd Daniel

On December 16, 1994 Link will celebrate three years of providing public transit in Chelan and Douglas county. They are a fare free system; one of just three in the state of Washington. Because of the high monthly fleet mileage they elected to try a fleet-wide, one month, 161,000 kilometer (100,000 mile), Biodiesel demonstration. The Biodiesel fuel was supplied free of charge from farmer checkoff dollars and regulated by the National Biodiesel Board. A 20% blend with number two low sulfur diesel powered their diesel fleet for twenty-eight days, or the entire month of February, 1994.

A few points of interest that were recorded during the demonstration were total fleet miles recorded at 167,000 kilometer (104,000 miles) on the 20% blend; oil sample results did not reflect anything unusual; there was no change in fuel economy; the average temperature was 12 C (22 F) degrees with no fuel clouding; emission levels (smoke) were lowered 17% fleetwide; and finally, they received very positive public response. The Link Biodiesel demonstration was called a success. Public and staff involvement, along with lower emissions, were the ingredients. National news coverage was an added benefit. It is their hope that better pricing and availability will develop and breed life into Biofuels!

"Truck in the Park" Demonstration, Howard Haines

The Montana Department of Natural Resources and Conservation (DNRC) in cooperation with the National Park Service (NPS) and the U. S. DOE Pacific Northwest and Alaska Regional Bioenergy Program will conduct an operational demonstration of a diesel truck powered by rape ethyl ester (REE). This fuel is produced by the University of Idaho (U of I) for use in tourism-related service in Yellowstone National Park. DNRC will assist the Park Service and private industry in developing options for managing the impact of the growth in tourism while preserving scenic resources.

Project Goals, Objectives, and Approach

The goals of this project are to:

- Develop a biomass-derived transportation fuel that is attractive for use in tourism-related industries and others that operate in environmentally sensitive areas.

- Provide a beachhead market for a developing industry, to encourage the development, production, and use of this biofuel within the region.

- Determine the feasibility of using Biodiesel at high elevation.

Industry

Navistar, Rodica Baranescu

Between 1991 and 1993 Navistar made 88,000 medium and heavy duty trucks. Last year they produced 178,300 engines. They are the largest producer of diesel engines in North America. Navistar has a statement for Biodiesel fuel use, it reads: "Use of 100% Biodiesel fuel is not recommended due to performance and potential reliability issues." By Biodiesel, they imply mostly methyl esters of vegetable oil. As to warranty position on this issue Navistar says, "Blends of Biodiesel with conventional diesel fuel in amounts up to 20% may be suitable for use. However, the user assumes warranty liability for any failure directly resulting from the suitability of a 'BIO' fuel blend and/or associated additives." They state that "This position is consistent with the use of any fuel additive." The Warranty Procedures and Administrative Policies procedure reads "...If the use of additives causes a failure, the cost to repair or replace the failed part or component is not reimbursable. Users and fuel suppliers maintain a responsibility for the quality of fuel regardless of Biodiesel impacts. Further, durability and emissions impact testing will be required to better assess the vulnerabilities of Biodiesel fuel usage in International engines." In one of the warranty statements it states "Warranty coverage will not be voided by installation or use of special equipment additives or other chemicals designed to improve vehicle performance, non-Navistar parts, or by modification of any part of the vehicle. However, if the use of such devices, modifications or additives causes a failure the cost to repair or replace the failed part or component is not reimbursable." We believe we don't know enough today about the behavior, especially the long term behavior, of Biodiesel fuel.

The Engine Manufacturers Association brainstorming session identified the following critical issues in the development and commercialization of Biodiesel: fuel characteristics, water adsorption and additive compatibility, cold flow characteristics of the fuel, fuel specifications for Biodiesel, engine performance and emissions, engine certification for Biodiesel, engine optimization for Biodiesel, emissions speciation for Biodiesel, compatibility with engine materials, Effects of the fuel on lubricating oil, maintainance of Biodiesel engines in comparison to diesel engines, economics and infrastructure needs, availability of the fuel and potential markets.

Cummins Engine Co., Karl Koontz

Cummins is celebrating the 75th year of building engines. Cummins produced 250,000 diesel engines last year. In the U.S., Cummins is number one in engines over 200 horsepower and number five over-all in diesel engine production.

The Cummins fuel specification bulletin lists recommended fuel specifications as well as alternative fuel specifications, and basically says that alternatives are not normally used in Cummins engines and may be used only where a recommended fuel is not available. Biodiesel is generally placed in the alternative fuel category at this time. Our standard fuel recommendation is No. 2 diesel fuel; No. 1 diesel blending for winter requirements.

The owner is responsible for the operation and maintenance of the engine as specified in the Operation and Maintenance manual, providing proof of that maintenance. Under limitations, "We are not responsible for failure or damage resulting from abuse, neglect," and "not responsible for failures caused by incorrect fuels, by water or dirt, or other contaminants in the fuel." Our warranty covers defects in Cummins workmanship and materials; we have built the engines with good parts that have been assembled properly and tested. It doesn't say you can't wear it out; it doesn't say you can't damage it. We look at the fine line as those consumables such as fuel and oil as user's choices, and at different times and emergencies, it may be necessary to deviate from our recommendations; however, all our engines are designed, tested, proven, and fully warranted to run on our recommended consumables: fuel, oil, and coolant. So, in short, the choice of these things implies acceptance of responsibility by the operator. These will not cancel our warranty. We follow ASTM recommended No. 2-D diesel fuel and recommend blends of Numbers 2-D and 1-D in the winter. This fuel needs to be kept above 1.3 degrees centigrade to provide adequate lubrication to the fuel system.

Cummins Concerns and Questions dealing with warranties:

1. Fuel properties
2. Cold flow issue
3. Seal and gasket compatibility
4. Engine deposits
5. Oil acidity
6. Ignition delay
7. Effect on combustion and engine temperature
8. Effect on fuel systems
9. Effect on power and fuel consumption
10. Effect on each of the seven Cummins engine families
11. Reliability
12. Emissions testing
13. Durability, wear and deposits
14. Experience in 240,000-320,000 kilometer (150,000- 200,000 miles)

Mercedes Benz, Ansgar Shafer

Mercedes Benz employs 200,000 people world-wide. The U.S. affiliate is Freightliner. Mercedes Benz has world-wide, the largest market share of heavy duty trucks.

Almost 14 to 15 years ago they found that vegetable oils themselves are not suitable alternative fuels. The transesterification of vegetable oils into methyl esters is a well known, optimized and commercially used large-scale standard process in the chemical industry. These esters are usable in all existing CI engines. If any, only minor engine modifications are required (e.g. elastomeric materials for fuel lines). This is the best researched and most developed vegetable oil based alternative fuel. The reality of transesterification is that there are all types of impurities. For example there are non-reacted triglycerides, partially reacted monoglycerides and diglycerides, free fatty acids, and glycerol. There is also methanol, water, and the rest of the catalyst. All these things have to be removed because they all are threatening the engine. For example the unreacted material, triglycerides, are building

materials for (injector) deposit formation. The free fatty acids are very dangerous for bearing metals, by so-called dry corrosion. The same thing applies to the free glycerol and the monoglycerides because they are very eager to react with bearing metals. The catalysts form ash. Methanol lowers the flash point.

A few important results from long term tests on different vegetable oil esters at Mercedes Benz. (These are tests of rapeseed oil methyl ester and palm oil methyl ester):

No sludging is apparent with a suitable lubricating oil;
Oil dilution is within relatively tight limits; no serious effects on relevant lubricating oil characteristics;
Inlet valves show a slight tendency to coke when the content of glycerides in the ester is too high;
The cylinder gap has a slight tendency to burn, but these were within acceptable limits;
The fuel injection system can remain unchanged; no nozzle coking is found when fuel quality is adequate: too high a glyceride content causes nozzle coking;
Some elastomeric materials (e.g. some fuel lines) are not sufficiently resistant to vegetable oil esters; the materials have to be changed;
The unusual exhaust gas smell is troublesome (some employees and customers could not tolerate the odor); an oxidation catalyst significantly diminishes the respective inconvenience.

Based on these experiences with methyl esters, Mercedes Benz has produced a service information bulletin regarding the use of rapeseed oil methyl ester produced according to the specification shown earlier. It is not for Biodiesel, because Biodiesel is not clearly defined. This service information is being circulated world-wide to all our affiliates, service centers, and dealers.

Mercedes-Benz trucks (not passenger cars) produced since 1988 with series 300 and 400 engines (DI CI) can be fuelled with RME.

The leak fuel lines of the injection nozzles on series 400 engines have to be replaced by an RME-resistant version and connected to the fuel feed line.

If RME is used in older vehicles, there is a risk that hoses and seals impaired by many years contact with diesel fuel will be attacked by RME and thus become leaky.

Commercial vehicles with MB series 600 engines (vans and pick-ups; IDI) cannot be operated with RME.

Mercedes-Benz does not provide warranty coverage for damage caused by using RME of inferior quality or by non-observance of the instructions for RME operation.

The same applies for industrial engines:

Industrial engines of series 300 and 400 are approved for RME operation

The fuel should correspond to the DIN standard DIN V 51606.

Operation with fuel of inferior quality may lead to malfunctions or engine damage.

Mixed-fuel operation using RME and diesel fuel is not approved.

Supplementary heaters: Some of them must not be operated on RME, others need to be modified for RME operation, others can be operated on RME without modification provided the control unit has been programmed appropriately. Generally, the supplementary heater can be operated via a separate fuel oil or diesel fuel tank; retrofitting is possible and even advisable for winter operation.

Lester Walker, Detroit Diesel

Detroit Diesel is a well known manufacturer of diesel engines. Specification sheets and warranty documents are very similar to what has already been discussed.

"Is the use of Biodiesel covered under engine warranties?" The answer is right out of our own individual statements: "Manufacturer warranties cover defects in materials and workmanship," much as was covered by our Cummins representative, "Those warranties extend to engines burning Biodiesel. These warranties do not cover engine problems related to fuel of any kind." Then there is a follow-up statement that says, "Tests and demonstrations have shown Biodiesel to be no different than petroleum diesel in terms of engine performance and wear."

The engine warranty, in most cases, is not set up to deal specifically with the use of a fuel. It is set up to cover defects in materials and defects in workmanship; engine problems that are traceable directly to the manufacturer. It's not uncommon when there is an engine warranty question that deals with a particularly severe warranty claim, for example, for the relevant parts of that engine to be returned to the factory or for a materials meeting to be set up to review and look at the condition of the parts to try to establish whether or not there is a root cause that relates to something that the manufacturer did.

Detroit diesel has the following concerns about using Biodiesel

Regulated emissions, especially NOx
Effect on fuel seals;
Durability testing of 1000 hours duration;
Field demonstration of over 160,000 kilometers (100,000 miles);
Tear down of engine from 160,000 kilometer (100,000 mile) demonstration;
Standardization of the fuel and fuel specification;
EPA approval.

Diesel Power Systems Group, Madan R. Goyal

The Biodiesel fuels, methyl ester of rape seed oil (RME) or Methyl ester of soybean oil, are believed to be fairly good solvents. The switch over from the diesel fuel to the use of Biodiesel is very likely to dissolve deposits from the fuel tank and fuel injection system and could cause serious fuel filter plugging and / or injector plugging problems. The protective coating from the inside of the fuel tank could also be removed by the Biodiesel fuel.

The technical data in the literature discuss the following important engine durability issues:

1. Fuel Quality
2. Material Compatibility
3. Long Term Storage
4. Low Temperature Operation
5. Phosphorus
6. Oil Dilution
7. Valve/Port deposits
8. Durability Summary

Workshop Summary

DRAFT STATEMENT ON WHERE WE ARE TODAY ON WARRANTY FOR USE OF BIODIESEL

Biodiesel (methyl or ethyl ester of plant oils or animal fats) is a new fuel which is being tested under a wide range of conditions including both neat and blended with petrodiesel. Users of this fuel should be aware, however, that currently there is no fuel specification for Biodiesel and, therefore, engine manufacturers cannot fully recognize it as equivalent to diesel. Users of this or any fuel not meeting manufacturers' published fuel specification requirements assume warranty liability for failure of components or emission certification traceable to the fuel. Non-fuel related warranty issues are not affected by the use of Biodiesel.

CRITICAL ISSUES RELATED TO ACCEPTANCE OF BIODIESEL BY ENGINE MANUFACTURERS

A) Fuel Characteristics and Specifications
-standard test methods
-fuel standard such as ASTM

B) Engine Performance and Emissions
-certified for use by EPA
-many 1000 hour+ and/or 160,000 kilometer (100,000 mile)+ engine durability tests
-test for air toxics

C) Fuel/Engine Interaction
-materials compatibility tests
-establishment of oil change intervals
-engine manufacturer tests

D) Economics/Infrastructure
-supply at competitive price
-identify uses where price is justified

E) It is clear that development of the required data must be a joint effort of research labs, private and public; engine manufacturers; the biodiesel industry; and governmental agencies such as CARB, EPA, DOE, etc.

EMISSIONS AND ENGINE PERFORMANCE FROM BLENDS OF SOYA AND CANOLA METHYL ESTERS WITH ARB #2 DIESEL IN A DDC 6V92TA MUI ENGINE

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Abstract

A Detroit Diesel 6V92TA MUI engine was operated on several blends of EPA #2 diesel, California ARB #2 diesel, soya methyl ester (SME) and canola methyl ester (CME). Various fuels and fuel blend characteristics were determined and engine emissions from these fuels and blends were compared. Increasing percentages of SME and CME blended with either ARB or EPA diesels led to increased emissions of NO_X, CO_2 and soluble particulate matter. Also noted were reductions in total hydrocarbons, CO and insoluble particulate matter. Chassis dynamometer tests conducted on a 20/80 SME/ARB blend showed similar emissions trends. The data suggest that certain methyl ester/#2 diesel blends in conjunction with technologies that reduce the soluble fraction of particulate emissions merit further exploration as emissions reducing fuel options for North American mass transit sectors (excepting California, which mandates ARB diesel).

Introduction

The present study was originally concerned with the use of SME as a fuel blend component with ARB diesel in heavy duty diesel engines for Southern California mass transit buses. During the final phase of the testing program we extended the engine dynamometer work to include tests on #2 diesel blends with canola methyl ester (CME). Both California ARB and U.S. EPA diesels (diesel fuel subject to October 1, 1993 U.S. EPA Standards) were blended with CME. A 20/80 SME/ARB blend was retested to substantiate our earlier work. Because of the widespread use of EPA diesel in the U.S. and Canada (as opposed to the relatively small California ARB diesel market) it was decided to also conduct tests on CME and SME in blends with EPA diesel.

Background - Research conducted using raw, degummed vegetable oils to fuel farm tractors during the early 1980s in Illinois, Idaho, Missouri and North Dakota demonstrated that diesel engines can operate with vegetable oils. Certain difficulties were encountered, such as injector coking. Additional research, in the U.S. and abroad, demonstrated that methyl esters derived from vegetable oils create fewer difficulties than the use of vegetable oil in heavy duty diesel engines. It was therefore suggested that on on-road vehicles (e.g., mass transit buses) be tested using vegetable oil methyl esters. A soybean oil derivative, soya methyl ester (SME) has recently received extensive attention in the U.S. Canola methyl ester (CME), derived from canola oil, has received similar attention in Canada. Produced through a catalyzed reaction between a vegetable oil and methanol, it was demonstrated that SME and CME can be used to fuel a diesel engine. Because both methyl esters contain less usable energy per unit volume, a diesel engine fueled on 100% SME or CME will develop approximately five percent less power than a similar engine fueled on diesel fuel. Although a power loss was noted (Schumacher, et. al.), there was no significant reduction in the torque.

We proposed to investigate, from a commercial user's perspective, the benefits and common-use problems, if any, of a domestically produced "transition fuel" for diesel engines that would cost-effectively provide an overall emissions reduction. SME and CME presented the potential to be this transition fuel. The initial phase of the project focused on SME blends instead of neat SME due to fuel cost issues, suspected materials compatibility problems and promising results from previous research on SME/diesel fuel blends. Work on CME was also conducted with blends but the blends were intentionally leaner in CME content.

SME testing consisted of fuels characterization, engine and chassis dynamometer work and limited on-road vehicle durability/compatibility tests. Neat ARB and EPA diesel and 20%, 30% and 40% SME/ARB blends were studied. Subsequent CME testing consisted of fuels characterization and engine dynamometer work. Neat ARB and EPA diesel as well as 6%, 20% and 40% CME/ARB blends and 6%, 10% and 20% CME/EPA blends were studied.

Results

Fuels characterization - Fuels characterization was conducted on ARB and EPA diesels, SME and SME/ARB fuel blends (see Table 1). Tests are also being conducted on various CME blends, but as of this writing the results are not yet available. The data were used to evaluate differences in these fuels and to serve as a basis of comparison for other methyl ester/diesel blends. The tests included gross heating value, distillation, pour point, API gravity, flash point, cetane number and viscosity measurements. Gas chromatographic (GC) analyses were also conducted on SMEs from two sources by several laboratories. Differences in fuel characteristics between EPA and ARB diesels proved to be minimal. Cetane numbers varied by approximately 0.5% and gross heating values varied by 0.25%. Flash points were 74.4 °C (166 °F) and 75.6 °C (168 °F) respectively.

Differences were found between SMEs from two different suppliers, Procter & Gamble (P&G) and Calgene. Prior to 1994, P&G produced SME using a "single distillation process." In spring of 1994, P&G reportedly began using a "double distillation process" in an effort to improve product quality. Though only "double distilled" SME was used for the dynamometer and on-road testing portions of this project, GC tests were also conducted on single distilled SME (by Dr. Marvin O. Bagby, USDA). Results from these tests show a smaller percentage of double and triple saturated fatty acids from soya oil and a greater percentage of lauric and myristic acids (C_{12} and C_{14}) in the single distilled product than in the double distilled esters (see Figure 1). No methanol was observed in any of the tested samples. This indicates that there are significant differences in fuel quality depending on the supplier.

A low flash point test result (55.5 °C, 132 °F) of a 20/80 SME/ARB blend was brought to our attention by the California Department of Food & Agriculture, Division of Measurements Standards. Such a low flash point can preclude the blend from use in marine engines and raises concerns for on-road use. Further tests were conducted by Dr. Jon Van Gerpen of Iowa State University, Department of Mechanical Engineering, on eleven blends ranging from 0% to 100% SME. Results show that there may be a flashpoint lowering effect of SME/ARB blends in percentages ranging from less than 10% to approximately 25% (see Figure 2). Subsequent tests have shown the drop in flash point not to be significant enough to create a fuel blend safety concern.

Table 1. Fuel Characteristics

Fuel	ARB Diesel	EPA Diesel	P&G SME	Calgene Methyl Ester	Calgene/ARB 20/80	P&G/ARB 20/80
Gross Heating Value (Btu/lb)	19,555	19,604	17,115	16,951	19,145	19,272
Pour Point (°F)	-12	-15	35	32	-13	0
Flash Point (°F)	168	166	>230	>230	141	140
Cetane Number	43.1	44.0	45.7	51.1	48.4	50.4
API Gravity (@ 60 °F)	34.4	34.2	28	27.9	35.3	35.3
Viscosity (@ 104 °F, cSt)	2.73	2.87	4.33	4.31	2.68	2.65

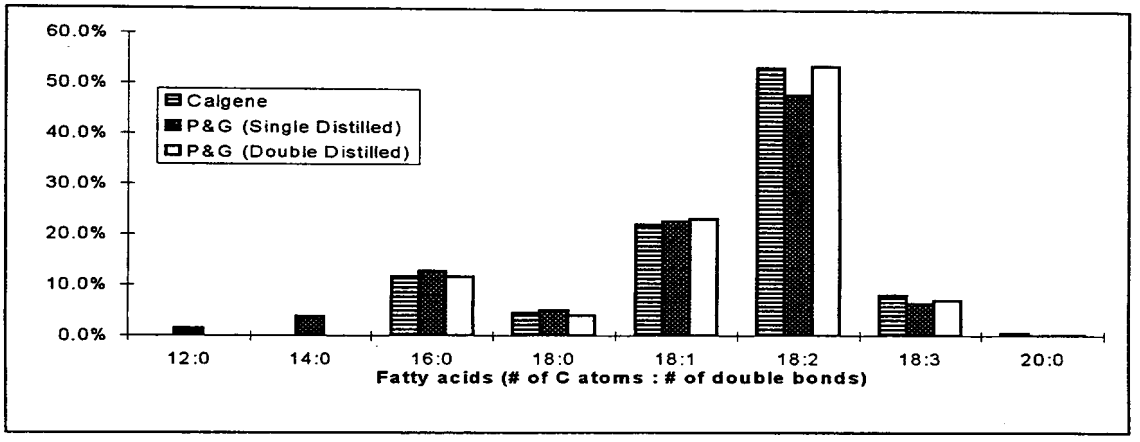
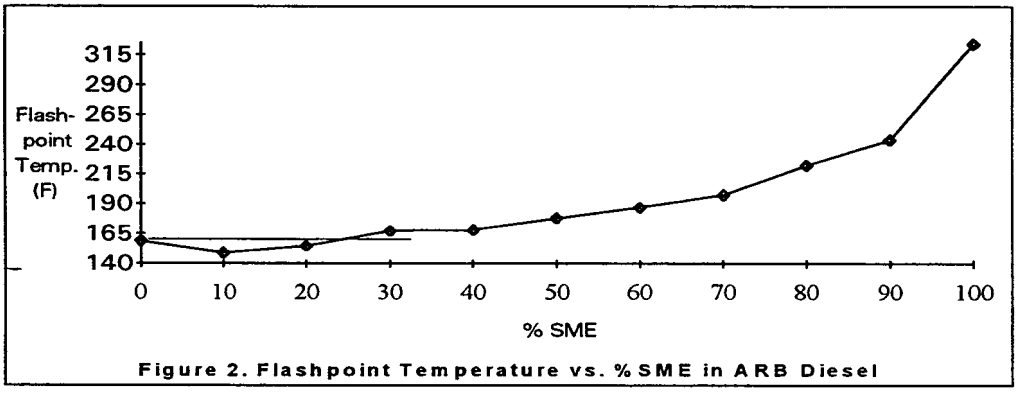


Figure 1. Percentage of Carbon Atoms in Fatty Acid Chains in Three Soya Methyl Ester Products



Additional research is suggested to substantiate these initial results. The above work further suggests a need to establish a commonly accepted fuel standard. In the absence of a fuel standard, further engine emissions and performance work will be of limited value.

Engine dynamometer testing - Engine dynamometer tests were conducted using the EPA heavy-duty engine transient cycle. Analysis of power parameters, including engine speed, torque, brake horse power and fuel flow rate indicate a gradual decrease in power as the percentage of SME was increased from 20% to 40% (see Tables 2 and 3). These changes are within expectations. The same performance trends were found with CME blends.

Table 2. Peak Power Comparisons

Test	ARB Diesel	20/80	30/70	40/60
Engine Speed (rpm)	2,003	2,003	2,003	2,002
Engine Power, bkW (bhp)	195 (261)	198 (266)	196 (262)	192 (258)
Engine Torque, N-m (ft-lb)	928 (685)	946 (698)	933 (688)	918 (677)
Fuel Flow, kg/hr (lb/hr)	47.8 (105.4)	49.4 (108.9)	49.3 (108.7)	49.0 (108.0)

Table 3. Peak Torque Comparisons

Test	ARB Diesel	20/80	30/70	40/60
Engine Speed (rpm)	1,201	1,202	1,202	1,202
Engine Power, bkW (bhp)	144 (193)	145 (194)	144 (193)	143 (191)
Engine Torque, N-m (ft-lb)	1142 (842)	1149 (848)	1143 (843)	1133 (836)
Fuel Flow, kg/hr (lb/hr)	32.9 (72.5)	38.4 (84.7)	33.6 (74.1)	33.8 (74.5)

Monitored exhaust emissions included: PM (total and insoluble), CO_2, CO, NO_x and total hydrocarbons (THC). ARB and EPA diesel baseline emissions were compared (see Figure 3). Results show that EPA diesel had lower PM, THC and CO emissions than did the ARB fuel. EPA NO_x emissions were 5.2% higher than ARB diesel.

Increasing percentages of SME and CME blended with either ARB or EPA diesels led to increased emissions of NO_x and CO_2 and reductions in THC and CO (see Tables 4-6, Figures 4-6). Increases in soluble PM and reductions in insoluble PM were also observed (see Figures 7-9). Insoluble particulates, composed mainly of pure carbon, contribute significantly to visible exhaust smoke. The decrease in insoluble PM corroborates visual accounts of reduced smoke opacity from vehicles fueled on similar methyl ester/diesel blends. A comparison in PM emissions was made between ARB and EPA diesels and 20/80 blends of SME/ARB, CME/ARB and CME/EPA (see Figure 10). The comparison illustrates the similarity in PM emissions between SME and CME/ARB blends and the reductions in both total and insoluble PM, compared to either ARB or EPA diesels, when using a CME/EPA blend.

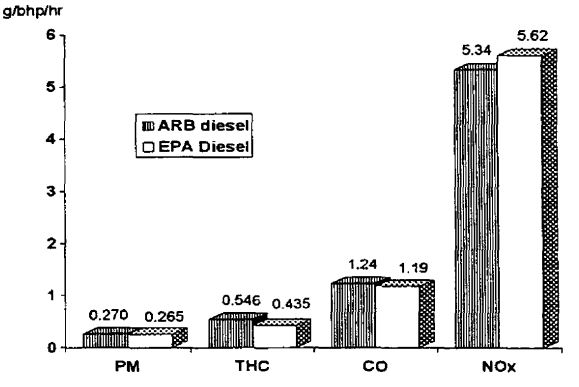


Figure 3. Comparison of ARB and EPA Diesel Baseline Emissions

It should be noted that during the CME testing phase of this project a second 20/80 SME/ARB blend was tested. The results of this second SME test corroborated previous exhaust emissions trends except in the case of PM, where the previous test had shown total PM emissions increasing. The second set of tests showed total PM emissions slightly decreasing compared to the ARB baseline. The PM total in these two cases was mainly a function of the difference in the soluble fraction between the two tests. The same trend illustrating the respective reduction and increase of the insoluble and soluble fractions of PM was observed in both sets of tests.

Table 4. Comparison of Exhaust Emissions from CME/EPA Blends (*g/bhp/hr*)

Fuel Blend	Total PM	Soluble PM	Insoluble PM	THC	NO_x	CO	CO_2
100% EPA	0.265	0.133	0.132	0.435	5.62	1.19	653
6/94	0.244	0.143	0.102	0.411	5.72	1.06	652
10/90	0.243	0.140	0.103	0.376	5.81	1.02	649
20/80	0.238	0.145	0.090	0.363	5.87	1.04	652

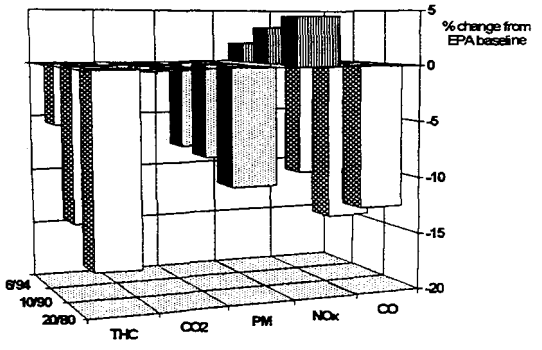


Figure 4. Emissions Trends Observed During CME/EPA Engine Dynamometer Testing

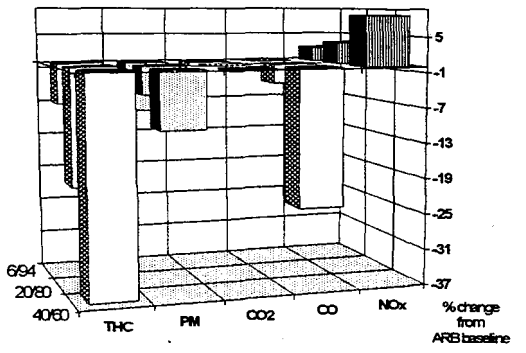


Figure 5. Emissions Trends Observed During CME/ARB Engine Dynamometer Testing

Table 5. Comparison of Exhaust Emissions from CME/ARB Blends (*g/bhp/hr*)

Fuel Blend	Total PM	Soluble PM	Insoluble PM	THC	NO_x	CO	CO_2
100% ARB	0.270	0.141	0.128	0.546	5.34	1.24	653
6/94	0.247	0.138	0.110	0.508	5.47	1.24	649
20/80	0.257	0.158	0.099	0.437	5.54	1.20	653
40/60	0.244	0.178	0.066	0.346	5.82	0.95	651

Table 6. Comparison of Exhaust Emissions from SME/ARB Blends (g/bhp/hr)

Fuel Blend	Total PM	Soluble PM	Insoluble PM	THC	NO_x	CO	CO_2
100% ARB	0.257	0.134	0.123	0.57	4.43	1.22	671
20/80	0.270	0.160	0.110	0.48	4.70	1.12	688
30/70	0.258	0.172	0.086	0.42	4.78	1.03	688
40/60	0.258	0.181	0.077	0.38	4.89	0.95	686

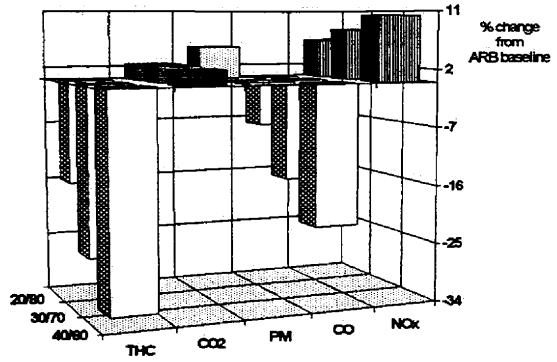


Figure 6. Emissions Trends Observed During SME/ARB Engine Dynamometer Testing

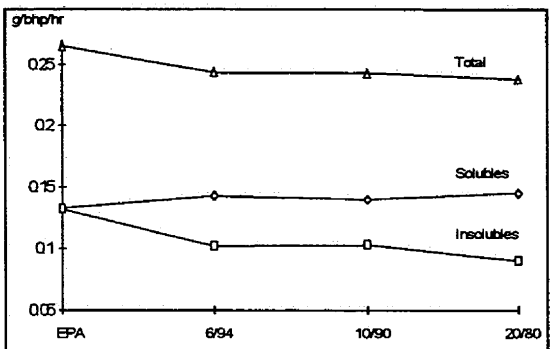


Figure 7. Comparison of Total, Soluble and Insoluble Particulate Emissions Between CME/EPA Blends and 100% EPA

In early 1993 it was demonstrated (Scholl, et al.) that NO_X emissions resulting from an SME/diesel blend increased. Our data corroborate this result. The same study also showed that NO_X emissions could be reduced via delays in engine timing. This suggests the possibility of an emissions reduction package that could lower emissions across the spectrum of relevant criteria pollutants, i.e., a methyl ester/ #2 diesel blend (which reduces THC, CO and insoluble PM), a delay in engine timing (negating the NOx increase resulting from the methyl ester fuel blend) and a high activity oxidation catalyst to reduce the increased soluble fraction of PM.

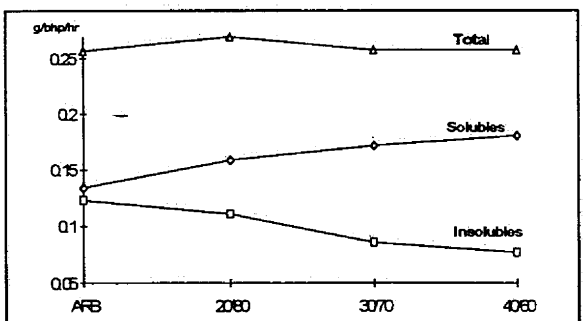


Figure 8. Comparison of Total, Soluble and Insoluble Particulate Emissions Between SME/ARB Blends and 100% ARB

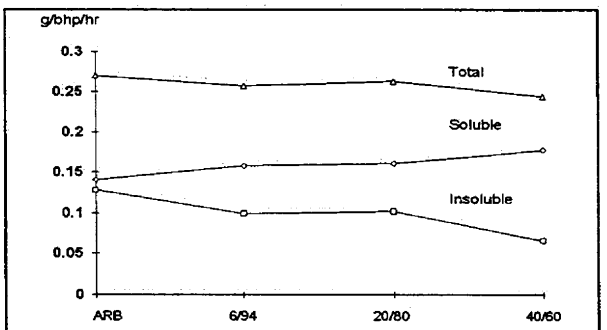


Figure 9. Comparison of Total, Soluble and Insoluble Particulate Emissions Between CME/ARB Blends and 100% ARB

Chassis dynamometer testing - Chassis dynamometer testing was conducted on a 20/80 SME/ARB diesel blend at the Emissions Testing Facility of the Los Angeles County Metropolitan Transportation Authority using the Central Business District Cycle. Although no definitive comparisons can be drawn between chassis and engine dynamometer tests because of the vast differences in procedural parameters and conditions, the trends in the data were largely similar (see Figure 11). Total hydrocarbons (THC), CO and PM emissions decreased by 16.7 percent, 20.2 percent and 6.1 percent respectively while NO_X emissions increased by 4.5 percent over the ARB diesel baseline.

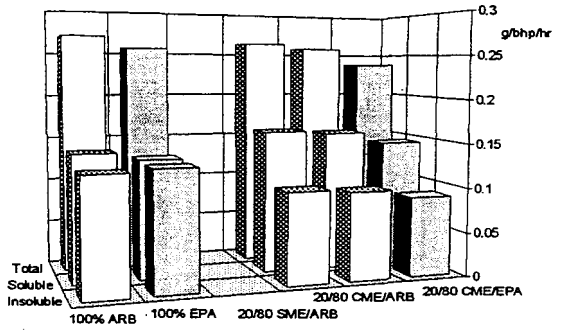


Figure 10. Comparison of Particulate Fractions Between Various EPA and ARB Blends

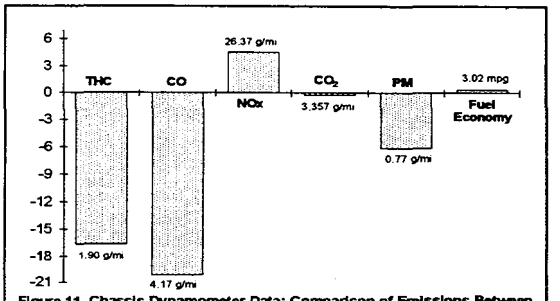


Figure 11. Chassis Dynamometer Data: Comparison of Emissions Between a 20/80 SME/ARB Blend and 100% ARB

On-road testing - On-road testing consisted of the daily refueling (using 20/80 and 25/75 SME/ARB fuel blends) of a passenger vehicle in an actual mass transit application within the Los Angeles basin. These tests were conducted to determine the blends' effects on engine performance and wear. The vehicle ran approximately 10,000 miles on the two blends. From the weekly oil samples taken, no abnormal engine wear was noted. Drivers of the test bus were surveyed regarding changes in power and handling before and after the bus was fueled with the blends. The drivers did not differentiate between before and after conditions.

Materials compatibility testing - Materials compatibility testing was limited to the components used in the assembly and operation of the fuel blending and pumping station. The material used for hoses was polyurethane ("Superthane," purchased from NewAge Industries). For a period of five months a sample of SME was sealed inside a ten inch long section of the product at room temperature. After two months the outside surface of the hose began to "sweat," indicating that the ester had penetrated the hose material. It was also observed that sealed plastic containers used to store SME deflated over time. This may indicate the presence of a chemical reaction between the ester and some component of the atmosphere trapped within the vessel. It was also observed that SME degrades upon exposure to air. SME from drums opened for sampling purposes and left alone changed color and became cloudy. This "shelf life" was approximately five months.

SME was also found to be an excellent paint remover. The penetrant qualities of SME are well documented. Because the fuel drums were painted, and because paint dissolved by the SME could have been introduced into the fuel blend through the drums' ventilation holes, care had to be taken in removing any SME spills from the tops of the fueling drums.

Conclusions and Recommendations

Conclusions - Soya and canola methyl ester/ #2 diesel blends, in conjunction with technologies that reduce the soluble fraction of particulate emissions merit further exploration as emissions reducing fuel options for North American mass transits. At the present time, however, methyl ester/#2 diesel fuel blends are not deemed to be a viable mass transit "transition fuel" for Los Angeles basin and California conditions. This is based on the following facts:

1. **On a 6V92TA MUI engine SME and CME/ARB diesel blends emit greater amounts of NO_x than does ARB diesel alone.** California emissions standards cannot be met using the tested fuel blends in the 6V92TA MUI engine model. (This model represents a significant percentage of the existing transit fleet inventory).

2. **SME/ARB diesel blends are not cost effective for mass transits under current Southern California economic conditions.** Fuel cost is a critical operations issue for mass transits. The Southern California delivered soya methyl ester cost was much higher than anticipated ($5 per gallon vis-à-vis an originally estimated $2.50 per gallon).

3. **Fuel characteristics variations were found from one SME batch to the next.** Although it is known that engine performance and emissions will be affected by fuel variations in general, it is not known to what degree methyl ester fuel variations will manifest themselves. A national fuel standard is necessary.

4. **Materials compatibility and engine durability issues need to be addressed.** Though limited engine durability testing showed no unacceptable engine wear, materials used in fuel transfer (e.g., hoses) exhibited signs of incompatibility with SME.

5. **Soya methyl ester appears to have a definite duration "shelf life."** More research is suggested in this area.

Recommendations - Given the data collected in this project, we recommend further research, testing and analysis in the following areas:

1. Testing on:
   - Long-term engine performance and wear on various methyl ester/#2 diesel blends.
   - Methyl ester/diesel blends plus high activity oxidizing catalysts.
   - Materials compatibility.

2. Research on:
   - Methyl ester shelf life.
   - Methyl esters from other feedstocks (i.e., restaurant waste oils, palm oil, almond oil, etc.).
   - Methyl ester performance when fungicides are added to the fuel blend. Since methyl esters are biodegradable they can serve as an energy source for microbial growth.

3. Development of:
   - Methyl ester fuel standards. In the absence of such a standard, further engine emissions work will be of limited value.

Methodology

This study concentrated on five key areas:

- fuels characterization,
- engine dynamometer tests,
- chassis dynamometer tests,
- on-road vehicle engine performance testing and field use issues in a mass transit application,
- materials compatibility.

A list of the testing facilities used in this project appears in Table 7.

Diesel Engines - We selected an engine model for emissions and performance testing that best represented the California mass transit fleet inventory for the next 5-10 years: a 1983 Detroit Diesel 6V92TA Mechanical Unit Injection (MUI) engine. According to 1991 DDC estimates, the 6V92TA was the engine most commonly used by California mass transit properties and represented approximately 85%-90% of the then existing fleet inventory. These engines had a remaining useful life of 5-10 years. Of these engines, approximately 80% were MUI models. An older MUI engine (as opposed to a more modern Detroit Diesel Electronic Control design) was chosen because MUI technology represented the present state of diesel engine technology in use by the majority of mass transit properties at that time. The underlying thought was that these older, less clean burning engines would stand to benefit most from a cost-effective, relatively low emissions interim fuel. According to March 1995 estimates, the large majority of engines (70%-75%) used by the California mass transit industry continue to be 6V92TA models. Of these, 70%-75% are thought to be MUIs. The particular engines used for this project were rebuilt to 1987 EPA D-bus standards (16-C upgrade, see Table 8). Additional 16-C engine specifications included 9F80(T) injectors timed at 1.470, a throttle delay setting of 0.636", a speed rating of 2,000 rpm and a high idle speed of 2,150 rpm.

Fuels Characterization - Fuels characterizations on both ARB diesel and SME were conducted by several laboratories in accordance with ASTM testing standards. These tests included gross heating value, distillation curve, pour point, API gravity, flash point, Cetane number and viscosity tests (see Table 9). In addition, GC analyses were conducted on three batches of SME obtained from two suppliers as well as on the various blends with diesel fuels in an effort to fully document fuel composition and quality. Additional flash point tests on eleven SME/ARB diesel blends (0% to 100% SME) were conducted by Dr. Jon Van Gerpen, Iowa State University, Department of Mechanical Engineering. The flash points were determined using a Pensky-Martens closed tester using standard ASTM test methods.

Table 7. Testing Facilities

Laboratory	Testing Conducted
ORTECH International, Inc.	Engine Dynamometer
MTA-ETF	Chassis Dynamometer
CORE Laboratories	Fuels Characterization
U.S. Dept. of Agriculture	Fuels Characterization
State of California Division of Measurement Standards	Fuels Characterization
Titan Laboratories	Oil Analysis

Table 8. List of Components for Upgrade #16-C by VDDA to a 6V92 TA MUI Engine

Component	Description
90F80(T) Injectors	Special new Transit Spec., low emission, optimized output.
Blower	Changed to 100% by-pass. Blower output self modulates according to turbocharger output. Lower flow at top end. Reduced NOx, smoke, PM_{10}.
Turbocharger	Improved efficiency, quicker response. Matched to blower to output. Better fuel consumption. Lower PM_{10}, NOx, smoke.
Oil Filter Element	Changed to 12 micron to improve filtration, less wear.
Hose Clamps	Proper hose installation.
Air Inlet Housing	Changed to accommodate new turbocharger.
Lock Plate	Prevents Cam Bolt from losing torque after installation.
Cylinder Kit	High tension oil expander ring, barrel faced fire ring, dome to skirt seal, close clearance skirt. Reduced oil consumption.

Table 9. Tests used in CORE Laboratories Fuel Characterization

Test	Test Method
Distillation curve	ASTM D-86
Heating Value (Gross)	ASTM D-613
Pour Point	ASTM D-97
API Gravity	ASTM D287
Flash Point	ASTM D-93
Cetane # (neat)	ASTM D-613
Viscosity	ASTM D-445

Fuels - ARB diesel was donated by Texaco's Bakersfield refinery (material/trade name: Texaco Low Sulfur CARB Diesel 2). Texaco ARB diesel was most suitable for this project as it fully conforms to the 10% maximum aromatics content requirement for ARB diesel (effective October, 1, 1993). SME was purchased from Calgene Chemical (material/trade name: OLEOCAL ME-130) and from P&G. The P&G SME was initially purchased via Interchem and subsequently via Fosseen Manufacturing. CME was manufactured by the Protein Oils and Starches (POS) Pilot Plant in Sasketchewan and donated to us by Canodev Research, Inc.

Engine Dynamometer Testing - Engine dynamometer testing was conducted at ORTECH International, Inc. (ORTECH) following the Federal protocol prescribed for the EPA heavy-duty engine transient cycle. Power parameters monitored included: engine

speed, torque, brake horse power, and fuel rate. Temperatures monitored included: combustion air, turbocharger out, coolant in, coolant out, oil sump and fuel temperatures. Pressures monitored included: exhaust back pressure, intake restriction, oil and fuel pressures. For each blend, the emissions monitored included: PM (total and soluble), CO_2, CO, NO_x, total hydrocarbons (THC) and brake specific fuel consumption (BSFC).

All instrumentation was calibrated following standard operating procedures. Baseline emissions tests were performed and gaseous and particulate emissions were collected with both EPA and ARB diesel fuels. Prior to running each set of tests, the engines were conditioned on each new fuel by purging the fuel system and operating the engine under full load for 1/2 hour. A 2-Point Power Check was performed followed by three hot transient cycles during which gaseous and particulate samples were obtained. Three hot transient cycles were run for each fuel blend. Emissions results from the three hot cycles were then averaged.

Chassis Dynamometer Testing - Chassis dynamometer tests were performed at the Metropolitan Transportation Authority Emissions Testing Facility (MTA-ETF) in Los Angeles using an ARB baseline and a 20/80 SME/ARB blend. The same fuels were used for the chassis dynamometer tests as for the engine dynamometer tests. The selected test protocol was the Central Business District (CBD) cycle. Actual vehicle on-road operating conditions were simulated through use of a standard road load equation. Input parameters were developed by the MTA-ETF based on coast downs conducted by the Southwest Research Institute and documented in SAE Paper No. 840349, *Dynamometer Simulation of Truck and Bus Road Horsepower for Transient Emissions Evaluations*. The selected inertia weight for the test vehicle was the vehicle tare weight plus 23 passengers and driver times 150 lbs. It was assumed that there were no road gradients. The velocity and acceleration of the vehicle were established by the dynamometer protocol. Emissions were monitored in units of grams per mile and included hydrocarbons, CO, NO_x, particulate matter and CO_2.

On-Road Testing - On-road vehicle compatibility tests were performed at Gardena Municipal Bus Lines (GMBL) in Gardena, California. These consisted of daily refueling of a passenger vehicle with a 20/80, and later with a 25/75 SME/ARB blend. Engine oil was sampled on a weekly basis to determine the presence of other than normal engine wear. Elements surveyed in the samples included twenty elements (metals and metalloids) that are commonly assumed to be indicative of engine wear. Material compatibility tests were conducted at ADEPT's facilities and at the GMBL bus refueling station.

There were challenges inherent in the fuel blending and bus refueling procedures. Local fire and air quality ordinance requirements dictated the following constraints: no use of electricity nor use of an above ground tank for fuel storage. An automatic dispensing nozzle was mandated. In addition, a flow of at least 14 gallons of fuel per minute was needed so as to not disrupt GMBL's fleet refueling schedules.

We finally designed and used a solar powered refueling station. The refueling system consisted of the following components:

- four interconnected 55-gallon drums,

- a 12-volt drum pump,
- a flow totalizer,
- a deep cycle marine battery connected to a solar panel, and
- sixteen feet of polyurethane hose.

We were unable to use the automatic dispensing nozzle because the 12-volt drum pump was unable to deliver enough pressure to insure adequate flow through the nozzle. It was necessary to store the SME off-site and to transport it to GMBL on a weekly basis. The bus was refueled by first calculating (based on daily vehicle mileage and fuel consumption) the amount of SME needed to make up the appropriate blend. SME was then pumped from the blending and dispensing system into the bus fuel tank, which was then topped off from ARB diesel from GMBL's underground tanks.

References

Interchem, "SoyDiesel Research Report," 1993.

Scholl, K. W. and S. C. Sorenson, "Combustion of Soybean Oil Methyl Ester in a Direct Injection Diesel Engine," SAE Technical Paper Series, 930934, 1993.

Schumacher, Leon G., et. al., "Fueling A Diesel Engine With Methyl Ester Soybean Oil," 1993.

CUMMINS 5.9L BIODIESEL FUELED ENGINES

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Abstract

The Agricultural Engineering Department at the University of Missouri-Columbia has fueled a 1991 and a 1992 Dodge pickup Cummins engine with 100 percent methyl-ester soybean oil (biodiesel) for more than 172,545 km (107,215 mile). The 1991 pickup has been driven 89,888 km (55,854 mile) and the 1992 pickup has been driven approximately 82,658 km (51,361 mile). Fueling the 5.9 L (360 in^3) engines with 100% biodiesel initially increased engine power by 3% (1991 engine) and reduced power by 7% (1992 engine). However, both pickups produced less power while fueled on biodiesel during the latest series of chassis dynamometer testing. The pickups averaged 6.9 km/L (16.6 mile/gal). Analysis of engine lubrication oil showed that the engines were wearing at a normal rate. Black exhaust smoke normally observed when a diesel engine accelerates was reduced when the diesel engine was fueled with 100% biodiesel. Increased EPA exhaust emissions requirements for diesel engines have created much interest in the use of biodiesel as a fuel for diesel engines.

Introduction

Much of the biodiesel research that has been conducted within the United States since 1990 has involved the use of a blend of biodiesel and petroleum diesel fuel. The National Biodiesel Board has proactively researched the environmental and performance effects of fueling compression ignition engines with a 20 percent blend (B20). A small number of engines have been fueled with 100 percent biodiesel (B100) (Peterson et al., 1994, National Biodiesel Board, 1995), a fuel that is biodegradable, lower in toxicity than fossil fuels, and a renewable agricultural commodity. Although the University of Idaho is fueling two 5.9L engines with B100, very little analysis of engine wear and exhaust emissions have been conducted on over-the-road (OTR) vehicles fueled with B100. This research provides much needed information for niche markets (such as the fueling of marine vessels on pristine waters) that will benefit by the fueling of compression ignition engines with B100

Related Literature

Ziejewski et al., (1984), Reece et al., (1993), Scholl et al., (1993), and Schumacher et al., (1992, 1993) reported reductions in smoke density when fueling with biodiesel or biodiesel as compared to #2 diesel. Reece et al., (1993) also noted reductions in smoke density when fueling with a 20% biodiesel/80% #2 diesel blend. Ziejewski fueled with sunflower derived biodiesel and Reece fueled with rapeseed derived biodiesel. Scholl and Schumacher used soybean derived biodiesel. Srinivasa et al., (1991), however, noted increases in smoke density when fueling with karanja based biodiesel.

Marshall (1993), Schumacher et al., (1992), Mittelbach et al., (1985), Mittelbach et al., (1988), and Scholl and Sorenson (1993) noted reductions in hydrocarbons and carbon monoxide. Schumacher and Scholl and Sorenson fueled with soybean derived biodiesel. Mittelbach fueled with rapeseed derived biodiesel in 1985, but used waste cooking oil during the 1988 investigation. Marshall used animal derived fats as his source of biodiesel. Niehaus (1985), however, noted increases in carbon monoxide and hydrocarbon exhaust emissions. Niehaus also noted decreases in oxides of nitrogen exhaust emissions.

Ziejewski et al., (1984), Niehaus et al., (1985), Schumacher et al., (1992), Reece and Peterson (1993), and Marshall (1993) observed reductions in power ranging from one to seven percent. Schumacher observed increased power (three percent) using a 1991 Cummins 5.9L DI turbocharged engine. Increased power was observed by Feldman and Peterson (1992) during a 200 hour EMA test using a 3 cylinder, DI, naturally aspirated diesel engine with the injection timing advanced two degrees.

The review of these data and a study conducted by Krahl et al. (1994) suggest that trends in engine exhaust emissions and performance exist when the engine is fueled on 100 percent biodiesel. Shifting the timing as performed by Feldman and Peterson appears to be an appropriate and acceptable method that should be used to optimize the compression ignition engine for biodiesel fueling.

Purpose and Objectives

The purpose of this investigation was to determine the effects of fueling a diesel engine with 100% biodiesel as compared to fueling the engine with petroleum diesel fuel. Specific objectives that were investigated included: fuel efficiency, engine wear, power, and exhaust emission levels.

Materials and Methods

A 1991 and a 1992 Dodge pickup equipped with Cummins, six-cylinder, direct injected turbocharged, 5.9 L (360 in^3) diesel engines were the OTR vehicles used in these tests. The engines were fueled with diesel fuel during the first months of operation. Fueling with biodiesel began after 4,827 km (3,000 mile) of operation for the 1991 pickup and after 2,413.5 km (1,500 mile) of operation for the 1992 pickup. An analysis of the fuel used can be found in Table 1.

Power determinations were made using a Super Flow Corporation model SF-601 chassis dynamometer. The engine was tested for power at 1700, 1900, 2100, 2300, 2500, and 2700 rpm. The chassis dynamometer was used to load the engine to peak pound foot ratings as determined by Cummins Engine Company. The pickup was operated for six minutes at each rpm. The load was then reduced by the dynamometer operator, allowing the engine to accelerate to the next rpm interval as designated by the SAE power test procedures.

Initially, the 1991 pickup engine lubricating oil (15w-40) and the engine lubricating oil filter were changed at approximately 4,023 km (2,500 mile) intervals. Engine lubricating oil was sampled at 805 km (500 mile) intervals and analyzed by MFA Oil Inc. laboratories. Analysis showed no indication of lube oil dilution, therefore, oil sampling interval and the oil change interval were subsequently lengthened to 1,609 km (1,000 mile) and 4,827 km (3,000 mile) respectively. The 1992 pickup engine lubricating oil sampling procedures and change intervals have been maintained at 1,609 km (1,000 mile) and 4,827 km (3,000 mile) intervals.

The biodiesel analysis was conducted by Cleveland Technical Center, Kansas City, MO for Interchem Environmental, Inc. The low sulfur diesel fuel was analyzed by Phillips Chemical Company.

Internal parts of the engine were visually examined using a boroscope on three separate occasions by MU technicians. MFA technicians used an atomic absorption spectrophotometer to analyze the lubricating oil samples for wear metal content.

The engines were not modified. Fuel storage and fuel delivery systems were modified. An aftermarket fuel tank was installed for biodiesel fueling. An electric fuel valve (and switch) was installed to permit the operator to switch between biodiesel and petroleum diesel fuel. Stainless steel heat exchangers were installed to warm the fuel during cold weather operation. Rubber based components in the original fuel lines and in the 1991

Table 1. Fuel properties of Biodiesel and Reference Diesel fuel.

Fuel Property	ASTM Test Procedure	Fuel: Biodiesel	Fuel: Low Sulfur Reference Diesel
Density g/L	D1298	0.86-0.90	0.8466
Gross Heat Value MJ/Kg	D2382	37.2	42.4
Cloud Point	D2500	3.3 (38 F) Max.	-14 (+6°F)
Pour Point	D97	-2.2 (28 F) Max.	-23 (-10°F)
Flash Point	D92	149 (300 F) Min.	67 (152°F)
Viscosity @ 40°C	D445	4.00-5.50Cst	2.7Cst
Sulphur	D129	0.02% Max.	0.033%
Carbon Residue	D524	0.1% Max.	86.8%
Cetane Number	D613	48 Min.	46.7
Ash	D482	0.02% Max.	N/T
Free Glycerine	G.C.	0.03% Max.	N/Ap.
Total Glycerine	G.C.	0.2% Max.	N/Ap.
% Ester	G.C.	97.5% Min.	N/Ap.
Distillation in °C			
IBP		264 (508°F)	187 (369°F)
5		327 (622°F)	213 (416°F)
10		331 (628°F)	222 (431°F)
20		N/T	233 (451°F)
30		335 (636°F)	244 (471°F)
50		337 (638°F)	264 (507°F)
70		340 (644°F)	285 (545°F)
80		N/T	298 (568°F)
90		343 (650°F)	314 (597°F)
95		350 (662°F)	328 (622°F)
End		351 (664°F)	338 (640°F)

N/T = Not tested, N/Ap = Not applicable, G.C. = Gas Chromatograph

injection pump deteriorated when exposed to biodiesel. These components were replaced with either viton (fluorinated rubber), steel, aluminum, or nylon reinforced tubing.

Results and Discussion

Fuel efficiency during biodiesel fueling fluctuated, depending on how the pickup was operated. The overall fuel economy for the 1991 pickup was 7.0 km/L (16.9 mile/gal) and for the 1992 pickup was 6.8 km/L (16.3 mile/gal). The highway fuel economy while the vehicles were operating on 100% biodiesel as compared to diesel fuel was 9.5 km/L (22.8 mile/gal) vs 9.9 km/L (23.9 mile/gal). Biodiesel fuel economy was nearly identical to that obtained when the engine was fueled with diesel fuel under comparable conditions. These data are summarized in Table 2.

Table 2. Operational data of the 1991 and 1992 Dodge pickups equipped with Cummins 6BT & 6BTA, 5.9L, direct injected engines fueled with Biodiesel.

Cummins Engine	1991 6BT 5.9L	1992 6BTA 5.9L
Fuel Economy Range	5.0-10.3 km/L (12-24.8 mile/gal)	3.7-9.5 km/L (8.95-23 mile/gal)
Total Pickup Travel Distance	89,888.0 km (55,854.0 mile)	82,658.0 km (51,361.0 mile)
Travel Distance on Biodiesel	85,060.0 km (52,854.0 mile)	80,243.5 km (49,861.0 mile)
Engine Run Time	1524.8 h	1259.3 h
Total Fuel Consumption	10,450.4 L (2,760.7 gal)	9,562.3 L (2,526.1 gal)
Fuel Economy	7.0 km/L (16.9 mile/gal)	6.8 km/L (16.3 mile/gal)
Fuel Flow	7.2 L/h (1.9 gal/h)	8.3 L/h (2.2 gal/h)

The engine lubricating oil analyses indicated that engine wear was normal. The levels of chromium, copper, silicon, and iron were either below or the same as expected when fueled on diesel fuel. No abnormal coking was noted on the injectors, on top of the pistons, on cylinder walls or on the valve stems when the engine was visually examined using a boroscope. The engine did not appear to be wearing at an accelerated rate.

Table 3 presents the engine oil analysis. These data were compared with engine lubricating oil samples taken from diesel powered farm tractor engines (Schumacher et al., 1991). As noted by Schumacher (1995), the analysis of the oil samples for the 1991 and 1992 5.9L engines was not statistically different. Data from the pickups were subsequently combined and analyzed to determine if differences existed between the pickup engines and farm tractor engines. The tractor engine oil samples that had greater than 113 h of use were excluded from this analysis. These samples were excluded since none of the pickup oil samples had been used in excess of 113 h. Note that the number of hours on the lubricating oil is not statistically different between groups. As noted by Schumacher in previous analysis, chromium and copper engine wear metals were not significantly different. Levels of iron, lead, and silicon were statistically different when compared to the oil samples that were taken from engines that had been fueled with diesel fuel.

Table 3. T-test analysis between engines grouped by tractor and pickup.

Wear metal		N	Mean (ppm)	StDev (ppm)	t-value	t-prob.
Iron	(T)	62	39.40	26.47	8.24	0.000
	(P)	90	9.77	12.11		
Lead	(T)	62	10.10	10.47	5.84	0.000
	(P)	90	1.99	3.82		
Copper	(T)	62	9.44	29.98	1.29	0.200
	(P)	90	4.33	9.72		
Chromium	(T)	62	3.16	3.74	1.96	0.052
	(P)	90	1.90	4.12		
Silicon	(T)	62	4.82	2.79	8.42	0.000
	(P)	90	1.50	1.66		
Hours on oil	(T)	62	55.97	34.24	0.67	0.506
	(P)	90	52.52	26.47		

T) Oil samples from farm tractors, operated on 100% diesel fuel.
P) Oil samples from Dodge pickups, operated on 100% methyl-ester soybean oil.

The date and hours on each engine at the time of each chassis dynamometer test can be found in Tables 4 and 5. Power (kW and hp) comparison tests were measured at 1700, 1900, 2100, 2300, 2500, & 2700 rpm. The engines were loaded at peak torque rpm and then the load was reduced allowing the engine to increase speed (at 200 rpm intervals) until the engine reached 2700 rpm. Fueling the engines with B100 initially increased engine power by 3% (1991 engine) and reduced power by 7% (1992 engine). Both pickups produced less power, however, during the January 1995 series of chassis dynamometer testing. This information is found in Tables 4 and 5.

Exhaust emission levels were analyzed by MU personnel in conjunction with the most recent dynamometer testing. A Nova Model 7550P5B engine exhaust analyzer (calibrated using appropriate span gases) was used for this analysis. Variables tested include CO, CO_2, HC, NO_x, O_2, and opacity. Several test values were recorded for each variable at each test point rpm. The values at each rpm were then averaged to determine an overall level for each variable during the test. These results, as well as the results from the emissions testing on 2/2/94, are summarized in Tables 6 and 7.

The 1991 truck performed as expected. Carbon monoxide, CO_2, and opacity were all reduced while NO_x increased. The measured HC values for the January '95 testing were unchanged. This was attributed to the emissions analyzer. Except for carbon monoxide, the 1992 truck also performed as expected. Carbon dioxide emissions were similar to those noted previously in the literature. Opacity fluctuated significantly during the February 1994 testing. As noted in Table 7, this variance was believed to be a result of

measurement error. The reduction in opacity noted during the January 1995 testing was similar to data reported in the literature. As with the 1991 truck, the measured HC values did not change. Oxides of nitrogen levels and carbon monoxide levels for the 1992 truck increased. While the oxides of nitrogen increase was expected, the carbon monoxide increase was not. The CO increase was quite small and was not significantly different.

Table 4. Power tests produced by a 1991 5.9 L turbocharged, direct injected, Cummins diesel engine.

Engine Speed (rpm)	Test Date	Power #2 Diesel kW	Power #2 Diesel hp	Power Biodiesel kW	Power Biodiesel hp	% Change from #2 Diesel
1700	A	87.9	118.0	93.2	125.0	+5.9
	B	77.7	104.2	78.8	105.7	+1.4
	C	96.2	129.1	95.2	127.7	-1.1
1900	A	96.9	130.0	102.2	137.0	+5.4
	B	88.2	118.3	89.3	119.8	+1.3
	C	103.4	138.6	104.7	140.4	+1.3
2100	A	106.6	143.0	110.4	148.0	+3.5
	B	99.6	133.6	99.2	133.0	-0.4
	C	113.4	152.1	110.5	148.2	-2.6
2300	A	114.1	153.0	116.3	156.0	+2.0
	B	110.1	147.7	104.2	139.7	-5.4
	C	121.9	163.5	116.3	156.0	-4.6
2500	A	114.8	154.0	120.1	161.0	+4.5
	B	108.4	145.3	104.1	139.6	-3.9
	C	121.9	163.5	120.0	160.9	-1.6
2700	A	56.7	76.0	55.2	74.0	-2.6
	B	45.7	61.3	42.7	57.2	-6.7
	C	74.2	99.5	68.4	91.7	-7.8

A) Dyno test on 5/29/92, 507 hours on engine.
B) Dyno test on 2/2/94, 1155 hours on engine.
C) Dyno test on 1/4/95, 1436 hours on engine.

Table 5. Power tests produced by a 1992, 5.9 L turbocharged. direct injected, aftercooled, Cummins diesel engine.

Engine Speed (rpm)	Test Date	hp Power #2 Diesel kW	hp Power #2 Diesel hp	hp Power Biodiesel kW	hp Power Biodiesel hp	% Change from #2 Diesel
1700	A	85.8	115.0	79.8	107.0	-7.0
	B	66.1	88.7	56.5	75.9	-14.4
	C	78.9	105.8	80.8	108.4	+2.5
1900	A	96.9	130.0	89.5	120.0	-7.7
	B	81.1	108.8	71.0	95.2	-12.5
	C	90.9	121.9	88.9	119.2	-2.2
2100	A	105.9	142.0	101.4	136.0	-4.2
	B	90.1	120.8	74.0	99.2	-17.9
	C	96.6	129.5	95.5	128.1	-1.1
2300	A	106.6	143.0	102.9	138.0	-3.5
	B	97.9	120.8	83.9	112.5	-14.3
	C	99.5	133.4	94.8	127.1	-4.7
2500	A	104.4	140.0	96.9	131.0	-7.1
	B	95.7	131.3	82.2	110.2	-14.1
	C	97.3	130.5	93.3	125.1	-4.1
2700	A	60.4	81.0	57.4	77.0	-4.9
	B	44.3	59.4	44.3	59.4	0.0
	C	50.5	67.7	48.5	65.0	-4.0

A) Dyno test on 5/29/92, 5 hours on engine.
B) Dyno test on 2/2/94, 790 hours on engine.
C) Dyno test on 1/10/95, 1145 hours on engine.

Table 6. Exhaust emissions produced by a 1991 5.9L turbocharged, direct injected Cummins diesel engine (2/2/94 and 1/4/95) while fueled with 100 percent biodiesel and 100 percent low sulfur diesel fuel.

Variable	2/2/94 Diesel	2/2/94 B100	2/2/94 %Change	1/4/95 Diesel	1/4/95 B100	1/4/95 %Change
Carbon Monoxide, %	0.025	0.013	-47.2%	0.029	0.022	-24.1%
Carbon Dioxide, %	7.2	7.1	-0.8%	7.8	7.8	-0.5%
Hydrocarbons, ppm	6.6	5.4	-17.4%	10.0	10.0	0.0%
Nitrogen oxides, ppm	639.7	768.6	20.1%	967.0	106.3	9.9%
Oxygen, %	10.7	10.9	1.2%	10.3	10.5	2.0%
Opacity, %	3.3	1.4	-58.2%	2.8	1.8	-35.8%

Table 7. Exhaust emissions produced by a 1992 5.9L turbocharged, direct injected, aftercooled, Cummins diesel engine (2/2/94 and 1/10/95) while fueled with 100 percent biodiesel and 100 percent low sulfur diesel fuel.

	2/2/94			1/10/95		
Variable	Diesel	B100	%Change	Diesel	B100	%Change
Carbon Monoxide,%	0.015	0.019	25.0%	0.023	0.024	4.3%
Carbon Dioxide, %	6.6	6.4	-4.1%	7.4	6.9	-6.4%
Hydrocarbons, ppm	6.3	4.3	-31.0%	10.0	10.0	0.0%
Nitrogen oxides, ppm	635.7	681.1	7.1%	671.0	709.2	5.8%
Oxygen, %	11.3	11.8	5.0%	11.9	11.0	8.5%
Opacity, %	1.9	2.4	27.2%*	1.4	1.2	-15.4%

*This data point is believed to be a result of measurement error.

Conclusions

The following conclusions were drawn from the investigation:

1. The fueling of compression ignition engines on 100 percent biodiesel slightly reduced the power when compared to the power developed when fueled with fossil diesel fuel. This was also noted in our review of literature.

2. The specific power developed by a compression ignition engine fueled on 100 % biodiesel will vary depending on engine design and fuel delivery. Differences in the test results of the two engines continue to surface during each subsequent test.

3. Nitrile rubber OEM fuel lines and other fuel line components made out of nitrile rubber deteriorate rapidly when fueling an engine with 100% biodiesel.

4. CO, HC, particulate matter, and smoke exhaust emissions tend to be lower when fueled on biodiesel than when fueled on diesel fuel. NO_x exhaust emissions tend to be higher when fueled on 100% biodiesel.

5. Materials from engine wear were found to be lower in the analysis of the engine lubricating oil (Fe, Pb, Si) when the engine was fueled on 100% biodiesel as compared to petroleum diesel fuel.

Recommendations

1. Nitrile rubber OEM fuel lines and other rubber fuel line components should be replaced before fueling an engine with 100% biodiesel.

2. Additional research is needed to examine fuel line component compatibility with 100% biodiesel.

3. Research should be conducted to determine the most efficient means of reducing NO_x exhaust emissions when fueling with 100% biodiesel. As noted by Feldman and Peterson, an adjustment of the timing of the engine was beneficial when optimizing the engine for biodiesel fueling. Fuel injection timing should be evaluated closely as a means of reducing NOx emissions.

4. Research should be conducted to determine how HC, CO, and PM emissions change after the engine has been fueled in the real world for extended periods of time.

5. Engine lubricating oil analysis data collection should be replicated. Findings over time clearly suggest that lubricating oil samples taken at regular oil change intervals contain low levels of engine wear materials (when compared to standards previously established for petroleum diesel fuel).

References

Feldman, M. E. and Peterson, C. L. (1992). Fuel injector timing and pressure optimization on a DI diesel engine for operation on biodiesel. *Liquid Fuels From Renewable Resources - Proceedings of an Alternative Energy Conference*. Nashville, TN.

Krahl, J. G., Vellguth, G. And Munack, A. (1994). Ubersicht von Arbeiten zum Einsatz von Rapsol und Rapsolmethylester als Kraftstoffe unter Berucksichtinung umweltrelevanter Ausirkungen. Institute Fur Biosystemtechnik, Federal Agricultural Research Center, Braunschweig, Germany.

Marshall, W. F. (1993). Effects of methyl esters of tallow and grease on exhaust emissions and performance of a Cummins L10 engine. Itt Research Institute, National Institute for Petroleum and Energy Research, Bartlesville, OK. (Report prepared for Fats and Proteins Research Foundation, Inc, Ft. Myers, Beach, FL)

Mittelbach, M. P., Tritthart, P, and Junek, H. (1985). Diesel fuel derived from vegetable oils, II: emission tests using rape oil methyl ester. *Energy Agriculture*. 4: 208-215.

Mittelbach, M. P., Tritthart, P. (1988). Diesel fuel derived from vegetable oils, III. Emissions tests using methyl esters of use frying oil. *Journal of the American Oil Chemists' Society*. 65(7): 1185-1187.

Niehaus, R. A., Goering, C. E. Savage, L. D., and Sorenson, S. C. (1985). Cracked soybean oil as a fuel for a diesel engine. ASAE Paper No. 85-1560. ASAE, St. Joseph, MI.

Reece, D. L. and Peterson, C. L. (1993). A report on the Idaho on-road vehicle test with RME and neat rapeseed oil as an alternative to diesel fuel. ASE Paper No. 93-5018. ASAE, St. Joseph, MI.

Scholl, K. w. and Sorenson, S. C. (1993). Combustion of a soybean oil methyl ester in a direct injection diesel engine. SAE paper No. 930934. SAE, Warrendale, PA.

Schumacher, L.G., S.C. Borgelt, and W.G.Hires. 1995. Fueling a diesel engine with methyl-ester soybean oil. *Applied Eng. In Agr.* 11(1):37-40.

Schumacher, L.G., J.C. Frisby and W.G. Hires. 1991. Tractor PTO horsepower, filter maintenance and tractor engine oil analysis. *Applied Eng. in Agr.* 7(5):625-629.

Schumacher, L. G, Hires, W. G, and Borgelt, S. C. (1992). Fueling a diesel engine with methyl-ester soybean oil. *Liquid Fuels From Renewable Resources- Proceedings of an Alternative Energy Conference*. Nashville, TN.

Schumacher, L. G., Borgelt, S. C., Hires, W. G. and Humphrey, J. K. (1993). Biodiesel on the road- A report from Missouri. ASAE paper No. 93-5017. ASAE, St. Joseph, MI.

Schumacher, L. G., Borgelt, S. C., and Hires, W. G. (1993). Soydiesel/Biodiesel Blend Research. ASAE paper No. 93-6523. ASAE, St. Joseph, MI.

Srinivasa, R. P. and Gopalakrishnan, K. V. (1991). Vegetable oils and their methylesters as fuels for diesel engines. *Indian Journal of Technology*. 29: 292-297.

Ziejewski, M., Kaufman, K. R., Schwab, A. W, and Pryde, E. H. (1984). Diesel engine evaluation of an nonionic sunflower oil-aqueous ethanol microemulsion. *Journal of the American Oil Chemists Society*. 61 (10): 1620-1626.

AN ALTERNATIVE FUEL FOR URBAN BUSES - BIODIESEL BLENDS

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Abstract

Qualitative and quantitative biodiesel fueling performance and operational data have been collected from urban mass transit buses at Bi-State Development Agency in St. Louis Missouri. A total of 10 vehicles were selected for fueling; 5 - 6V92 TA Detroit Diesel engines have been fueled with a 20/80 biodiesel/diesel fuel blend and 5 - 6V92 TA Detroit Diesel control vehicles have been fueled on petroleum based low sulfur diesel fuel (LSD). The real-world impact of a biodiesel blend on maintenance, reliability, cost, fuel economy and safety compared to LSD will be presented. In addition, engine exhaust emissions data collected by the University of West Virginia Department of Energy (DOE) sponsored mobile emissions laboratory will be presented. Operational data from Bi-State Development Agency is collected by the University of Missouri and quality control procedures are performed prior to placing the data in the Alternative Fuels Data Center (AFDC). The AFDC is maintained by the National Renewable Energy Laboratory in Golden, Colorado. This effort, which enables transit operators to review a real-world comparison of biodiesel and LSD, has been funded by the National Biodiesel Board with funds provided by the United Soybean Board with national checkoff dollars and the National Renewable Energy Laboratory.

Introduction

The testing of biodiesel as a fuel for diesel powered transportation vehicles has been conducted in several locations across the United States since July, 1991. Little effort had been made to systematically, qualitatively, and quantitatively collect and record vehicle performance and operational characteristics. The collection of this information is essential to the commercialization of biodiesel in the United States.

Overview and Objectives

Vehicle performance, operation, and maintenance characteristics are used extensively during the commercialization of a transportation fuel. Information concerning the use of biodiesel as a transportation fuel is needed to provide legislators and agencies the knowledge to make informed decisions that will effect market development and impact the acceptance of biodiesel as a transportation fuel for diesel engines.

Specific objectives of the project included:

1. Establish cooperative relationships and collect qualitative and quantitative vehicle performance and operational data from a mass transit district.
2. Summarize retrieved information and format appropriately for the National Renewable Energy Laboratory (NREL) Alternative Fuels Data Center (AFDC) database.
3. Transfer data (ASCII format) electronically to NREL and place in the AFDC database (monthly).

Methods and Procedures

This project involved highly controlled data collection from one mass transit agency. Data were collected and compiled by researchers at the University of Missouri (MU). Data collected from the transit properties were compiled using Paradox, a relational database, and electronically transmitted using CCMAIL to the Alternative Fuels Data Center. The AFDC is an electronic database that is operated by NREL. The AFDC contains data collected from urban transit properties that are testing alternative fuels such as compressed natural gas (CNG), liquefied natural gas (LNG), methanol, ethanol, biodiesel, and in the very near future, propane.

Site Selection

As the managing agency of the AFDC, NREL has outlined several criteria that are to be used when selecting a mass transit agency to serve as a site for controlled data collection. The selected mass transit agency must be able to supply identical or comparable buses to ensure that good control vehicles are available. Characteristics that must be similar include length, engine model, mileage, transmission, weight, year, and chassis model. The mass transit agency should have an accurate, acceptable means of recording data. Finally,

NREL site selection is based on the overall ability to collect reliable data on the part of the operators and the ability to implement in-house quality assurance programs.

Biodiesel Blend Selection

Research conducted by Fosseen Manufacturing and Development (1993) suggested that the most appropriate blend when fueling the Detroit Diesel Corporation (DDC) 6V92 TA heavy duty engine was a 20/80 blend of biodiesel/diesel fuel. Based on their research, a 20/80 (%) blend (B20) was selected as the fuel of choice for the urban buses involved in this project. In their research, substituting 20 percent of the petroleum diesel with biodiesel substantially reduced the emissions of the engine while minimizing the incremental increase in fuel costs associated with biodiesel fueling.

Information Collection Procedures

Bi-State Development Agency, the regional transit agency of St. Louis, was selected as the host site for this data collection project. A total of 10 vehicles were selected for fueling: 5 - 6V92 TA DDC engines were fueled with a B20 biodiesel/diesel fuel blend and 5 - 6V92 TA DDC engines were fueled with petroleum based low sulfur diesel fuel (control group).

Visits were made to the cooperating mass transit agency to perform an initial vehicle inspection and explain both the importance of and how to accurately collect this information. All test buses are being used in normal daily service. Data were collected to determine the actual impact of a biodiesel blend on maintenance, cost, fuel economy and safety (In-service Data Collection, Table 1).

Several steps were taken to increase the quality and reliability of the information generated from this project. Unit injectors for fuel in each of the ten test buses were replaced with new unit injectors in April, 1994. At the close of the demonstration in September, 1995, selected unit injectors will be returned to DDC for examination by their analytical laboratory. Injectors were replaced to ensure that any problems that occurred could be attributed to the test conditions. In addition, each of the ten test buses were placed in Bi-State's warranty program. This in-house program allowed MU researchers to track every event that happened to the test buses. In addition, Bi-State designated one employee to oversee the implementation of the data collection program.

Data are currently being collected using Bi-State's existing operating, dispatching, maintenance, and fueling systems. The data are collected, reported weekly and forwarded to the University of Missouri Agricultural Engineering Department. Maintenance data are being coded by MU researchers according to type; scheduled, unscheduled, or road call. The work performed and parts replaced are coded using the American Trucking Association format to facilitate data entry and to allow the researchers to compare data from fleets that are testing other alternative fuels. Vehicle performance problems, route information, and safety data are being monitored by Bi-State and forwarded to MU.

Fuel has been sampled and will be analyzed by Analysts, Inc. after each new shipment of biodiesel and low sulfur diesel fuel has been delivered. Engine oil samples were taken

Table 1. In-service data collection variables for mass transit buses recorded in the Alternative Fuels Data Center database, National Renewable Energy Laboratory, Golden, CO.

Type of Data	Frequency Recorded	Data Items
Maintenance Data	For Each Work Order	Shop Order Number
		Repair Description
		Type of Maintenance -scheduled -unscheduled -road call
		Labor Hours
		Date of Repair
		Odometer Reading
		Parts Replaced
		Parts Cost
		Work Done
		Removed From Service
		Date Returned to Service
Fuel Data	Each Time a Bus is Fueled	Type and Amount of Fuel
		Odometer Reading
		Date
	Each Time the Bulk Fuel Storage is Refilled	One Sample of Biodiesel and Diesel Fuel Analyzed
Oil Data	Each Time Oil is Added	Make, Type, Viscosity of Oil
		Amount of Oil
		Odometer Reading
	Each Time Oil is Changed	Make, Type, Viscosity of Oil
		Amount of Oil
		Odometer Reading
		Oil Sample
Vehicle Deficiency Report	At Each Problem Occurrence	Standard Reporting
Bus Route and Operating Cycle Data	Each Day	Daily Route Assignments for Each Bus
Safety Data	As Needed	Number and Nature of Each Accident

using the approved sampling methodology. The oil samples were analyzed by an analytical laboratory and recorded by MU technicians.

Vehicle operating costs, maintenance costs, initial purchase price and vehicle salvage value is being monitored for each vehicle. These data provide an accurate assessment of the vehicle operating costs in actual fleet conditions and allows comparisons with other alternative fuels.

Treatment of Data

MU researchers have utilized macros within the Paradox relational database to check discrepancies within the data. Bi-State has been consulted when any discrepancies and/or inaccurate data has been noted.

Progress of Project

Although start-up for this project was planned for November, 1993, the actual start date was delayed until April 14, 1994 (the anticipated end date is September 15, 1995). The facility selection and the selection of the test buses were made in concert with DDC and NREL. Table 2 reports the buses that were selected for fueling.

Table 2. Bi-State Development Agency bus number, fuel, and mileage after rebuild for the NREL data collection sponsored by the National Biodiesel Board and the National Renewable Energy Laboratory.

Bus Number	Fuel	Mileage after Rebuild	Kilometers after Rebuild
8441	B20	37,155	59,795
8443	B20	33,600	54,074
8452	B20	13,959	22,465
8447	B20	20,546	33,066
8449	B20	10,938	17,603
8446	LSD	33,140	53,334
8450	LSD	12,175	19,594
8451	LSD	36,830	59,272
8455	LSD	29,653	47,722
8529	LSD	57,522	92,573

Each bus selected was powered with a DDC 6V92 TA two stroke engine utilizing a turbocharger and a blower. Nine of the engines were manufactured in 1988. One engine was manufactured in 1989. Each engine was rated at 277Hp at 2100 rpm and developed 880 ft-lbs of torque at 1200 rpm. Each bus had an Allison V731 transmission, was 40' in

length, had a curb weight of 27,500 pounds and a GVWR of 39,500 pounds. Each bus engine had been rebuilt and had less than 93,300 kilometers (58,000 miles) on the engine rebuild. New unit injectors were installed in all ten of the bus engines. The change-out of these injectors was done at the request of DDC. Each vehicle selected has been tracked via Bi-State Development's maintenance tracking program. Previous maintenance records have been noted and recorded for comparison purposes. The mean number of km on the buses after rebuild was 45,950 km.

Fuel economy for the buses can be observed in Table 3. The overall average fuel economy is slightly lower for the biodiesel fueled buses. The total miles driven by the diesel powered buses is approximately 18 percent higher. The biodiesel powered buses have not been driven on the week-ends and consequently have traveled fewer miles.

Table 3. Fuel economy and total miles by bus number for the National Biodiesel Board and National Renewable Energy Laboratory sponsored bus data collection at Bi-State Development Agency (1/27/95).

Bus Number	Blend	Average Fuel Economy (mpg) 4/14/94-1/27/95	Total Miles
8441	B20	3.52	37,539
8443	B20	3.56	35,991
8452	B20	3.99	37,390
8447	B20	3.49	35,916
8449	B20	3.70	35,298
	Total miles driven		182,134
	Average fuel economy (mpg)		3.65
8446	LSD	3.76	46,349
8450	LSD	3.69	29,718
8451	LSD	4.14	49,633
8455	LSD	3.93	45,573
8529	LSD	3.84	44,455
	Total miles driven		215,728
	Average fuel economy (mpg)		3.87

The actual maintenance costs can be found in Table 4. The total costs associated with maintaining the diesel powered buses are lower than the buses that have been fueled with B20. The researchers anticipated that differences in maintenances costs could surface during the investigation. Maintenance costs, however, should be interpreted with caution due to the fact that these costs have varied much during the data collection.

Table 4. The maintenance costs for buses fueled for forty-two weeks on a twenty percent blend of biodiesel and petroleum diesel fuel. (4/15/94 -1/27/95).

Blend	Cost	Total Miles	Cost/ Mile	Cost/ Month
B20	$11,661.25	182,134	$0.0640	$1,203.14
LSD	$12,177.11	215,728	$0.0565	$1,256.37

Emissions Testing

In order to collect all of the data requested by NREL for this project, chassis dynamometer testing of the buses was conducted. The DOE Mobile Emissions Laboratory coordinated by West Virginia University was utilized to collect these data. Emissions tests were conducted during June of 1994 and during March of 1995. Wheel horsepower and fuel rate were recorded at rated and peak torque speed during the chassis dynamometer tests. The Central Business District (CBD) test cycle was used when collecting the data. Test results were recorded in grams per mile for the following: hydrocarbons, carbon monoxide, carbon dioxide, nitrogen oxides, and particulates. The results for the testing conducted on June 6, 1994 are reported in Table 5.

An examination of the emissions data yielded unexpected results. The PM levels did not change and the emissions of nitrogen oxides were nearly 10 percent lower when fueled on a B20 blend. If one examines the data without the data reported for bus number 8441 however, the data were more similar to data reported in the literature (Schumacher, et al, 1993). Examining the data without bus 8441 reveals a 2 percent increase in oxides of nitrogen and a 29 percent reduction in total particulate (PM).

Engine Lubrication Oil Analysis

The used lubrication engine oil analysis data were summarized for all diesel control and B20 fueled buses. The samples were taken when each engine was serviced. Approximately 12,000 miles of operation were placed on each oil sample. The oil analysis data are shown in Table 6.

Summary

The National Biodiesel Board and the National Renewable Energy Laboratory together with the University of Missouri Agricultural Engineering Department are collecting real world data that will be placed in the Alternative Fuels Data Center.

Bi-State Development Agency of St. Louis was selected as the site for a highly controlled data collection activity. Vehicles were selected and fueling began April 14, 1994. Fueling is scheduled to conclude September 15, 1995. NREL and DDC were actively involved in the site and vehicle selection process.

Table 5. Mobil Emissions Testing Conducted at St. Louis, MO, June 6, 1994 as a part of the NREL - NBB - DOE funded Biodiesel data collection project. Data were collected by West Virginia University using the CBD Test Cycle.

Bus Number	Blend	Grams per Mile CO	NOx	HC	PM	CO_2
8441	B20	29.4	15.6	1.6	3.09	3276
8443	B20	12.1	39.5	1.6	0.65	2851
8452	B20	29.5	37.2	1.7	1.38	3280
8447	B20	23.5	43.5	1.7	0.87	3335
8449	B20	22.7	38.9	2.0	1.16	3045
8446	LSD	23.3	38.3	3.2	3.10	3222
8450	LSD	35.0	39.8	1.6	1.28	2909
8451	LSD	42.2	42.5	1.8	1.24	3113
8455	LSD	26.5	41.3	2.2	1.09	2971
8529	LSD	14.5	32.9	1.7	0.44	2554
Average LSD		28.3	40.0	2.1	1.4	2954
Average B20		23.4	34.9	1.7	1.4	3157
% Change		-17.2	-10.3	-18.1	0.0	6.893

The buses have experienced small but observable differences in fuel economy and maintenance costs. Emergency road calls were few in number for both B20 and diesel fuel control buses. An analysis of the engine lubricating oil indicated that the wear metals normally found in the B20 fueled buses were mostly quite similar to the diesel control buses.

The emissions data collected by West Virginia University were quite similar to that found in the literature Fosseen and Goetz (1993) after examining the data without the B20 outlier. The unmodified DDC 6V92TA engines produced lower levels of carbon monoxide, hydrocarbons, and particulate matter. Slightly higher levels of nitrogen oxides were noted, however, the increase was not different from the emissions that were recorded for the diesel control buses.

Table 6. Averaged lubricating oil analysis results of the NREL - NBB - DOE funded Biodiesel data collection project.

Category	B20	LSD	Relative Change from LSD (LSD=100%)
Iron (ppm)	147.0	89.0	165
Chromium (ppm)	4.8	3.5	137
Lead (ppm)	14.5	19.5	74
Copper (ppm)	32.9	28.5	115
Tin (ppm)	5.9	4.0	148
Aluminum (ppm)	1.0	0.1	1000
Silicon (ppm)	17.4	19.0	92
Boron (ppm)	19.8	17.3	115
Sodium (ppm)	25.7	69.8	37
Magnesium (ppm)	555.0	559.2	99
Calcium (ppm)	995.0	1030.0	97
Barium (ppm)	3.0	3.3	91
Phosphorous (ppm)	1047.0	1053.3	99
Zinc (ppm)	1150.0	1197.5	96
Molybdenum (ppm)	1.1	1.2	92
Vanadium (ppm)	4.7	49.9	9
Viscosity at 100°C	16.7	15.1	111
Solids % by wt.	0.7	0.7	100
Total Base Number	6.9	7.4	

Please note: The data are presented in whole numbers, the averages presented have been rounded to the tenth decimal point for comparison purposes.

Bibliography

Fosseen, D. and Goetz, W. (1993). Methyl soyate evaluation of various diesel blends in a DDC 6V-92. Fosseen Manufacturing and Development. Radcliffe, IA. (Report prepared for National Biodiesel Board, Jefferson City, MO)

Schumacher, L. G., S.C. Borgelt, and W.G. Hires. (1993). Fueling a 7200 John Deere tractor with blends of methyl ester soybean oil and petroleum diesel fuel. Proceedings of the Mid Central Conference Meeting. St. Joseph, MO. Paper #MC94-109. (40)

CONVERSION OF VEGETABLE OILS AND ANIMAL FATS INTO PARAFFINIC CETANE ENHANCERS FOR DIESEL FUELS

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Abstract

The two principal methods of producing biodiesel fuels are a) transesterification of vegetable oils and animal fats with a monohydric alcohol,and b) direct hydrotreating of tree oils,vegetable oils and animal fats.

The patented hydrotreating technology is based on the catalytic processing of biomass oils and fats with hydrogen, under elevated temperature and pressure conditions. The typical mix of hydrotreated products is as follows: 5-15% light distillate (naphtha),40-60% middle distillate (cetane), 5-15% heavy distillate and 5-10% burner gas. The naphtha fraction may be used as a gasoline supplement. The middle distillate is designed for use as a cetane booster for diesel fuels. Both heavy distillate and light hydrocarbon gases are usable as power boiler fuels.

Typically, the cetane enhancer would be admixed with diesel fuel in the range of 5 to 30% by volume. This new diesel blend meets the essential quality characteristics of the basic diesel fuel,for direct use in diesel engines without any modifications.

The basic hydrotreatment technology has been evaluated further in the laboratory on degummed soya oil, yellow grease and animal tallow. The preliminary findings suggest that the technology can provide efficient conversion of these materials into cetane enhancers for diesel fuels.

Introduction

Cetane number is a measure of the ignition quality of diesel fuel [1]. It is analogous to the Octane number for the rating of gasoline. Normal hexadecane, n-$C_{16}H_{34}$, has a Cetane Number rating of 100. The use of high Cetane Number fuel in diesel engines can be expected to provide lower emissions of pollutants. The present specification of Cetane Number of Canadian diesel fuel is only 40 minimum [2]. Higher Cetane Number in diesel fuel is achieved typically through the use of nitrate-based ignition additives and/or by more intensive refining of petroleum in the manufacture of diesel fuel [3].

The two principal methods of producing biodiesel fuels are a) transesterification of vegetable oils and animal fats with a monohydric alcohol, and b) direct hydrotreating of tree oils, vegetable oils and animal fats.

Most biomass oil can be esterified with methanol (or ethanol) into a suitable diesel fuel additive. The exception is tall oil, a product of the wood pulp industry; it can not be esterified efficiently because its specific chemical composition. In the use of ester-based fuels, the diesel engine has to be modified to accept the non-specification fuel product.

The proprietary Canadian technology is based the catalytic hydrogen treatment of biomass oils under elevated temperature and pressure conditions [4,5]. The basic technology is very similar to that practiced routinely in the petroleum refining industry. Unlike the conventional esterification approach, the hydrotreatment process does not produce any non-fuel hydrocarbon by-products.

Figure 1 illustrates the basic processing scheme. In commercial practice, it is contemplated that distillation would be applied to produce a naphtha cut (b.p. <200 deg.C), a middle distillate (200 deg.C <b.p. <340 deg.C), and a heavy end (b.p. >340 deg.C). The desired chemical profile of the hydrocarbon products obtainable from a specific feedstock can be manipulated by the choices of hydrotreatment conditions and/or by distillation cuts.

The cetane (middle distillate) product is paraffinic in nature. Typically, it has a Cetane Number of 55 to 90, depending on product design. It is anticipated that the blending of this cetane enhancer into standard (petroleum-based) diesel fuel would be in the range of 5 to 30% by volume.

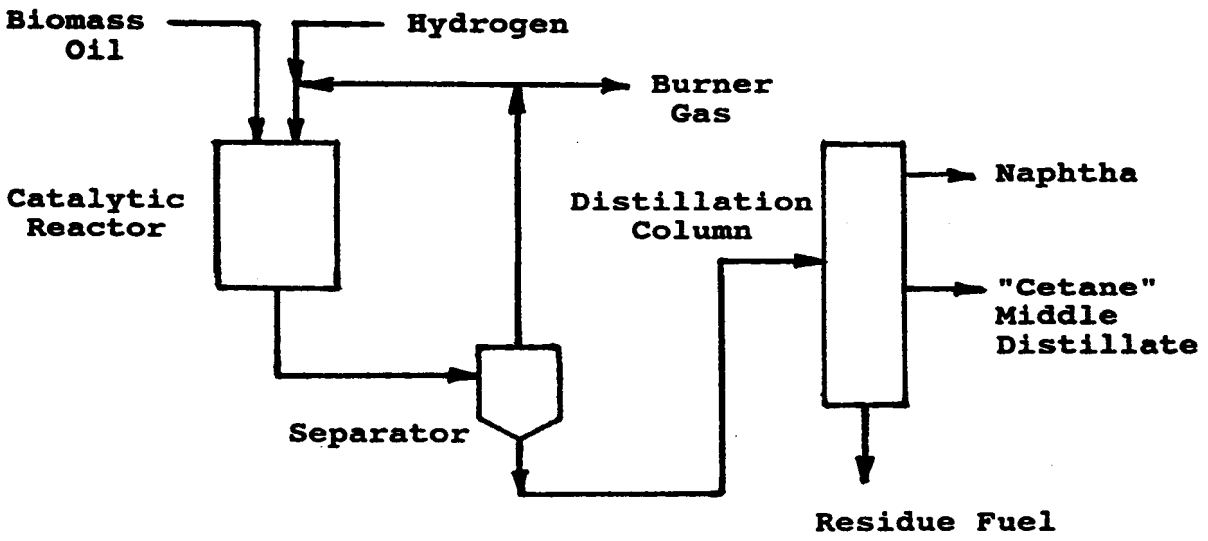

Figure 1 - Schematic of Canadian Hydrotreatment Technology for the Production of Cetane Enhancers for Diesel Fuels.

For both biodiesel production technologies,the feedstock cost is very important. Virgin vegetable oil is an expensive feedstock for biodiesel fuel production because of its normal use as food oil. For example,vegetable oil such as soyabean oil and palm oil is priced in the range of US$450 to US$500/tonne [6]. Even "off-spec" green canola oil may be priced at more than $300/tonne. The present economics of biodiesel fuel is heavily dependent on generous subsidies given to farmers for growing oilseed (non-food) crops and/or substantial concession on excise tax on fuel [7,8].

In previous papers,we have demonstrated tall oil [9] and canola oil [10,11] to be excellent feedstock for hydrotreatment into fuel-grade liquid hydrocarbons. In this study,we have investigated the feasibility of using degummed soya oil,and waste oils and fats as hydrotreatment feedstocks.

Experimental

Samples of biomass oil were hydrotreated at the micro-pilot plant at the laboratory of the Saskatchewan Research Council,Regina. The typical hydrotreatment operating conditions were 300 to 400 deg. C and 2 to 10 mPa. The samples tested are given in Table I.

Table I - Samples of Biomass Oil Tested

Type	Commercial Source
Degummed Soya Oil	Iowa,United States
Yellow Grease	Ontario,Canada
Animal Tallow	British Columbia,Canada

Typically,the neat hydrotreated sample was then analyzed using gas chromatography (GC) and gas chromatography-mass spectrometry (GC/MS) at the Arbokem Inc. laboratory in Vancouver. The GC and GC/MS test conditions used have been described elsewhere [12].

The feedstock oil was routinely saponified,and the resulting fatty acids were methylated with methanol in the presence of BF_3 catalyst. Pentadecanoic acid (C15:0) or heptadecanoic acid (17:0) ester was used as the internal standard. Hydrotreated samples did not require any derivatization. Tetradecane or hexadecane was used as the internal standard in the GC analysis of hydrotreated samples.

Results and Discussion

Degummed Soya Oil

This sample of degummed soya oil (DSO) was provided by the National Soydiesel Development Board (Jefferson City, MO). It is envisaged that degummed soya oil would be priced lower than degummed,refined soya oil,as a feedstock for cetane production.

The predominant fatty acids in the DSO were C18:1 (18.7%) and C18:2 (62.2%). As shown in Figure 2,C17 and C18 parafffins are the principal components of hydrotreated DSO. The normal paraffins in the range of C6 to C24 account for about 88% of the total hydrocarbons. Small amounts of branched/cyclic alkanes and alkenes were also detected in the hydrotreated liquid product. The middle distillate is estimated to have a Cetane Number >90.

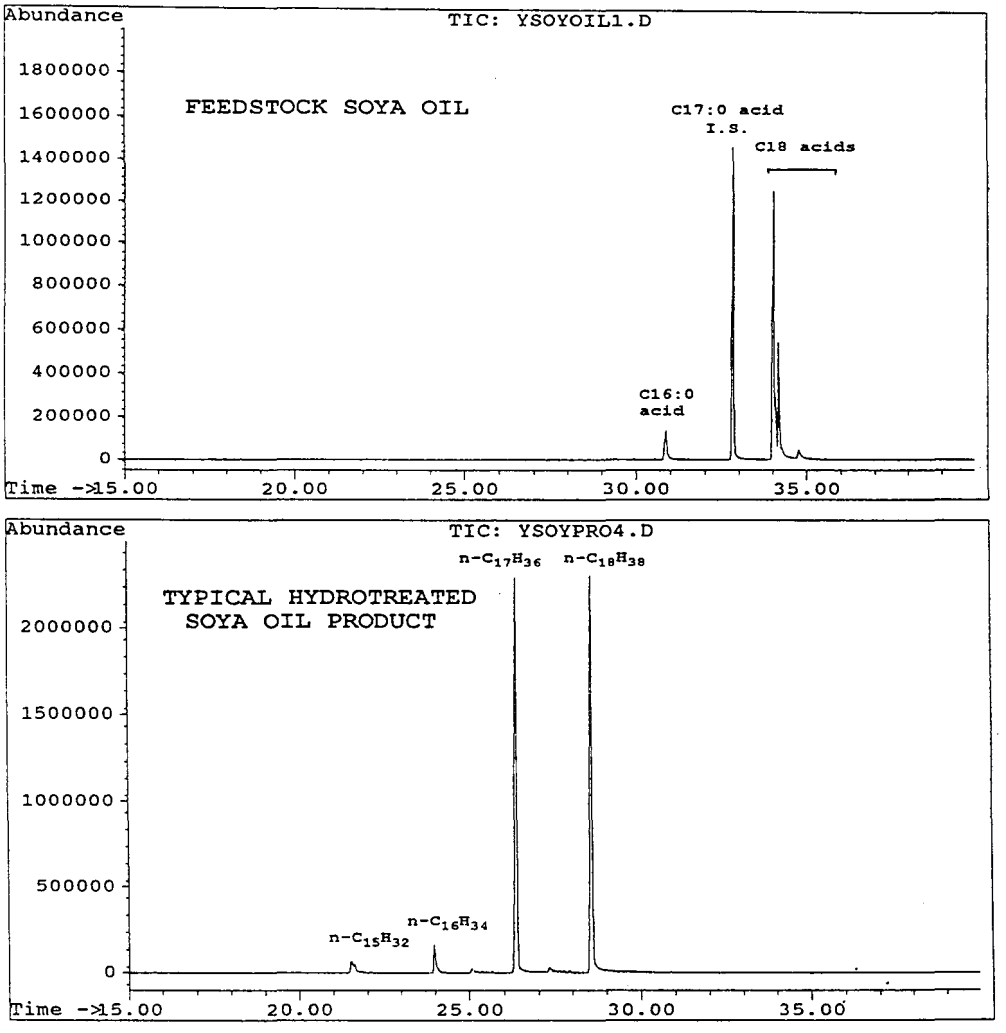

Figure 2 - Typical GC Traces of Degummed Soya Oil Before and After Hydrotreatment.

Yellow Grease and Animal Tallow

The yellow grease sample was provided by Rothsay Ltd. of Toronto. And the animal tallow sample was provided by West Coast Reduction Ltd. of Vancouver. The fatty acid composition of these two samples are given in Table II.

The normal paraffins as measured in the C6 to C24 range account for about 94% of the total liquid hydrocarbons produced from the hydrotreatment of yellow grease. Figure 3 shows the predominant normal paraffins to be heptadecane and octadecane. The middle distillate derived from this product is estimated to have a Cetane Number >90.

Table II - Fatty Acid Composition of Two Waste Products

Fatty Acid,%	Yellow Grease	Animal Tallow
C12:0	0.2	ND
C14:0	0.9	3.4
C14:1	ND	0.6
C15:0	ND	0.6
C16:0	14.1	25.4
C16:1	1.9	3.1
C17:0	0.4	1.7
C18:0	10.6	17.4
C18:1	57.8	41.2
C18:2	12.2	3.3
C18:3	0.4	ND
C20:0	0.5	0.5
C20:1	0.7	0.5
C22:0	0.3	0.3
Other	ND	1.9
Total	100.0	100.0

Note: ND = not detected

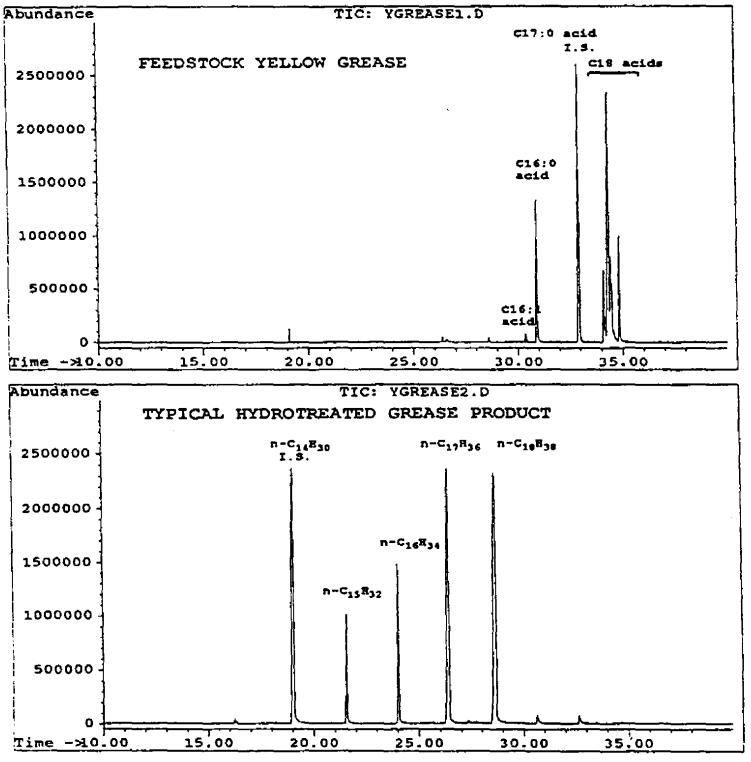

Figure 3 - Typical GC Traces of Yellow Grease, Before and After Hydrotreatment.

The hydrotreatment of animal tallow sample gave 92% yield of normal paraffins in the range of C6 to C22. As shown in Figure 4,the 4 principal peaks are C15,C16,C17 and C18 normal alkanes. The estimated Cetane Number of the corresponding middle distillate is >90. The presence of C15 and C16 normal alkanes would provide a beneficial lowering of the cloud point of the neat middle distillate.

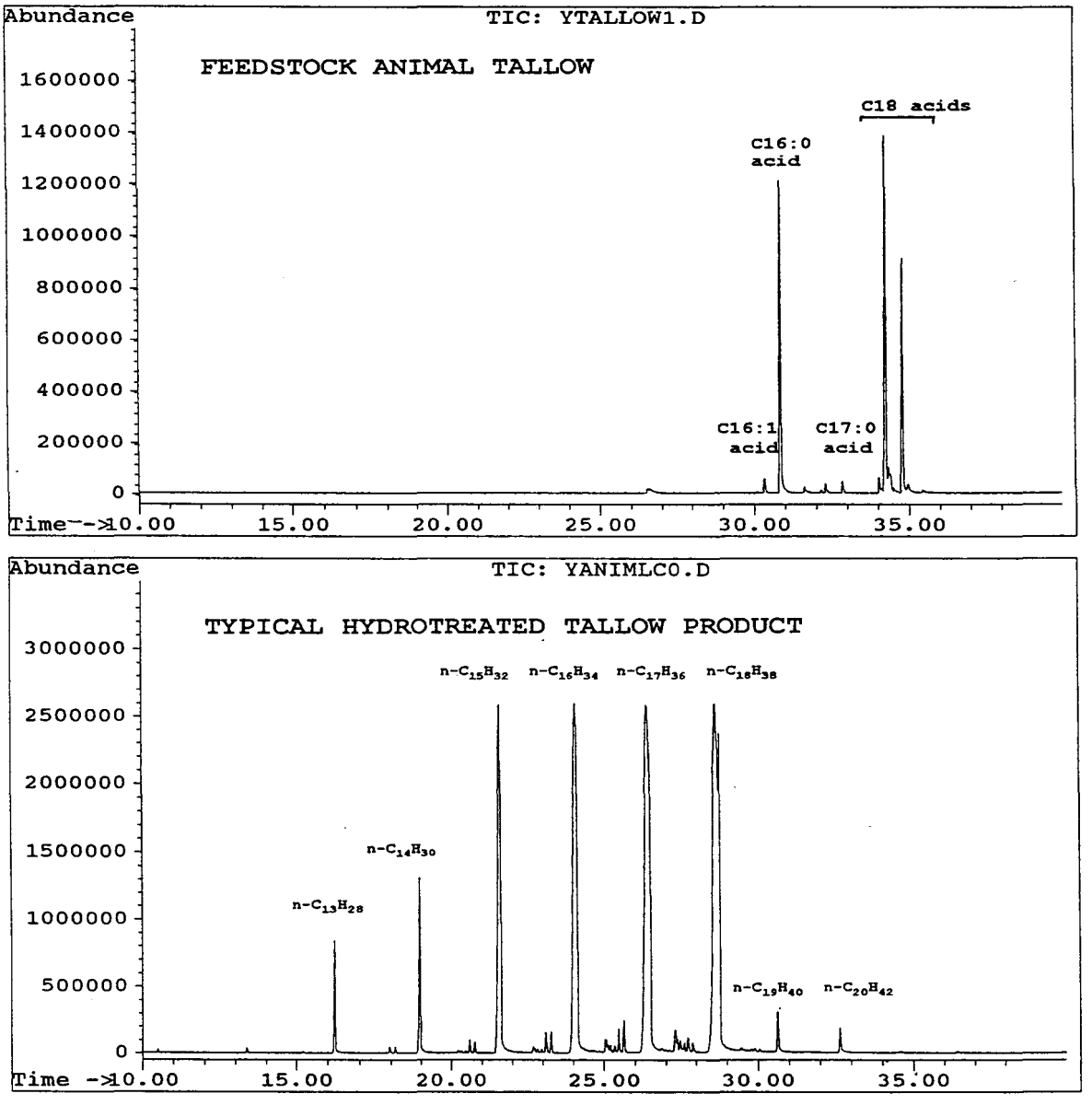

Figure 4 - Typical GC Traces of Animal Tallow Before and After Hydrotreatment.

Concluding Remarks

The novel hydrotreatment technology provides another means for the biomass oil industry to meet the increasing demand for cleaner-burning diesel fuels.

The present study demonstrated that various types of virgin and waste biomass oils can be used as feedstock for the production of cetane enhancers. In commercial practice,the neat hydrotreated product would be separated by distillation into specific fuel products. The middle distillate fraction with predominantly normal paraffins would have Cetane Number in excess of 90.

Acknowledgment

The skillful technical work of the staff of the Saskatchewan Research Council (SRC Regina) is recognized. The project work at SRC was funded by CANMET-Natural Resources Canada.

The cooperation of the Ag Processing Inc. (Sergeant Bluff,IA),National Soydiesel Development Board (Jefferson City,MO),Fats and Protein Research Foundation Inc. (Bloomington,IL),West Coast Reduction Ltd. (Vancouver,BC) and Rothsay Ltd. (Toronto,Ontario) in providing test samples are gratefully acknowledged.

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Literature Cited

1. ASTM D613-86,"Standard Test Method for Ignition Quality of Diesel Fuels by the Cetane Method".

2. Almdal,W.W. et al.,"All-Synthetic Diesel Fuel from Athabasca Bitumen: Properties,Testing and Operating Experience",Proc. ACS Division Fuel Chemistry Meeting, 34,4:1149-1159 (1989).

3. Stumborg,M. et al.,"Catalytic Conversion of Vegetable Oils to Diesel Additives",Proc. XVI Energy from Biomass and Wastes Conference,IGT,Orlando,FL,March 2-6,1992.

4. Craig,W. and Coxworth,E.,"Conversion of Vegetable Oils to Conventional Liquid Fuel Extenders",Proc. 6th Canadian Bioenergy R&D Seminar,Richmond,B.C.,February 16-18,1987.

5. Craig,W.K. and Soveran,D.W.,"Production of Hydrocarbons with a Relatively High Cetane Rating",U.S. Patent 4,992,605 (February 12,1991).

6. Chemical Marketing Reporter,May 1,1995.

7. Howell,S.,"Biodiesel Boom or Bust?",Proc. Bio-Oils Symposium,SCDC,Saskatoon,Canada,March 2-3,1994.

8. Korbitz,W.,"Status of BioDiesel Production in Europe", Proc. Bio-Oils Symposium,SCDC,Saskatoon,Canada,March 2-3, 1994.

9. Wong.,A.,"Tall oil-based cetane enhancer for diesel fuel", Pulp Paper Can. (in press,1995).

10. Wong,A. et al.,"Technical and Economic Aspects of Manufacturing Cetane-Enhanced Diesel Fuel from Canola Oil",Proc. Bio-Oils Symposium,SCDC,Saskatoon,Canada, March 2-3,1994.

11. Stumborg,M. et al.,1994. "Hydroprocessed Vegetable Oils for Diesel Fuel Improvement",paper presented at the 2nd Alternative Energy Conference: Liquid Fuels,Additives and Lubricants from Biomass,Kansas City,MO,June,1994.

12. Feng,Y. et al.,"Chemical composition of tall oil-based cetane enhancer for diesel fuels",Proc. 1st Biomass Conference of the Americas,Burlington,VT.,September,1993.

HYDROGENATED SOY ETHYL ESTER (HySEE) FROM ETHANOL AND WASTE VEGETABLE OIL

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Abstract

Biodiesel is gaining recognition in the United States as a renewable fuel which may be used as an alternative to diesel fuel without any modifications to the engine. Currently the cost of this fuel is the factor that limits its use. One way to reduce the cost of biodiesel is to use a less expensive form of vegetable oil such as waste oil from a processing plant. These operations use mainly hydrogenated soybean oil, some tallow and some Canola as their frying oils. It is estimated that there are several million pounds of waste vegetable oil from these operations. Additional waste frying oil is available from smaller processors, off-grade oil seeds and restaurants.

This paper reports on developing a process to produce the first 945 liters (250 gallons) of HySEE using recipes developed at the University of Idaho; fuel characterization tests on the HySEE according to the ASAE proposed Engineering Practice for Testing of Fuels from Biological Materials, X552; short term injector coking tests and performance tests in a turbocharged, DI, CI engine; and a 300 hour screening test in a single cylinder, IDI, CI engine.

Introduction

Due to increasing environmental awareness, Biodiesel is gaining recognition in the United States as a renewable fuel which may be used as an alternative to diesel fuel without any modifications to the engine. Biodiesel fuels can be produced from ethanol and vegetable oil, both agriculturally derived products. As such, they provide several advantages: they are renewable, they are safer, they are biodegradable, they contain little or no sulfur and they reduce engine exhaust smoke. Currently, the cost of this fuel is a primary factor that limits its use. One way to reduce the cost of Biodiesel is to use a less expensive form of vegetable oil such as waste oil from a potato processing plant.

Idaho produces approximately 120 million cwt of potatoes from over 152,000 ha annual. Nearly 60 percent of these are processed, the vast majority being made into french fried potatoes. These operations use mainly hydrogenated soybean oil, some beef tallow, and canola. It is estimated that there are several million pounds of waste vegetable oil from these operations each year. Additional waste frying oil is available from smaller processors, off-grade oil seeds and restaurants.

One of these processors, produces over 2 billion pounds of frozen potatoes per year at plants in Oregon, Idaho and North Dakota. This company built two ethanol plants in the late 1980's, which potato waste is the feedstock. One plant provides an opportunity for a Biodiesel facility using waste vegetable oil and ethanol to produce hydrogenated soy ethyl esters (HySEE). The market value of waste frying oils is about $0.11 per liter ($0.40 per gallon). Ethanol has a plant value of about $0.28 per liter ($1.05 per gallon). It is projected that this facility could produce Biodiesel at only slightly over $0.25 per liter ($1.00 per gallon) making it economically comparable to diesel fuel.

Biodiesel is being demonstrated as a motor fuel in an ongoing project entitled, "Demonstration of the On-the-Road Use of Biodiesel." This project is a cooperative effort between the University of Idaho and the Idaho Department of Water Resources. Hydrogenated soy ethyl ester (HySEE) has good possibilities for use as a diesel fuel substitute because:

- Biodiesel made from waste french fry oil may be cost competitive with diesel fuel and other diesel substitutes.
- Ethyl Esters may reduce emissions which may help open markets in urban areas.
- Ethyl Esters are made from ethanol and vegetable oil. They are therefore completely biomass derived products.
- Ethanol is nontoxic, making it safer to work with than methanol.

Objectives

1. Produce 1000 liters (250 gallons) of HySEE using the University of Idaho's Agricultural Engineering transesterification process.
2. Perform fuel characterization tests on the HySEE according to the ASAE proposed Engineering Practice for Testing of Fuels from Biological Materials, X552.
3. Conduct short term injector coking tests as reported in Korus, Jo and Peterson (1985) using HySEE with three replicate runs on a John Deere 4239T test engine. This test includes torque tests and mapping engine performance.
4. Conduct a 300 hour engine durability screening test using the Agricultural Engineering Department's Yanmar TS70C single cylinder diesel engines.

5. Compare regulated emissions data including total hydrocarbons (HC), carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NOx), and particulate matter (PM) for HySEE and diesel control fuel.

Materials and Methods

Fuel Production

The potato processing company supplied a sufficient amount of waste hydrogenated soybean oil to produce 1000 liters (250 gallons) of HySEE. This was produced at the University of Idaho's Agricultural Engineering Laboratory farm scale processing facility using a recipe developed by the Agricultural Engineering Department personnel. Phillips 66 Company low sulfur diesel reference fuel was used as the baseline fuel for the John Deere engine testing and emissions testing, and D2 from a local vendor was used for the 300 hour Yanmar engine testing.

Fuel Characterization

The fuels were characterized by evaluating the parameters required in ASAE EP X552. The tests for specific gravity, viscosity, cloud point, pour point, flash point, heat of combustion, total acid value, catalyst, and fatty acid composition were performed at the Analytical Lab, Department of Agricultural Engineering, University of Idaho. The boiling point, water and sediment, carbon residue, ash, sulfur, cetane number, copper corrosion, Karl Fischer water, particulate matter, iodine number, and the elemental analysis were performed at Phoenix Chemical Labs, Chicago Illinois. The high performance liquid chromatograph (HPLC) and titration analysis for total and free glycerol, percent of oil esterified, free fatty acids, and mono-, di-, and trigylicerides were performed by Diversified Labs Inc., Chantilly, Virginia.

Engine Performance Tests

All engine performance tests were conducted in the engine performance lab at the University of Idaho. The equipment used and tests conducted are described below. The short term tests were performed with an in-line four cylinder John Deere 4239T turbocharged, direct injected diesel engine. It has a displacement of 3.9 liters (239 cubic inches), a high RPM of 2650, 61 kW (82 hp) at 2500 RPM, and 290 Nm (214 ft lbf) torque at 1500 RPM. It is attached to a General Electric 119 kW (159 hp) cradle dynamometer. The engine was not modified in any way for use with renewable fuels.

A Hewlett Packard data acquisition unit (model 3497-A) and a personal computer were used to collect data every thirty seconds for each of the test. Torque, power, opacity, fuel consumption, and temperatures of various engine parameters were monitored throughout the testing and saved into a data file.

Fuel Flow Equipment

The fuel delivery and return lines were adapted with quick couplers for fast and clean changing of the fuels. Individual 19 liter (5 gallon) metal fuel tanks were modified with a fuel filter and flexible fuel lines which could be connected to the engine quick couplers. Fuel flow rate was determined by direct weighing. The fuel containers were placed on an electric 45.4 kg (100 lb) scale accurate to 23 grams (0.05 lb) with RS232 capability.

Opacity Meter

A Telonic Berkley model 200 portable opacity meter was connected to the data acquisition unit. The opacity meter consists of a light source positioned on one side of the exhaust stream and a

photo resistor mounted on the opposite side. The meter provides an output voltage ranging from 0 to 1.00 volts. One hundred percent opacity (1.00 volt) corresponds to no light transmission whereas 0 percent opacity (0.0 volts) corresponds to complete light transmission.

Injector Coking Test
Carbon build-up within the combustion chamber and ring belt area is a potential problem with alternative fuels. The injector coking test uses an easily removable part from the combustion chamber (the injector) and a short engine test to determine the carbon deposition on direct injection diesel nozzles. The injector coking tests were performed using the procedure described in "A Rapid Engine Test to Measure Injector Fouling in Diesel Engines Using Vegetable Oil Fuels" (Korus et al, 1985). The engine was operated for ten minutes at each interval for data collection.

Torque Tests
In addition to the injector coking test, a torque/horsepower test was triplicated. The torque tests were performed with the engine operating from 2600 RPM to 1300 RPM in 100 RPM increments with the same data collection procedure as previously described. The engine was operated for 2 1/2 minutes at each RPM for data collection.

Mapping Engine Performance
The engine mapping performance test was also triplicated. The engine mapping tests were performed using the procedure described in "Procedure for Mapping Engine Performance-Spark Ignition and Compression Ignition Engines" (SAE J1312, 1990). The mapping tests were performed at 2500, 2250, and 2000 RPM with loadings of 100, 75, 50, 25, and 0 percent of maximum power. The engine was operated for 5 minutes at each data collection interval.

300 Hour Engine Endurance Test with HySEE and Diesel
Two Yanmar TS70C single cylinder, 4-cycle, horizontal diesel engines were used for this test. These engines have a bore and stroke of 80 mm and 75 mm respectively, a displacement of 0.376 liter, a continuous rating output of 6 horsepower at 2200 RPM and a compression ratio of 21.2 to 1. The engines have a precombustion chamber combustion system and a condenser type cooling system with a cooling water capacity of 2.0 liters. The engines drive alternators which are connected to a pair of electric load banks. A timing circuit switches the load between the engines every twenty minutes. Each engine ran for 300 hours, one with 100 percent HySEE and the other, with 100 percent Number 2 diesel (D2). The testing began June 7 and ran continuously for 150 hours until June 13 with the exception of oil changes. The first 150 hours of testing was with both engines operating at the same load. The second 150 hours they operated at the same high RPM.

Emissions Testing
The emissions tests were conducted at the Los Angeles County Metropolitan Transit Authorities (MTA) Emissions Testing Facility (ETF) with a 1994 Dodge pickup which has a direct injected, turbocharged and intercooled, 5.9 L Cummins diesel engine. This facility has instrumentation to measure all regulated emissions: total hydrocarbons (HC), carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NOx), and particulate matter (PM). A comprehensive description of this facility is in Peterson et. al. (1994).

Procedures

Fuel Production
The HySEE fuel production process utilizes 70 percent stoichiometric excess ethanol (absolute, 100 percent pure), or a molar ratio of 5.1:1 ethanol to oil ratio. The total free fatty acids are determined and neutralized with the calculated addition of catalyst. Based on the amount of input

oil by weight, 1.3 percent of KOH is used plus the amount to neutralize the free fatty acids.

The waste hydrogenated soybean oil is heated to 49 degrees Celsius (120 degrees Farhrenheit). The catalyst is dissolved into the alcohol by vigorous stirring in a small reactor. The oil is transferred into the Biodiesel reactor and then the catalyst/alcohol mixture is pumped into the oil and the final mixture stirred vigorously for two hours. A successful reaction produces two liquid phases: ester and crude glycerol. Crude glycerol, the heavier liquid will collect at the bottom after several hours of settling. Phase separation can be observed within 10 minutes and can be complete within two hours after stirring has stopped. Complete settling can take as long as 20 hours. After settling is complete, water is added at the rate of 5.5 percent by volume of the oil and then stirred for 5 minutes and the glycerol allowed to settle again. After settling is complete the glycerol is drained and the ester layer remains. Washing the ester is a two step process which is carried out with extreme care. A water wash solution at the rate of 28 percent by volume of oil and 1 gram of tannic acid per liter of water is added to the ester and gently agitated. Air is carefully introduced into the aqueous layer while simultaneously stirring very gently. This process is continued until the ester layer becomes clear. After settling, the aqueous solution is drained and water alone is added at 28 percent by volume of oil for the final washing.

Engine warm-up and cool-down

Three different engine test protocols were followed using facilities at the University of Idaho. Each test started with a warm-up and ended with a cool-down period. The warm-up period consisted of a two minute interval on D2 at low idle. Then there was an eight minute interval with the fuel to be tested. During this eight minute period there is a gradual increase in load and RPM to the rated horsepower and load. The cool-down period consisted of 10 minutes on D2 at low idle. For both the warm-up and cool-down periods the return fuel line was placed into a separate container.

Engine Durability Screening Test

The two TS70C Yanmar engines used for the engine durability screening test were rebuilt prior to the beginning of the 300 hour test. New cylinder liners, pistons, rings and rod bearings were installed. The cylinder head was rebuilt and the head was thoroughly cleaned of all carbon deposits. The engine oil was changed and sampled every 50 hours of operation. The oil samples were sent to Cleveland Technical Center in Spokane, Washington for analysis. The engine valves were adjusted at each oil change interval during the first 150 hours of operation. At the end of the 300 hour test the engines were disassembled and inspected for evaluation of the effect of the fuel on engine components. Coking of the pintle injector, precombustion chamber and piston ring grooves were evaluated by inspection.

Emissions Testing

Two problems had to be overcome in developing a test design. The first was that the number of potential test runs was unpredictable. The test facility was scheduled for one week during which time all testing had to be completed. The second hurdle was a tendency for emissions to vary with ambient conditions. A randomized block design with unequal sample numbers was developed. In this design the main fuels were randomized and tested first and tests of fuel blends were included in later tests in each block. As it turned out, sufficient time was available to test each fuel and desired blends. Two runs of HySEE were included in the test design. The cycle used was the double arterial cycle of 758 seconds duration. Five test runs were included on the same cycle using Phillips low sulfur diesel control fuel. A Fisher's Protected LSD analysis using SAS (Statistical Analysis System) was carried out for the analysis of the data.

The emissions test procedure was as follows:

1. The test fuel delivery tube was connected to the input lines and the return line was connected to a waste tank. The engine was started and run for 50 seconds.
2. The engine was stopped and the return line was connected to the test fuel tank.
3. The engine was restarted and idled for approximately 10 minutes until the MTA technicians were ready to run the test.
4. The vehicle was operated under load until the operating temperatures stabilized.
5. The test was started and the cycle completed.
6. While the technicians were taking data, weighing particulate filters, etc., the fuel was switched to the next fuel to be tested.

Results

Fuel Production

Waste vegetable oil was obtained from the french fry plant owned by Simplot, Inc., Caldwell, Idaho. The waste oil was placed in drums and is solid at normal room temperatures. The oil is heated in the drums by electric heaters and is then transferred into the biodiesel reactor for transesterification. The ethanol-KOH mixture is added to the heated waste grease. The amount of ethanol and KOH must be adjusted upward to account for vaporization of the ethanol as it is heated and the free fatty acid content of the waste oil. Separation of the ester and glycerol is a constant problem. The final product produced in these tests was found to be 92.26% esterified and contained 0.3% glycerine, 0.99% total glycerine. Monoglycerides were 1.49%, diglycerides 4.23% and triglycerides 0.99%. Alcohol content was only 0.012%. The remaining catalyst measured 32 microg/gm.

Fuel Characterization

A complete summary of the fuel characterization data is listed in Table 1 for the HySEE and the reference diesel fuel used for this study.

Viscosity - HySEE had a viscosity 1.9 times that of D2.

Cloud and Pour Point - HySEE had a cloud point 19 degrees Celsius higher than D2 and a pour point 23 degrees higher than D2.

Sulfur - HySEE had 1.56 times less sulfur than the low sulfur diesel fuel used for comparison.

Heat of Combustion - HySEE has 12.3 percent less energy on a mass basis than D2. Since HySEE has a 4.1 percent higher specific weight, the energies average 8.2 percent lower on a volume basis.

HySEE has an apparent molecular weight of 306.95 compared to D2 at 198. As the molecular weight increases so do the cetane number and viscosity.

Injector Coking

A visual inspection of the injector tips would indicate no difference between the HySEE and diesel fuel. However, the numerical scales show that diesel has an injector coking index of one and HySEE has an index of 3.05 (for comparison in these tests, Rape Ethyl Ester had an injector coking index of 3.16) The coking index is an average of three runs, four injectors for the four cylinder

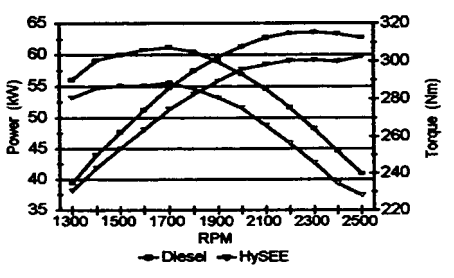

Figure 1. Power and Torque versus RPM

engine, and two orientations for a total of 24 samples averaged for each fuel (Table 2). The overall injector coking is low, especially when compared with older tests that included runs with raw vegetable oil.

Torque Tests

Figure 1 compares power and torque for HySEE and diesel fuel. HySEE has a 4.85 percent decrease in power compared to that of diesel at rated load. Peak torque is less for HySEE than for diesel but occurs at lower engine speeds and generally the torque curves are flatter. At 1700 RPM the torque is reduced 6 percent while at 1300 RPM it is reduced only 3.2 percent.

Percent opacity was 18.97 for diesel fuel at 1400 RPM and only 4.95 for HySEE at the same load. At the rated load the diesel fuel produced 2.5 times higher opacity than HySEE.

The following table is the average of the completed tests at 1500 RPM.

	HySEE	Diesel
Opacity (%)	4.7	11
Power (hp)	44 (59.6)	46 (61.7)
Torque N.m (ft-lb)	283 (209)	292 (215)
Fuel Consumption kg/min(lb/min)	0.20(0.45)	0.20(0.44)
Fuel Consumption L/hr(gal/hr)	14.1 (3.72)	14.11 (3.73)
Thermal Efficiency (%)	32.7	30.6

At 1700 RPM the torque output for the diesel was 227 foot pounds and 213 for the HySEE.

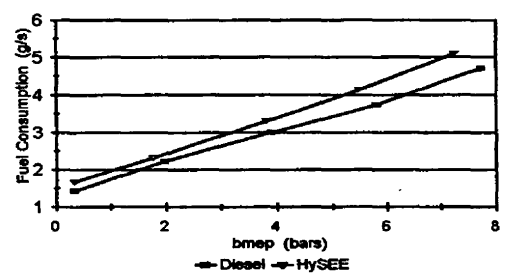

Figure 2. Fuel Consumption versus bmep at 2500 RPM

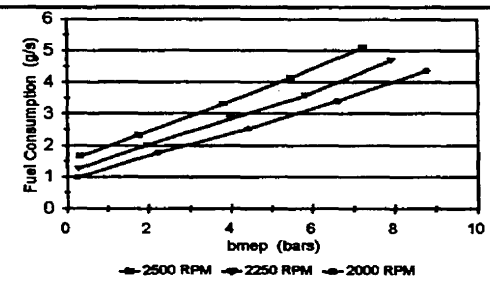

Figure 3. Fuel Consumption versus bmep for HySee at 3 RPM's from Engine Mapping Test

Mapping Engine Performance

Figure 2 presents an engine mapping graph for diesel fuel and HySEE at 2500 RPM. Figure 3 is the fuel map for HySEE at each of the three RPM's. Figure 4 is a graph of the thermal efficiency versus brake mean effective pressure. Brake mean effective pressure (bmep) is the theoretical constant pressure which can be imagined exerted during each power stroke of the engine to produce power equal to the brake power and is useful for comparing performance parameters in

engines. For a specific engine, as used in these tests, BMEP is directly related to power so these two graphs also show the fuel consumption as a function of increasing power.

Engine Durability Screening Test

HySEE Engine – The initial power was set at 2800 watts with the engine operating at 2100 RPM under a load condition and 2250 RPM under a no-load condition. During the second night of operation the ambient conditions were such that the HySEE gelled and shut the engine down for approximately two hours. A drum heater was added to the drum of fuel, a new fuel filter was installed and the engine was restarted. On June 30, the circuit breaker tripped and 19.4 hours were not logged on the hour meter. The engine was running at full RPM but was not loaded during this time. Ten hours, about one half of the time the circuit breaker was tripped, was added to the end of the test to compensate for the 19.4 hours for which there was no loading. On July 3 at 5:15 am the engine shut down again with the probable cause being cold weather gelling the fuel.

For the first 150 hours, when the engines were set at the same load, the engine high RPM under no-load condition was 2300 and under load was 2200 RPM. The engine produced a load of 2820 watts and consumed fuel at a rate of 0.299 gallons per hour.

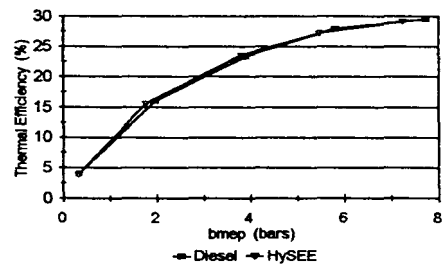

Figure 4. Thermal Efficiency versusbmep. Data is from the fuel mapping test at 2500 RPM

During the second half of the test, both engines were set at the same high RPM's, the engine high RPM under no-load condition was 2270 and under load was 2140 RPM. The engine produced a load of 2950 watts and consumed fuel at a rate of 1.1 liters per hour (0.3 gallons per hour). For the entire test a total of 344 leters (91 gallons) of fuel were consumed and 309 hours were logged. The engine was shut down and restarted twice for oil changes.

After completing the 300 hour endurance testing the engine was disassembled and inspected for wear and compared to the engine operating on 100% diesel fuel.

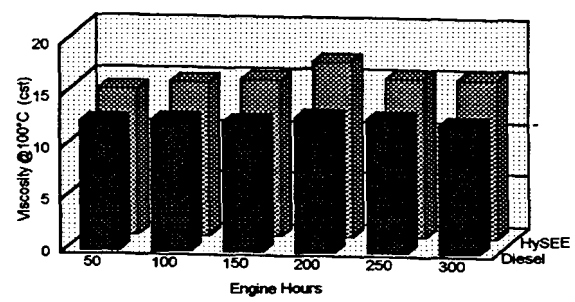

Figure 5. Engine oil viscosity at 50 hour oil change intervals

Diesel Engine – The initial power was set at 2800 watts with the engine operating at 2200 RPM under a load condition and 2300 RPM under a no-load condition.

During the 150 hours of the test, when the engines were set at the same load, the engine high RPM under no-load condition was 2300 and under load was 2200 RPM. The engine produced a load of 2820 watts and consumed fuel at a rate of 0.84 liters per hour (0.22 gallons per hour).

During the second half of the test, both engines were set at the same high RPM's, the engine high

RPM under no-load condition was 2270 and under load was 2160 RPM. The engine produced a load of 2860 watts and consumed fuel at a rate of 0.84 liters per hour (0.22 gallons per hour). For the entire test 255 liters (67.5 gallons) of fuel were used and 302 hours were logged. The engine was shut down and restarted twice for oil changes.

The HySEE diesel engine consumed 25% more fuel than that of the diesel fueled engine. The HySEE fueled engine shutdown twice, presumably due to cool weather, and produced a significantly greater amount of visible exhaust smoke.

The engine oil analysis for the diesel engine indicated no abnormal conditions. The engine oil analysis for the engine fueled with HySEE at each interval indicated no abnormal conditions except at the 200 hour interval. The engine oil viscosity was reported as being in the SAE 50 range while the base oil is 15W-40. Figures 5, 6, and 7 are graphs of the viscosity, iron and silicon versus engine hours from the oil analysis. The higher iron concentration may be due to the higher silicon concentration in the HySEE engine.

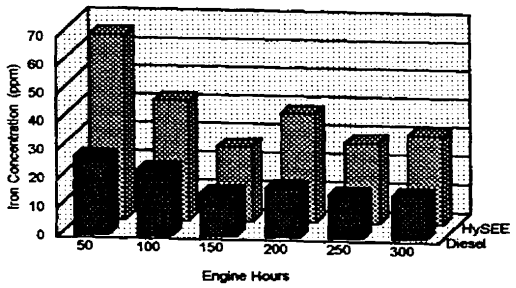

Figure 6.
Concentration of iron in engine oil analysis

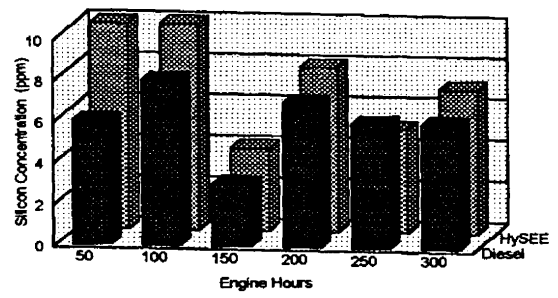

Figure 7.
Concentration of silicon in engine oil analysis

Engine Disassembly

At the completion of the 300 hour endurance test the two engines were disassembled and inspected. The first two piston ring grooves of the diesel fueled engine had slightly more carbon build-up than did the HySEE fueled engine. The second two piston ring grooves were identically clean. The top three piston ring groove surfaces for the diesel fueled engine showed more wear than the HySEE fueled engine and the oil ring (bottom ring) showed more wear. The piston rings were equally free in both engines. The deposits on the piston head were black to gray on the diesel fueled engine and black for the HySEE fueled engine with each having equal amounts of carbon build-up. The HySEE fueled intake valve had more deposits in the stem area than did the diesel fueled engine, other than that the intake and exhaust valves looked similar. No other differences in the engine components were observed.

Emissions Tests

The summary data for the two 100% HySEE arterial tests and five 100% diesel tests are shown in the following table.

Fuel	HC gm/mile	CO gm/mile	NOx gm/mile	CO_2 gm/mile	PM gm/mile
Diesel	0.823	3.33	6.27	654.91	0.3050

Diesel	0.757	3.20	6.21	646.75	0.2364
Diesel	0.751	2.90	6.19	651.32	0.2638
Diesel	0.849	3.20	6.25	649.23	0.3124
Diesel	0.837	3.24	6.25	650.16	0.3213
HySEE	0.360	1.69	5.35	655.90	0.3364
HySEE	0.373	1.73	5.26	652.44	0.3200
Diesel Average	0.803	3.17	6.23	650.47	0.2878
HySEE Average	0.367*	1.71*	5.31*	654.17	0.3282

*Numbers followed by an asterisk are significantly different from diesel ($p<.05$).

On the average HySEE showed a slight reduction in NOx, a significant reduction in HC and CO, and a slight increase in PM and CO_2. The PM data, even though different, was sufficiently variable that it was not statistically significantly different from diesel.

CONCLUSIONS

A complete set of fuel characteristics for HySEE and diesel are presented. Performance tests demonstrated that HySEE can be used to successfully fuel a diesel engine. In general, the testing performed has shown that torque and power are reduced about 5 percent compared to D2 and fuel consumption is increased 7 percent.

Specific conclusions of this study are:

1. Fuel characterization data show some similarities and differences between HySEE and D2. a) Specific weight is higher for HySEE, viscosity is 1.9 times that of D2 at 40°C (104°F), and heat of combustion is 12% lower than D2. b) Sulfur content For HySEE is 36% less than D2.
2. The average HySEE injector coking index was 3.07 and D2 was 1.00. Visually, all injector coking was low especially compared with older tests that included raw vegetable oils.
3. Opacity was decreased by as much as 71 percent compared to D2.
4. At rated load, engine power produced by HySEE decreased by 4.8 percent compared to D2.
5. Peak torque for HySEE at 1700 RPM was reduced by 6 percent compared to D2 while at 1300 RPM it was reduced only 3.2 percent, demonstrating a flatter torque curve characteristic of Biodiesel.
6. The average fuel consumption (g/s) on a mass basis was 7 percent higher than that of D2. The differences in fuel consumption and power reflect the differences in heat of combustion and density between the two fuels.
7. Thermal efficiencies for HySEE and D2 were not significantly different.
8. Emissions tests showed a 54 percent decrease in HC, 46 percent decrease in CO, 14.7 percent decrease in NOx, 0.57 percent increase in CO_2 and a 14 percent increase in PM when HySEE was compared to D2. The HC, CO and NOx differences were statistically significant.

References

References cited available on request to the authors.

PRODUCING BIODIESEL FOR THE "TRUCK IN THE PARK" PROJECT

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Abstract

One of the principal advantages of Biodiesel is it's environmental compatibility. It's biodegradability and reduced toxicity make it an ideal candidate fuel for environmentally sensitive areas. Biodiesel has potential as a fuel for equipment operating in or near waterways, sensitive wildlife habitat and other environmentally sensitive areas. The national park system has a mandate to maintain the environment in the areas they supervise. Use of Biodiesel could be one more tool in achieving that goal.

This paper is a progress report of a joint project between the University of Idaho, The Montana Department of Natural Resources and Conservation, Wyoming Department of Energy, the PNW and Alaska Regional Bioenergy Program, Chrysler Corporation and the National Park Service to fuel an on-road vehicle for service in Yellowstone National Park. A 5.9L Cummins powered Dodge pickup, supplied by Dodge Truck, is being operated by NPS with fuel produced by the University of Idaho. Tests include regular dynamometer testing, emissions tests, injector coking analysis, oil analysis, detailed operational records and fuel characterization tests according to the ASAE proposed Engineering Practice for Testing of Fuels from Biological Materials, X552.

Introduction

In 1993, 7.5 million people visited Montana, a state with about 830,000 residents. Many of these visitors came to Montana for its recreational amenities, including access to two major national parks, Yellowstone and Glacier. Their impact on its transportation energy use profile, is significant. As of yet, comparatively little research has been done either nationally or regionally concerning alternative fuel use in the recreational or tourist sector. It is obvious that areas of great natural beauty may in the long term be damaged by the effects of transportation fuel use. This is especially true for the national parks and other high-use areas in the western region of the U. S.

This project will address the environmental impact of Biodiesel use in tourism. The Montana Department of Natural Resources and Conservation (DNRC) in cooperation with the National Park Service (NPS) and the U.S. DOE Pacific Northwest and Alaska Regional Bioenergy Program will conduct an operational demonstration of a diesel truck powered by rape ethyl ester (REE). This fuel is produced by the University of Idaho (U of I) for use in tourism-related service in Yellowstone National Park. DNRC will assist the Park Service and private industry in developing options for managing the impact of the growth in tourism while preserving scenic resources. This demonstration is intended to:

- Help NPS and private industry develop options for reducing enviromental degradation without decreasing visitation to Yellowstone National Park.

- Support development of a process to convert vegetable oil into a transportation fuel.

- Encourage the development, production and use of this biofuel within the region by providing a beachhead market for a developing industry.

- Determine the extent and probable impact, benefits and concerns of using biodiesel in environmentally sensitive areas, and its interaction with other diesel fuel additives used in Yellowstone National Park.

- Determine the feasibility of using biodiesel at high elevations and cool temperatures at the beginning and end of the tourist season in Yellowstone National Park.

- Initiate a cooperative working relationship regarding alternative fuels among NPS, DNRC, the University of Idaho, and the U.S. DOE Regional Bioenergy Program.

Because of the value of consumers and tourist service providers place on the environment and recreational amenities, cleaner, less odoriferous fuels such as biodiesel, have the potential to compete with conventional diesel fuel. The biofuel developed by U of I is at the stage of development where a higher value market, such as this tourist-related application, is the next logical step on the way to commercialization.

Some previous market research supports investment in this and in future alternative fuel projects. First, the project will reach large numbers of tourists whose home towns have air quality problems. A 1989 survey of 600 guests at one of the lodges in Yellowstone National Park by Mings and McHugh (1989) of Arizona State University found that visitors to the

Park tended to come from large population states -- California, Illinois, and from nearby states -- Utah and Colorado. These states have large metropolitan areas that are non-attainment for air quality standards. Yellowstone Park is an ideal location to expose a large number of visitors to more environmentally benign fuels that could improve their experience, the air quality, and the amenity value of transit in their own communities. Second, according to the same survey, visitors to the Park tended to consider it to be a "truly special" and unique natural place, and often are making the trip of a lifetime. However, some have complained about the smoke and odor from the current fleet of buses, especially when these buses pass by campgrounds in the Park. Reduction of visible particulate and diesel odor are two goals of this project.

Finally, a 1991 survey of U.S. travelers conducted by the U.S. Travel Data Center for the Travel Industry of America, found that more than 85 percent claimed they are very likely or somewhat likely to patronize travel suppliers that help preserve the environment. The survey also found that travelers would spend an average of 8.8 percent more for environmentally responsible transportation services.

The current price of fleet diesel delivered at Yellowstone National Park is $1.02 per gallon. Depending on the proportion of fuel costs, capital and equipment, labor, and other costs in a tour or transit operation, a diesel fuel or blend could easily cost $1.10 or more and still be acceptable to many of the tourist transportation services and their customers, provided they were aware of the environmental benefits. If the operation and test of a biodiesel vehicle attains the objectives of reducing air quality impacts (odor and visible exhaust smoke), and if production costs can be lowered, then biodiesel has the potential of being a viable alternative fuel in higher value applications such as tourism.

Objectives

The objectives of this project are to:

1. Develop a biomass-derived transportation fuel that is attractive for use in tourism-related industries and others that operate in environmentally sensitive areas.

2. Provide a beachhead market for a developing industry, to encourage the development, production, and use of this biofuel within the region.

3. Determine the extent and probable impact, benefits, and concerns from using biodiesel in environmentally sensitive areas, including its interaction with other diesel fuel additives used in Yellowstone National park and any tendency to attract bears.

4. Make the first step toward environmentally friendly fuels in tourism, leading to anticipated use in tourist buses.

5. Operate the vehicle with the highest possible percentage of biodiesel in the spring to late fall (mid-April through mid-November) to acquire data on a cold weather operation.

6. Test the vehicle for regulated emissions both at the beginning and end of the demonstration with and without the standard catalytic converter.

Materials and Methods

Test Vehicle

A 3/4 ton 4x4 pickup truck with a 5.9 liter Cummins turbocharged and intercooled, direct injection diesel engine was donated by Dodge Truck to be operated in supervisory maintenance service for 100,000 miles within Yellowstone National Park (YNP). The vehicle is anticipated to be used a minimum of 200 miles a day four days a week from mid-April through mid-November. The project is expected to take two seasons to complete the mileage for the test. The demonstration will include diesel engine performance testing, normal service and maintenance, and periodic emissions testing. The specially marked demonstration vehicle will operate throughout the Park and will be seen by the 600 NPS employees, 3000 concession workers in Yellowstone Park, and a portion of the 3 million annual visitors.

The engine was not modified in any way for use with the vegetable oil fuels. The fuel delivery system was modified for convenience of changing fuels between test runs during emissions testing. The vehicle tests shall include regular dynamometer tests including injector inspection, opacity measurements, compression, injector pressure and borescope analysis. Vehicle maintenance shall include lubricating oil analysis for wear metals at each oil change interval (6400 km or 4000 miles.)

Fuel

The vehicle will be fueled with 100 percent Rape Ethyl Ester (REE) Biodiesel. The REE will be made and delivered by the U of I using a process that combines oil with ethanol and a catalyst to produce glycerol and the rape ethyl ester. The rape oil will be provided by Koch Agri Service, Great Falls, Montana and the ethanol by Simplot, Inc., Caldwell, Idaho. Each batch of REE will undergo the fuel characterization testing provided for in ASAE Engineering Practice EP - X552.

Bear Attractant Study

Because the reported smell of Biodiesel exhaust is often compared to "french fries" or similar foods. NPS personnel were interested in determining if the fuel or vehicle exhaust could be a potential attractant to Yellowstone Park grizzly and/or black bears. The Washington State University Bear Research Conservation and Education facility was used for the attractant study. The attractant study was supervised with Yellowstone Park Biologists. Two pens of black bears and 3 pens of Grizzly bears were used in the study. The test involved blowing each of the test substances into each pen for 20 minutes and observing the behavior of the bears. A video camera was set up to record the bear activity for further evaluation. The bear attractant sudy was conducted April 17-20, 1995. The test substances used in the study were diesel exhaust and REE exhaust from vehicles similar to the Truck in the Park test vehicle described earlier, air passed over a container of REE, air passed over a container of diesel, air alone, and air passed over a portion of a deer carcass. Each test was for 20 minutes with continued observation of the bear activity for an additional 5 minutes. Test substances were introduced into the pens with an air delivery system consisting of a 127 mm (5-inch) pipe and a fan.

Emissions Test

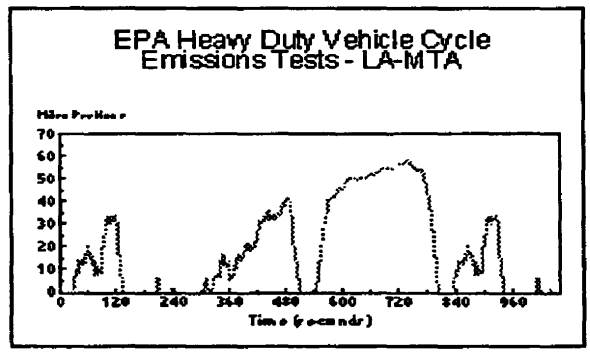
The emissions tests were conducted at the Los Angeles Metropolitan Transit Authority (MTA) Emissions Testing Facility (ETF) located in Los Angeles, California. This facility has

instrumentation to measure all regulated emissions: total hydrocarbons (HC), carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NOx), and particulate matter (PM). The ETF provides quality assurance test results and calibrations in accordance with California Air Resources Board (CARB) quality assurance recommendations. Peterson and Reece (1994) give a detailed description of the facility and an earlier test which is similar to the test and methods used for the "Truck in the Park" project and thus only a brief description of the facility and methods is provided in this paper.

The ETF is equipped with a Schenck Pegasus chassis dynamometer driven by a 600 horsepower (hp) direct current (DC) motor, a computerized control room, sophisticated emissions recovery capability, measurement and recording equipment, and various testing stations. The chassis dynamometer comprises a 72-inch diameter roller assembly connected to a DC motor and planetary gear box assembly. The complete assembly is suspended on flexible supports, facilitating measurement of the torque on the rollers.

Test Cycles

The test cycle utilized for this test program was the EPA Dynamometer Driving Schedule for Heavy-Duty Vehicles (Code of Federal Regulations 40, Part 86, Appendix I, Cycle D). The EPA cycle has a total time of 1080 seconds.

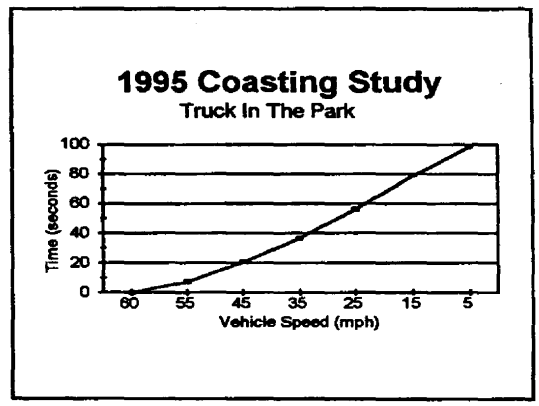


Test Vehicle

The vehicle tested was the 1995 Dodge pickup with a direct injected, turbocharged and intercooled, 5.9 liter Cummins diesel engine. The vehicle had accumulated 5,120 km (3180 miles) on diesel and approximately 2,253 km (1,400 miles) on rape ethyl ester at the time of this test. The vehicle was driven from Moscow, Idaho to Los Angeles, California on 100 % REE fuel for testing. Weight used during the test and for coast down was 3700 kg (8,140 pounds).

Road Load Simulation

University of Idaho personnel conducted a coast down evaluation of the test vehicle in Idaho prior to the scheduled ETF test date. Based on the coast down data, LA-MTA personnel developed a set of coefficients as a starting point for road load model development. Once the vehicle was installed on the dynamometer, coast downs were conducted and the model was refined to match the average on-road data. This refinement process was necessary to "factor out" the internal dynamometer resistance.



Fuels Tested
Fuels tested included:

Phillips D-2 low-sulfur diesel control fuel (DIESEL or D2); 100 % rape ethyl ester (100REE); 50% REE - 50% diesel (50REE); 20 % REE - 80 % diesel (20REE);

Each fuel was tested 3 times (2 times with 50REE without the catalytic converter) with and without the vehicle catalytic converter. Fuels were selected for testing in random order. The first test each day was a cold start test with 100D2 and 100REE with and without the vehicle catalytic converter for a total of 4 cold start tests.

Vehicle Installation
The test vehicle was installed on the chassis dynamometer in accordance with typical ETF practice. A total of seven sensors were installed. The test sensor locations were at the oil filter adapter housing, boost pressure at manifold, exhaust temperature at tailpipe adapter, fuel pressure at pump inlet, coolant temperature, and inlet air temperature.

Fuel Mass Flow Rate
Fuel use was determined by direct weighing. The fuel containers were placed on an electric scale accurate to the nearest .01 pound. Weight of fuel was read at the start and end of each test.

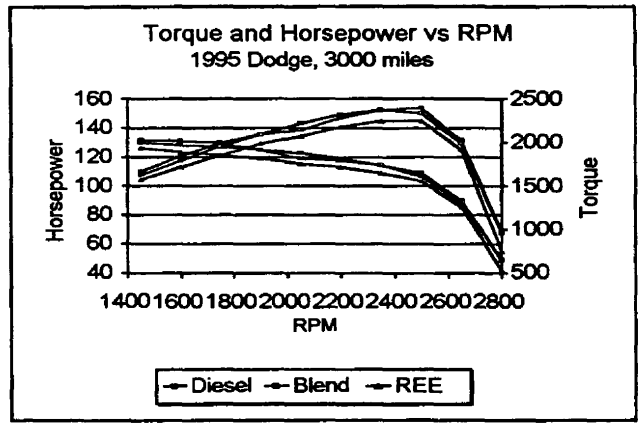
Test Design
Two problems had to be overcome in developing a test design. The first was that the number of potential test runs was unpredictable. The test facility was scheduled for one week during which time all testing had to be completed. The second hurdle was a tendency for emissions to vary with ambient conditions. The vehicle with catalytic converter was tested first, then the catalytic converter was removed and the tests repeated. As it turned out, sufficient time was available to test each fuel and desired blend three times both with and without the vehicle catalytic converter except for one run of 50REE.

Test Procedure
A complete description of the test procedure is given in Peterson and Reece (1994). Briefly, the test fuel delivery tube was connected to the input lines and the return line was connected to the waste tank. The engine was started and run for 50 seconds. The engine was stopped and the return line was connected to the test fuel tank. The vehicle was operated under load until the operating temperatures stabilized. The test was started and the cycle completed. While the technicians were taking data, weighing particulate filters, etc., the fuel was switched to the next fuel to be tested. Tests were conducted on March 20-24, 1995. A total of 29 EPA test cycles were completed, including one for cold start each day .

Presentation and Discussion of Results

On-Road Pickup
The pickup was delivered by Dodge Truck in February. The vehicle was prepared for the test by installing a 98 gallon in-bed fuel tank with a transfer pump; the three way valves were installed in the fuel supply and return lines for convenience of the emissions testing; lettering to promote the tests was placed on the vehicle exterior and a topper installed. The first dynamometer test was conducted at Western States Cat in Spokane Washington on March 9 at 2965 miles. Fuels tested in the first dynamometer test were 100REE, 100D2 and

20REE. Each of the fuels were tested three times and a snap idle test was performed after each test. The first dynamometer test resulted in a 5.6% drop in peak power and a 5.9% drop in average torque when 100REE (108 kw or 145 hp peak @ 2500 RPM) is compared to 100D2 (115 kw or 154 hp peak @ 2500 RPM) and a 1.5% drop in peak power and 2.1% drop in average torque when 20REE (112 kw or 150 hp peak @ 2500 RPM) is compared to 100D2. Opacity was reduced by 50% for 100REE and 16.5% for 20REE compared to 100D2.



At 3183 miles the fuel injectors were removed, cleaned and photographed. The injector valve opening pressures were checked, the engine compression checked and the cylinders borescoped. At this time the diesel fuel was drained from the vehicle main tank and filled with 100REE which then marked the beginning of the testing on Biodiesel.

Fuel Production

The REE fuel is being processed in a batch type reactor. The methyl ester process utilizes 100 percent molar excess alcohol (preferably absolute or 100 percent pure), or a molar ratio of 6:1 alcohol to oil ratio. Based on the amount of input oil by weight, 1.1 percent of potassium hydroxide (KOH) is used. Refer to Peterson et al. (1994) for a more complete description of the process. The ethyl ester process utilizes 70 percent stoichiometric excess ethanol (absolute, 100 percent pure), or a molar ratio of 5.1:1 ethanol to oil ratio. Based on the amount of input oil by weight, 1.3 percent of KOH is used . The catalyst is dissolved into the alcohol by vigorous stirring in a small reactor. The oil is transferred into the Biodiesel reactor and then the catalyst/alcohol mixture is pumped into the oil and the final mixture stirred vigorously for two hours. A successful reaction produces two liquid phases: ester and crude glycerol. Crude glycerol, the heavier liquid will collect at the bottom after several hours of settling. Phase separation can be observed within 10 minutes and can be complete within two hours after stirring has stopped. Complete settling can take as long as 20 hours. After settling is complete, water is added at the rate of 5.5 percent by volume of the oil and then stirred for 5 minutes and the glycerol allowed to settle again. After settling is complete the glycerol is drained and the ester layer remains. Washing the ester is a two step process which is carried out with extreme care. A water wash solution at the rate of 28 percent by volume of oil and 1 gram of tannic acid per liter of water is added to the ester and gently agitated. Air is carefully introduced into the aqueous layer while simultaneously stirring very gently. This process is continued until the ester layer becomes clear. After settling, the aqueous solution is drained and water alone is added at 28 percent by volume of oil for the final washing.

Fuel Characterization

The total REE produced to date for Yellowstone Park is 7,300 liters (1,935 gallons). Not

all of the Fuel Characterization parameters are available at this time, but the following is a partial analysis.

Fatty Acid Analysis:

16:0	2.67%	18:2	11.02%	22:0	4.37%
18:0	1.90%	18:3	8.11%	22:1	44.6%
18:1	12.00%	20:1	6.76%		

Water and Sediment	0.01%	Particulate Matter	
Ramsbottom Carbon		Total	2.44 mg/L
(as received because		non-combustible	0.40 mg/L
sample is non-distillable)	0.062 %	Nitrogen	14 ppm
Ash	0.011%	Carbon	77.15 %
Sulfur	0.022%	Hydrogen	9.52%
Cetane Rating		Oxygen	13.3%
(ASTM D613)	59.5	Iodine Number	97.5
Copper Corrosion	slight tarnish, 1A	Distillation Initial	
Karl Fischer Water	757 ppm	Boiling Point, C	227

Bear attractant

The bear attractant test will be reported by the Yellowstone Park biologists. Preliminary results indicated that the bears were very irritated by raw diesel fuel, diesel exhaust or REE exhaust being introduced into their pens. They ignored scent from the raw REE fuels and the air and were quite interested in the deer rumen.

Emissions

The summary data for each of the 29 EPA tests are not provided due to space. Since a large amount of data was collected, only summary data is reported in this paper. The data presented in the following table includes test fuel, HC, CO, CO_2, NOx, PM for both with and without the catalytic converter. All of the emissions data is reported as grams/mile.

With Catalytic Convertor

Percent REE	Fuel	HC	CO	NOx	CO2	PM
0	100D2	0.76	3.60	6.70	663.50	0.101
20	20/80	0.64	2.96	6.46	668.15	0.13
50	50/50	0.48	2.49	6.24	666.55	0.14
100	100REE	0.28	2.45	6.13	677.81	0.12

Without Catalytic Convertor

0	D2	0.854	3.68	6.75	669.54	0.18
20	20/80	0.712	3.03	6.24	646.55	0.20
50	50/50	0.482	2.40	6.55	687.05	0.25
100	100REE	0.324	2.40	5.91	654.81	0.26

These data show a significant reduction in HC, CO, and NOx as percent of vegetable oil is increased and a non-significant increase in PM. The PM data had the most variability of the data and an examination of the raw data shows that there is scatter sufficient to neutralize differences.

The next table shows the percent change in emissions compared to the diesel control fuel with and without the catalytic converter.

	Fuel	HC	CO	NOx	CO2	PM
With Catalytic Convertor						
	100D2	100%	100%	100%	100%	100%
	20/80	83%	82%	96%	101%	128%
	50/50	63%	69%	93%	100%	140%
	100REE	37%	68%	91%	102%	116%
Without Catalytic Convertor						
	100D2	100%	100%	100%	100%	100%
	20/80	83%	82%	92%	97%	106%
	50/50	57%	65%	97%	103%	135%
	100REE	38%	65%	88%	98%	144%

Other researchers have indicated that NOx and PM are inversely related, and that may explain the apparent difference in results from these tests. It has more generally been found that the esters increase NOx and decrease PM, however in these tests, generally speaking, the reverse was true. One might speculate that this trend is due to the fatty acid constituents of rapeseed esters tested or that it is a characteristic of this particular engine. In either case, the result was consistent. In these tests a reduction in HC (63%), CO (33%), NOx (10%), CO_2 unchanged and increases in PM (30%). The catalytic converter had an affect on only the HC and PM. It reduced HC for diesel 10.5% and for REE 13.6%. It also reduced PM for diesel 45% and for REE 56%. Repeatability for HC, CO, CO_2, and NOx was very good. When one experiments with a number of fuels on a limited budget, setting up a test procedure is extremely critical. It would have been more desirable to have replicated each fuel two or three times in succession and to have replicated each fuel in time in random fashion as well. However, time did not allow this luxury.

Conclusions

The "Truck In The Park" project will provide a unique opportunity to observe use of Biodiesel (REE) as a fuel in an environmental setting. As of this writing the truck has been driven over 17,700 km (11,000 miles) under a wide variety of conditions. The temperature has been near - 18 C (0 F) on several occasions. The bear attractant study indicated that no out-of-the-ordinary problem should be experienced with park wildlife because of the fuel. The first dynamometer test resulted in a 5.6% drop in peak power @ 2500 RPM and a 5.9% drop in average torque when 100REE (108 kw or 145 hp) is compared to 100D2 (115 kw or 154 hp) and a 1.5% drop in peak power @ 2500 RPM and 2.1% drop in average torque when 20 REE (112 kw or 150 hp) is compared to 100D2. Opacity was reduced by 50% for 100REE and 16.5% for 20REE compared to 100D2. The first emissions test has been completed and resulted in the following:

1) Reductions in HC (63%), CO (33%), NOx (10%) when 100REE is compared to 100D2.

2) CO_2 remained unchanged and PM increased (30%) when 100REE is compared to 100D2.

3) The catalytic converter had an affect on only the HC and PM. It reduced HC for

diesel 10.5% and for REE 13.6%. The catalytic converter reduced PM for diesel 45% and for REE 56%.

References

References cited available on request to the authors.

ACUTE TOXICITY OF BIODIESEL TO FRESHWATER AND MARINE ORGANISMS

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Abstract

Biodiesel fuels are reported to be nontoxic resulting in less potential hazard to fish and other aquatic life in case of accidental spills. This paper reports on static tests with rapeseed methyl ester (RME) and rapeseed ethyl ester (REE) performed according to EPA/600/4-90/027. The acute aquatic toxicity tests were conducted with both rainbow trout and daphnia magna by CH2M Hill in Corvallis, Oregon under contract to the University of Idaho.

The LC50 (the point at which 50% have died and 50% are still alive determined by interpolation) values for each of the substances tested with daphnia magna in parts per million were as follows: control (table salt (NaCl)) = 3.7, D2 = 1.43, RME = 23, REE = 99, and Methyl Soyate = 332. Duplicate tests with rainbow trout were run with 10 organisms per replicate. LC50 numbers were not reported because of the failure to kill a sufficient number of fish at the concentrations tested, even with the diesel control fuel. The 20 percent and 50 percent blends had scattered losses of fish but none of the tests had less than 85 percent survival at any concentration after 96 hours.

Introduction

Current test guidelines for acute aquatic toxicity produced by the United States Environmental Protection Agency (EPA), American Standard Testing of Materials (ASTM), and other federal and state governing agencies are not generally applicable to oil products.

As part of the ongoing research of Biodiesel at the University of Idaho's Department of Agricultural Engineering a test of acute aquatic toxicity to freshwater organisms was conducted by CH2M Hill in Corvallis, Oregon. Biodiesel fuels are reported to be nontoxic resulting in less potential hazard to fish and other aquatic life in case of an accidental spill. Biodiesel has been shown to be readily biodegradable (Peterson et al., 1994). To satisfy a growing interest in renewable, biodegradable, and non-toxic fuel sources, ecotoxicity testing was conducted on methyl and ethyl esters of rapeseed oil and blends of these esters with number two diesel fuel.

Literature Review

Cheng et al. (1991) compared hydraulic oils of mineral oil, vegetable oil, polyglycol, and a synthetic ester for biodegradability, toxicity, and fluid performance parameters. They used an oil-water dispersion procedure by the Ministry of Agriculture, Fisheries and Food, England, and provided mechanical agitation to continually disperse the test materials as small droplets in the water column. This procedure simulates physical dispersion by wave and current action. Rainbow trout were exposed to five concentrations of each test material and a control. Toxicity was expressed as the concentration of material in ppm to kill 50% of the fish after 96 hours of exposure (LC50). They reported that the base stocks for the vegetable oil formulations were nontoxic (> 1000 ppm) but the formulated products did not meet this criteria because of one or more of the additives. The LC50 with rainbow trout for mineral oil was 389 ppm; vegetable oil, 633 ppm; polyglycol, 80 ppm; and synthetic ester, > 5000 ppm.

Lockhart et al. (1984) studied rainbow trout in forty-eight hour-LC50 (acute lethal toxicity) tests exposed to water-soluble fractions (WSF) for a range of crude and refined oils. The results were compared to the concentrations of volatile very low-boiling (<115°C) and low-boiling (115-270°C) hydrocarbons determined by a two-stage analytical method. The results suggest that toxicity of the water-soluble fractions is associated largely with the substituted benzenes and naphthalenes, with boiling points between 115 and 270°C.

Lockhart et al. (1984) found that the LC50 values were highly dependent on the particular exposure conditions. Thus, survival of rainbow trout and their LC50 values were consistently higher in test containers that were open to the atmosphere than in sealed closed containers. Aeration of test containers, by bubbling air through the WSF, virtually eliminated toxicity to the trout in even the most toxic test preparations. The results were discussed in terms of the design of bioassays relevant to ice-covered environments and to other situations where volatilization may be low or reduced.

Weber, C.I. (1993) documents the EPA methods for acute toxicity of effluents and receiving waters to freshwater and marine organisms for the use in the National Pollutant Discharge Elimination System Permits Program. Summaries of the test conditions for the daphnids, daphnia magna, fathead minnows, rainbow trout, brook trout, the mysid, sheepshead minnows, and silversides are given. Three test types are given: static non-renewal, static renewal, and flow-through. Test duration may vary from 24 to 96 hours depending on the objective of the test. The tests are designed to provide dose-response information, expressed as the percent effluent concentration that is lethal to 50 percent of the test organisms (LC50) within the prescribed period of time (24-96 hours), or the highest effluent concentration in which survival is not statistically different from the control.

Nearly identical procedures are outlined in 40 CFR part 797.1300 (Daphnid acute toxicity test) and part 797.1400 (fish acute toxicity test), and ASTM E 729-88. These procedures include, with the LC50 (median lethal concentration), an EC50 (median effective concentration), and an IC50 (inhibition concentration).

Materials and Methods

Toxicity Tests

The University of Idaho Department of Agricultural Engineering contracted with CH2M Hill in Corvallis, Oregon to conduct two static definitive bioassays. The first bioassay was a 48-hour bioassay using the water flea, daphnia magna. A 96-hour bioassay using rainbow trout was conducted for the second study. Two rounds of tests were conducted for this study. All tests were performed according to: Methods for Measuring the Acute Aquatic Toxicity of Effluents to Freshwater and Marine Organisms EPA600/4-90/027F.

Fuels

Fuel nomenclature is as follows: (1) Phillips D2 low-sulfur diesel control fuel (D2); (2) 100 percent rapeseed methyl ester (RME); (3) 100 percent rapeseed ethyl ester (REE); (4) 50 percent RME - 50 percent D2 (50RME); (5) 50 percent REE - 50 percent D2 (50REE); (6) 20 percent RME - 80 percent D2 (20RME); 20 percent REE - 80 percent D2 (20REE); and 100 percent soybean methyl ester (SME).

Test quantities of each Biodiesel fuel tested were supplied by the University of Idaho. The rapeseed oil was expelled at the University of Idaho's Agricultural Engineering farm scale process facility. The RME, REE, and SME fuels were produced using the process developed by University of Idaho researchers. Phillips 66 Company 0.05 low sulfur diesel fuel was used as the baseline for the Biodiesel fuels.

Test Methods

All static tests were performed according to: Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms, Weber C., et al. (1991); EPA/600/4-90/027.

Test Organisms

Daphnia Magna

The daphnia magna were obtained from CH2M Hill's in house cultures and were less than 24 hours old prior to initiation of the test. All organisms tested were fed and maintained

during culturing, acclimation, and testing as prescribed by EPA (1989). The test organisms appeared vigorous and in good condition prior to testing. The daphnia magna were placed below the test surface at test initiation due to the non-soluble nature of the sample.

Rainbow Trout
The rainbow trout used in the first round of tests were obtained from Thomas Fish Company, Anderson, California, and were 22 days old and 32±2 mm in length. The rainbow trout were acclimated to test conditions (dilution water and temperature) for 10 days prior to test initiation. The rainbow trout used in the second round of tests were obtained from Spring Creek Trout Hatchery, Lewiston, Montana, and were 24 days old and 28±1 mm in length. The rainbow trout were acclimated to test conditions (dilution water and temperature) for 12 days prior to test initiation. All the test organisms appeared vigorous and in good condition prior to testing.

Dilution Water
Daphnia Magna
The water used for acclimation and dilution during the static testing was reconstituted moderately hard water with a total hardness of 98 as $CaCO_3$, alkalinity of 64 mg/l as $CaCO_3$, and a pH of 8.0 to 8.2.

Rainbow Trout
The water used for acclimation and dilution during the rainbow trout static testing was reconstituted moderately hard water with a total hardness of 92-98 as $CaCO_3$, alkalinity of 70-74 mg/l as $CaCO_3$, and a pH of 7.9 to 8.0.

Test Concentrations
Daphnia Magna
The concentrations tested in definitive test on REE were 33, 167, 833, 4170, and 20800 ppm of sample and dilution water for the control. The concentrations tested in the definitive test on RME were 67, 333, 1330, 6670, and 26700 ppm of sample and dilution water for the control. The concentrations tested in the definitive test on D2 were 6.67, 13.3, 33.3, 66.7, and 1333 ppm of sample and dilution water for control. The concentrations tested in the definitive test on Methyl Soyate were 13.3, 33.3, 66.7, and 6667 ppm of sample and dilution water for control. The fuel mixture concentrations were run in quadruplicate with five organisms per replicate. Additional concentrations of 1.43 and 3.33 ppm were set up for D2 with 10 organisms in on chamber. The fuel was stirred into the water before the daphnia magna were introduced into the chamber. There was a sheen of fuel on the top of each chamber.

Rainbow Trout
The concentrations tested for round 1 in the definitive test on D2, 20RME, and REE were 100, 300, 600, 1200, and 2400 ppm with dilution water for control. The concentrations tested for round 2 in the definitive test on RME and 50REE were 100, 500, 750, 1000, and 7500 ppm and the 50RME sample was tested at 100, 500, 600, and 7500 ppm due to a shortage of the sample.

The rainbow trout bioassays were run in 5-gallon glass aquaria, with a volume of 5 liters. The samples were run in duplicate with 10 organisms per replicate. The photo period was 16 hours light 8 hours dark. The temperature range was 12±1°C. Loading of test organisms was 0.53g wet fish weight per liter in round one, and 0.26g wet fish per liter in round two. Mortality was measured by lack of response to tactile stimulation and lack of respiratory movement. The fuel was stirred into the water before the Daphnia Magna were introduced into the chamber. There was a sheen of fuel on the top of each chamber.

Monitoring of Bioassays

The static tests were monitored at test initiation for pH, hardness, alkalinity, conductivity, and dissolved oxygen, and every 24 hours thereafter for mortality and at test termination for pH, conductivity, and dissolved oxygen. Temperature was monitored continuously throughout the test periods. The response measured for the Daphnia Magna was mortality over the 48-hour exposure period. The median lethal response (LC50) was calculated using Toxis version 2.2.

Results

Daphnia Magna

The raw data is summarized in Table 1 below for 100 percent REE. Some of the mortality seen in the tests may have been caused by the physical nature of the test substances. The raw data sheets noted when the Daphnia Magna were trapped on the oil sheen at the surface of the test containers. The LC50 for the REE sample was 99 ppm.

Table 1
REE
Summary of Results
Percent Survival

Concentration (ppm)	0 hr	24 hr	48 hr
Control	100	100	100
33	100	80	65
167	100	70	40
833	100	65	30
4170	100	65	25
20800	100	50	20

Table 2 summarizes the results of the RME sample. The LC50 for RME was 23 ppm.

Table 2 RME Summary of Results Percent Survival			
Concentration (ppm)	**0 hr**	**24 hr**	**48 hr**
Control	100	100	100
67	100	90	40
333	100	95	40
1330	100	60	20
6670	100	35	5
26700	100	30	30

Table 3 summarizes the results of the D2 sample tested. The LC50 for the D2 sample was less than 1.43 ppm.

Table 3 D2 Summary of Results Percent Survival			
Concentration (ppm)	**0 hr**	**24 hr**	**48 hr**
Control	100	100	100
1.43	100	30	0
3.33	100	0	0
6.67	100	10	0
13.3	100	10	0
33.3	100	0	0
66.7	100	0	0
1333	100	0	0

Table 4 summarizes the results of the Methyl Soyate. The LC50 for the Methyl Soyate was 332 ppm.

Table 4 Methyl Soyate Summary of Results Percent Survival			
Concentration (ppm)	**0 hr**	**24 hr**	**48 hr**
Control	100	100	100
13.3	100	90	85
33.3	100	95	80
66.7	100	85	75
667	100	80	45
6667	100	45	10

The methyl and ethyl esters are not water soluble and form a sheen on the water surface. This sheen could be easily skimmed off, but the Daphnia Magna get captured in this sheen. Fifty percent of the Daphnia Magna in common table salt had died at a concentration of 3.7 parts per million (ppm). With diesel, 50 percent of them had died at less than 1.43 ppm and CH2M Hill reported all were dead at this concentration. When this test was first completed, CH2M Hill reported that the LC50 for diesel fuel was less than 6 ppm because all the Daphnia Magna had died. They were asked to test lower concentrations. They tested four more concentrations less than 6 ppm and the diesel fuel still killed all the Daphnia Magna. For the RME the LC50 was 23 ppm, and at 26,700 ppm 30 percent of them were still alive. With REE the LC50 was 99 ppm and 20 percent were still alive at 20,800 ppm. With methyl soyate the LC50 was 332 ppm; however, only 45 percent were alive at 667 ppm. This difference between rapeseed esters and SME may be due to the high Erucic acid content of the rapeseed. If one takes the worst case, the 23 ppm for REE, and compare it of the 1.4 ppm for diesel fuel, the acute aquatic toxicity is 15 times less. What is even more significant is the 20 percent and 30 percent that are still alive at very high concentrations of Biodiesel.

Rainbow Trout

The raw data is summarized in Tables 5 to 10 below for 100 percent D2. The LC50 for D2 was not determined. This data compares cadmium chloride (CdCl), diesel fuel, and methyl and ethyl esters of rapeseed.

Table 5 D2 Summary of Results Percent Survival					
Concentration (ppm)	**0 hr**	**24 hr**	**48 hr**	**72 hr**	**96 hr**
Control	100	100	100	100	100
100	100	100	95	95	90
300	100	100	100	100	100
600	100	100	100	100	100
1200	100	100	100	95	85
2400	100	100	100	95	80

Table 6 20%RME - 80%D2 Summary of Results Percent Survival					
Concentration (ppm)	**0 hr**	**24 hr**	**48 hr**	**72 hr**	**96 hr**
Control	100	100	100	100	100
100	100	100	100	100	100
300	100	100	100	100	100
600	100	95	95	95	95
1200	100	100	100	100	85
2400	100	100	100	100	95

Table 7 20%REE - 80%D2 Summary of Results Percent Survival					
Concentration (ppm)	**0 hr**	**24 hr**	**48 hr**	**72 hr**	**96 hr**
Control	100	100	100	100	100
100	100	100	100	95	95
300	100	100	100	100	100
600	100	100	100	100	100
1200	100	100	95	95	95
2400	100	100	95	95	90

Table 8 100% REE Summary of Results Percent Survival					
Concentration (ppm)	**0 hr**	**24 hr**	**48 hr**	**72 hr**	**96 hr**
Control	100	100	100	100	100
100	100	100	100	95	95
300	100	100	100	100	100
600	100	100	100	100	100
1200	100	100	100	100	100
2400	100	100	100	100	95

Table 9 100% RME Summary of Results Percent Survival					
Concentration (ppm)	0 hr	24 hr	48 hr	72 hr	96 hr
Control	100	100	100	100	100
100	100	100	100	100	100
500	100	100	100	100	100
600	100	100	100	100	100
1000	100	100	100	100	100
7500	100	100	100	100	100

The 50RME percent survival summary results were identical to the 100% RME results.

Table 10 50% REE - 50% D2 Summary of Results Percent Survival					
Concentration (ppm)	0 hr	24 hr	48 hr	72 hr	96 hr
Control	100	100	100	100	100
100	100	100	100	100	100
500	100	100	100	100	100
600	100	100	100	100	100
1000	100	100	100	100	100
7500	100	100	100	100	95

The 48-hour LC50 value and Control Chart limits for the reference toxicant (cadmium chloride) was at a concentration of 2.8 μg/l for the round one rainbow trout and 4.6 μg/l for the round two trout. The results indicate that the test organisms were within their expected sensitivity range. Comments included in round one test data at 24-hours was a general behavior of twitching and they were swimming on their sides and skittering; at 48-hours their condition was the same as at 24-hours. The trout in the 20REE containers at 100 and 300 ppm were swimming vertically, at 600 ppm the trout were on their sides at the bottom, and at 2400 ppm they were barely moving at the bottom of the tank. The trout in the REE containers were not as active as in the other three test substances. The end condition of survivors was reported as being poor. The only comment in round two was at 48-hours that the fish were dark and swimming vertical at concentrations as low as 500 ppm in the 50RME and 50REE with the end condition of survivors as being poor.

Conclusions

Biodiesel is not as toxic to Daphnia Magna as NaCl. When compared to the reference toxicant (sodium chloride) diesel fuel was 2.6 times more toxic, RME was 6.2 times less toxic, REE was 26 times less, and SME 89 times less toxic. When compared to number two diesel fuel RME is 16 times less toxic, REE is 69 times less toxic, and SME was 237 times less toxic. CH2M Hill has been asked to repeat the toxicity study with rainbow trout at the water accommodated fraction (WAF) and below to produce a LC50.

References

ASTM. 1993. Standard guide for conducting acute toxicity tests with fishes, macroinvertebrates, and amphibians. Designation: E 729-88, Annual Book of ASTM Standards, Vol. 11.04, American Society for Testing and Materials, Philadelphia, PA.

Cheng, V.M., A.A. Wessol, P. Baudouin, M.T. BenKinney, and N.J. Novick. 1991. Biodegradable and nontoxic hydraulic oils. Presented at the 42nd annual SAE Earthmoving Industry Conference and Exposition in Peoria, Il.

Lockhart, W.L., R.W. Danell, and D.A.J. Murray. 1984. Acute toxicity bioassays with petroleum products: influence of exposure conditions. Proceedings of the Symposium of Oil Pollution in Freshwater, Edmonton, Alberta, Canada.

Peterson, C.L., D. Reece, J. Thompson, S. Beck, and C. Chase. 1994. Development of biodiesel for use in high-speed diesel engines. Proceedings of the Sixth National Bioenergy Conference. Vol 1: 97-104.

Weber C.I. 1993. Methods for measuring the acute aquatic toxicity of effluents and receiving waters to freshwater and marine organisms. EPA/600/4-90/027F. Office of Research and Development, Washington DC 20460.

RECENT PROGRESS IN BIODIESEL PRODUCTION AND TESTING AT THE UNIVERSITY OF IDAHO

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Abstract

Biodiesel from vegetable oil and animal fats has been studied at the University of Idaho since 1979. Recent research is directed toward developing and demonstrating commercial technologies. During the last year an on-road vehicle was driven coast-to-coast on Biodiesel for a total of 14,068 km (8742 miles.) As part of this on-road testing, the vehicle was tested for emissions on a chassis dynamometer at the LA-MTA emissions test facility in Los Angeles, California. Tests included HC, CO, CO_2, NOx, and PM. The two cycles used in the tests included a modified arterial cycle and the EPA cycle for heavy duty vehicles. Biodiesel research has included producing both methyl and ethyl esters from tallow, canola, soybean oil and rapeseed oil. These eight fuels have been subjected to fuel characterization tests according to the ASAE proposed Engineering Practice, Reporting of Fuel Properties when Testing Diesel Engines with Alternative Fuels Derived from Biological Materials, X552; and short term injector coking tests and performance tests in a turbocharged, DI, CI engine. Two-hundred hour EMA endurance tests in 3-cylinder, DI, CI engines are in progress with each of the fuels.

Introduction

This paper presents a brief summary of three activities pursued by the Department of Agricultural Engineering during the past year. First is a summary of a Coast-to-Coast trip with 100 percent Biodiesel fuel. Second is a brief report of an emissions test conducted on methyl and ethyl esters of biodiesel using the transient chassis dynamometer at the Los Angeles Metropolitan Transit Authority emissions test facility (LA-MTA ETF). Third, is a summary of processing and testing of 8 fuels (methyl and ethyl esters of rapeseed, canola, soybean oil and tallow.) The first two activities were funded by the DOE Pacific Northwest and Alaska Regional Bioenergy program and the third was funded by the National Biodiesel Board.

Coast-To-Coast on Biodiesel

Driving a 1994 Dodge 2500, turbocharged and intercooled diesel pickup fueled with 100 percent ethyl ester of rapeseed oil (REE), personnel representing the University of Idaho, Agricultural Engineering Department drove from Moscow to the Pacific Ocean at Los Angeles, California and back to Moscow and then from Moscow to the Atlantic Ocean at Ocean City, Maryland just east of Washington, D.C and back to Moscow. This trip covered a total of 14,000 km (8,742 miles), 1,768 liters (467 gallons) of ethyl ester of rapeseed oil fuel was used and the truck averaged 8.0 km/liter (18.7 miles per gallon). No troubles or unusual events were encountered with the truck operation. The truck was completely unmodified as to engine or fuel system. The fuel required for the trip was all processed in the agricultural engineering laboratory at the University of Idaho and was carried on-board as no refueling facilities were available away from Moscow, Idaho. This is believed to be the first coast-to-coast and back run on Biodiesel.

In the latter half of 1994, the Pacific Northwest and Alaska Regional Bioenergy Program funded a program with the U of I, Agricultural Engineering program to examine many aspects of production and use of ethyl esters. As part of this program funds were provided to lease a diesel powered vehicle and to operate that vehicle on 100 percent ethyl ester of rapeseed oil fuel. An addendum to that project also provided funding for emissions tests of the vehicle at the Los Angeles Metropolitan Transit Authority Emissions Test Facility (LA-MTA). It was in the context of meeting the need to accumulate mileage on the vehicle, the requirement for travelling to Los Angeles with the truck, and the necessity of attending meetings in Kansas City and Milwaukee that provided the incentive for the Coast-to-Coast-to-Coast run with the pickup.

Details of Travel

The western leg of the trip began March 9, 1994. The starting point was in Moscow, Idaho. The estimated 3,860 km (2,400 miles) of the trip required approximately 570 liters (200 gallons) of fuel. In addition, fuel was required for the emission tests at LA-MTA so nearly 1130 liters (300 gallons) of fuel was on-board during the trip.

The eastern leg of the run was carried on between June 12 and July 4, 1994. For the estimated 9,600 km (6,000) miles of the trip approximately 1150 liters (300 gallons) of fuel was required. The trip started with a total of about 1,300 liters (340 gallons) of fuel weighing

over 1,090 kg (2,400 pounds). Approximately 100 liters (30 gallons) remained at the conclusion of the trip.

Unique Characteristics of the Run

1. The total distance travelled was 14,068 km (8,742 miles) with one fueling location in Moscow, Idaho.
2. All of the fuel used in the test was 100 percent ethyl ester of rapeseed oil produced in the Agricultural Engineering Department Laboratory at the University of Idaho.
3. All of the fuel was on-board the vehicle when it left Moscow. No fuel was shipped and/or delivered at other locations.
4. The vehicle ran normally with no engine or fueling system modifications.
5. No diesel fuel was used on the trip, none was carried or purchased and at no time was it felt necessary to attempt to use diesel fuel.
6. The vehicle was driven at normal highway speeds and no attempt was made to avoid any particular situation. Traffic included heavy city traffic, freeways, tollways, etc. On two different days the vehicle travelled over 1450 km (900 miles).

LA-MTA Emissions Test

In March of 1994, University of Idaho personnel conducted a series of chassis dynamometer emissions tests in cooperation with the Los Angeles County Metropolitan Transit Authority (LA-MTA). Emissions data generated from this facility includes the regulated emissions: total hydrocarbons (HC), carbon monoxide (CO), carbon dioxide (CO_2), oxides of nitrogen NOx, and particulate matter (PM).

Two test cycles were used in the test program. First, an arterial cycle , which consisted of eight replications of accelerating to 64 kmph (40 mph) and decelerating to 0 kmph (0 mph) and required 758 seconds was used for 26 tests. Second, the dynamometer driving schedule for heavy duty vehicles (Code of Federal Regulations 40, Part 86, Appendix I, Cycle D), a 1060 second test was used for 13 tests.

Fuels tested included ethyl ester of rapeseed oil (REE), methyl ester of rapeseed oil (RME), Phillips low sulfur diesel reference fuel (D2) and 20 percent and 50 percent blends of REE or RME with D2.

The vehicle tested was the 1994 Dodge pickup described above in the coast-to-coast run. A complete description of the test facility and the procedures used during the test is given in Peterson and Reece (1994).

The presentation of the data are tables 1 and 2, showing the percent change in the emissions compared to the diesel control fuel for ethyl and methyl ester of rapeseed oil for the average of the two cycles. Relative test results were the same for the two cycles even though the actual level of emissions was higher for the EPA cycle than for the arterial cycle. Table 3 compares REE and RME. These tables show that HC and CO were reduced approximately 50 percent by using rapeseed esters. CO_2 increased by an amount indicative of the reduction in CO while no significant change in PM was detected although the trend was lowered PM

at the 20 percent vegetable oil ester and increased PM at the 100 percent fuel mixture. Other researchers have indicated that NOx and PM are inversely related, and that may explain the apparent difference in results from these tests. It has more generally been found that the esters increase NOx and decrease PM, however in these tests, generally speaking, the reverse was true. Ethyl ester at the 100 percent and 50 percent level were lower in NOx than methyl ester.

Table 1. Percent changes in emissions compared to diesel control fuel for ethyl ester of rapeseed oil (REE) for combined Arterial and EPA cycles.

Combined Cycles	Emissions Percent Increase (+) or Decrease (-) for REE compared to Diesel Control Fuel		
Volume Percent of REE in Diesel Control Fuel	20% REE	50% REE	100% REE
HC	-18.0*	-32.3*	-54.6*
CO	-30.0*	-45.5*	-48.8*
NOx	-4.6*	-7.9*	-11.6*
CO_2	+0.5	+0.6	+1.1
PM	-1.3	+1.2	+8.0

*Numbers followed by an * are significantly different from diesel (p<=0.05).

Table 2. Percent changes in emissions compared to diesel control fuel for methyl ester of rapeseed oil (RME) for combined Arterial and EPA cycles.

Combined Cycles	Emissions Percent Increase (+) or Decrease (-) for RME compared to Diesel Control Fuel		
Volume Percent of RME in Diesel Control Fuel	20% RME	50% RME	100% RME
HC	-18.8*	-33.2*	-50.3*
CO	-27.4*	-39.4*	-46.5*
NOx	-2.9*	-5.3*	-8.5*
CO_2	+0.5	+0.7	+0.7
PM	-7.3	+9.7	+11.8

*Numbers followed by an * are significantly different from diesel (p<=0.05).

Specific conclusions of this study are:

1. HC was reduced by 52.4 percent when 100 percent vegetable oil fuel was compared to low sulfur diesel control fuel.
2. CO was reduced by 47.6 percent when 100 percent vegetable oil fuel was compared to low sulfur diesel control fuel.
3. CO_2 increased by 0.9 percent when 100 percent vegetable oil fuel was compared to low sulfur diesel control fuel.
4. NOx was reduced by 10.0 percent when 100 percent vegetable oil fuel was compared to low sulfur diesel control fuel.

Table 3. Percent changes in emissions comparing REE and RME for combined Arterial and EPA cycles.

Combined Cycles	Emissions Percent Increase (+) or Decrease (-) for REE compared to RME		
Volume Percent of REE in Diesel Control Fuel	20% REE	50% REE	100% REE
HC	-1.0	-1.3	-8.7
CO	-3.6	-9.9	-4.3
NOx	-1.7	-2.8*	-3.4*
CO_2	-0.1	-0.2	+0.3
PM	+6.5	+2.3	-3.3

*Numbers followed by an * are significantly different from diesel ($p<=0.05$).

5. PM increased by 9.9 percent when 100 percent vegetable oil fuel was compared to low sulfur diesel control fuel; however, this difference was statistically non-significant. PM was the lone parameter that had variations sufficient to make differences non-significant. The result is in harmony with the literature, which reports a trade-off between PM and NOx.
6. In these tests, 100 percent REE reduced HC (8.7 percent), CO (4.3 percent) and NOx (3.4 percent) compared to 100 percent RME.
7. Absolute value of emissions data were higher for the EPA Cycle than for the arterial cycle. HC increased from 0.57 to 0.87 gm/mile; CO from 2.34 to 2.865 gm/mile; CO_2 from 657.8 to 703.8 gm/mile; NOx from 5.88 to 6.41 gm/mile and PM from 0.305 to 0.44 gm/mile.

Eight Biodiesel Fuels from Various Feedstocks

Test quantities of ethyl and methyl esters of four renewable fuels were processed, characterized and performance tested. Canola, rapeseed, soybean oils, and beef tallow were the feedstocks for the methyl and ethyl esters. Previous results have shown methyl esters to be a suitable replacement for diesel fuel; however, much less has been known about the ethyl esters. The study examines short term engine tests with both methyl and ethyl ester fuels compared to number 2 diesel fuel (D2). Three engine performance tests were conducted including an engine mapping procedure, an injector coking screening test, and an engine power study. A complete report of this study is given in Peterson et al. (1994).

Two hundred sixty five liters (70 gallons) of each of the esters were produced using the process developed by University of Idaho researchers. The feedstocks for these fuels were as follows: rapeseed from Dwarf Essex variety seed; canola from Stonewall variety seed; beef tallow purchased from Iowa Beef Products in Kennewick, Washington; and soybean oil purchased from Foodservices Brokerage Co. in Spokane Washington. In addition to these eight fuels, seventy five gallons of methyl soyate were purchased from Interchem, Inc., Overland Park, Kansas (Midwest Biofuels). The rapeseed and canola oils were expelled at

the University of Idaho's Agricultural Engineering farm scale process facility. Each fuel, excluding the methyl soyate, was processed at this facility. Phillips 66 Company low sulfur diesel reference fuel was used as the baseline fuel.

Fuel Preparation

The eight Biodiesel fuels were processed in a batch type reactor. The methyl ester process utilizes 100 percent molar excess alcohol (preferably absolute or 100 percent pure), or a molar ratio of 6:1 alcohol to oil ratio. Based on the amount of input oil by weight, 1.1 percent of potassium hydroxide (KOH) is used. The ethyl ester process utilizes 70 percent stoichiometric excess ethanol (absolute, 100 percent pure), or a molar ratio of 5.1:1 ethanol to oil ratio. Based on the amount of input oil by weight, 1.3 percent of KOH is used. The following transesterification procedure is for the methyl and ethyl ester production. The catalyst is dissolved into the alcohol by vigorous stirring in a small reactor. The oil is transferred into the Biodiesel reactor and then the catalyst/alcohol mixture is pumped into the oil and the final mixture stirred vigorously for two hours. A successful reaction produces two liquid phases: ester and crude glycerol. Crude glycerol, the heavier liquid will collect at the bottom after several hours of settling. Phase separation can be observed within 10 minutes and can be complete within two hours after stirring has stopped. Complete settling can take as long as 20 hours. After settling is complete, water is added at the rate of 5.5 percent by volume of the oil and then stirred for 5 minutes and the glycerol allowed to settle again. After settling is complete the glycerol is drained and the ester layer remains. Washing the ester is a two step process which is carried out with extreme care. A water wash solution at the rate of 28 percent by volume of oil and 1 gram of tannic acid per liter of water is added to the ester and gently agitated. Air is carefully introduced into the aqueous layer while simultaneously stirring very gently. This process is continued until the ester layer becomes clear. After settling, the aqueous solution is drained and water alone is added at 28 percent by volume of oil for the final washing.

Fuel Characterization

The fuels were characterized by evaluating the parameters required in ASAE EP X552. The tests for specific gravity, viscosity, cloud point, pour point, flash point, heat of combustion, total acid value, catalyst, and fatty acid composition were performed at the Analytical Lab, Department of Agricultural Engineering, University of Idaho. The boiling point, water and sediment, carbon residue, ash, sulfur, cetane number, copper corrosion, Karl Fischer water, particulate matter, iodine number, and the elemental analysis were performed at Phoenix Chemical Labs, Chicago Illinois. The HPLC and titration analysis for total and free glycerol, percent of oil esterified, free fatty acids, and mono-, di-, and trigylicerides were performed by Diversified Labs Inc., Chantilly, Virginia.

Engine Performance Tests

All engine performance tests were conducted in the engine performance lab at the University of Idaho. The equipment used and tests conducted are described below. The short term tests were performed with an in-line four cylinder John Deere 4239T turbocharged, direct injected diesel engine. It has a displacement of 3.9 liters 239 cubic inches), a high RPM of 2650, 61 kw (82 hp) at 2500 RPM, and 290 Nm (214 ft lbf) torque at 1500 RPM. It is

attached to a General Electric 119 kw (159 hp) cradle dynamometer. The engine was not modified in any way for use with the renewable fuels. The injector coking tests were performed using the procedure described in "A Rapid Engine Test to Measure Injector Fouling in Diesel Engines Using Vegetable Oil Fuels" (Korus et al., 1985). The torque tests were performed with the engine operating at 2600 RPM to 1300 RPM in 100 RPM increments. The engine mapping tests were performed using the procedure described in "Procedure for Mapping Engine Performance-Spark Ignition and Compression Ignition Engines" (SAE J1312, 1990). The mapping tests were performed at 2500, 2250, and 2000 RPM with loadings of 100, 75, 50, 25, and 0 percent of maximum power.

Experimental Design

The engine performance data was collected using a randomized complete block experimental design. Each fuel was tested once in each block in random order for each of the three blocks. This resulted in a total of 30 injector coking tests, 30 torque tests, and 30 fuel mapping studies.

Specific conclusions of this study are:

1. Fuel characterization data (Table 4) show some similarities and differences between Biodiesel fuels and diesel. a) Specific weight is higher for Biodiesel, heat of combustion is lower, viscosities are 1.3 to 2.1 times that of D2. b) Pour points for Biodiesel fuels vary from 1 to 25 degrees Celsius higher for Biodiesel fuels depending on the feedstock. c) Sulfur content for Biodiesel is 20 to 50 percent that of D2.

2. The percent oil esterified as determined by an outside lab was lower than expected. Methyl esters averaged 97.5 percent and ethyl esters 94.3 percent esterified.

3. Total glycerol was higher than expected averaging 1.1 percent. Methyl esters averaged 0.87 percent and the ethyl esters 1.4 percent.

4. The esters all have higher levels of injector coking than diesel fuel, Figure 1. Ethyl esters had higher levels than did the methyl esters. Injector coking was more related to apparent molecular weight and viscosity than to total glycerol. Visually all injector coking was low especially compared with older tests that included raw vegetable oils.

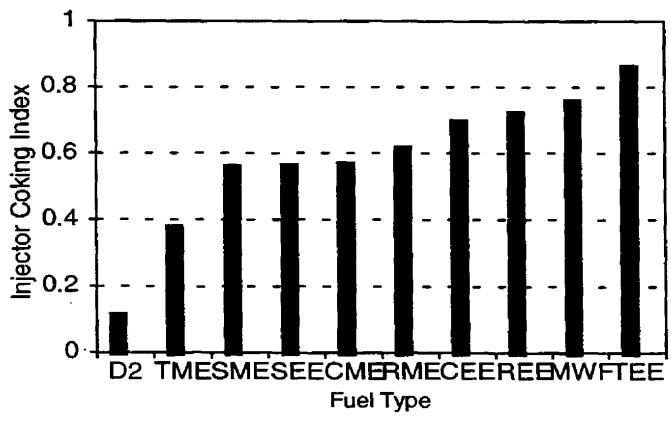


Figure 1. Injector coking versus fuel type for 9 biodiesel fuels and D2.

5. Smoke density, as determined by an opacity meter, Figure 2, decreased an average of 75 percent for the Biodiesel fuels compared to D2. CEE and CME produced the most smoke of the Biodiesel fuels and TME and SME the least smoke.

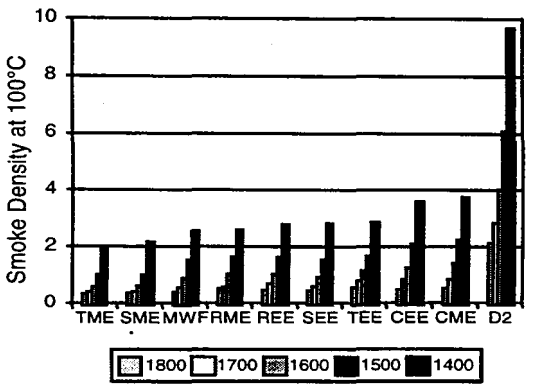


Figure 2. Average smoke density as determined by the opacity meter for each of the 9 Biodiesel fuels and Diesel. Data is from the torque test at 1800 to 1400 rpm.

6. At rated load, engine power produced by the Biodiesel fuels decreased an average of 4.9 percent compared to D2. Figure 3, is the power and torque data for the ethyl esters; the methyl esters produce similar results.

7. Peak torque for Biodiesel at 1700 RPM was reduced 5 percent on the average compared to D2 while at 1300 RPM it was reduced only 3 percent, demonstrating the flatter torque curve characteristic of Biodiesel.

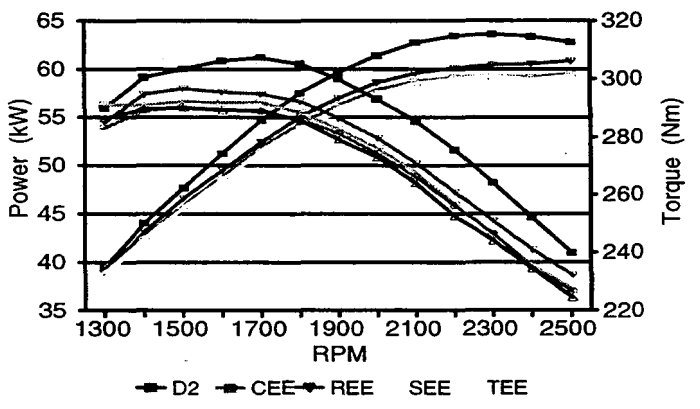


Figure 3. Power and Torque for Ethyl Ester Biodiesel Fuels and D2.

8. The average Biodiesel fuel consumption (g/s) on a mass basis was 7 percent higher than that of D2, Figures 4 and 5. On a volume basis (l/s) the consumption would be 6.7 percent higher than that of D2.

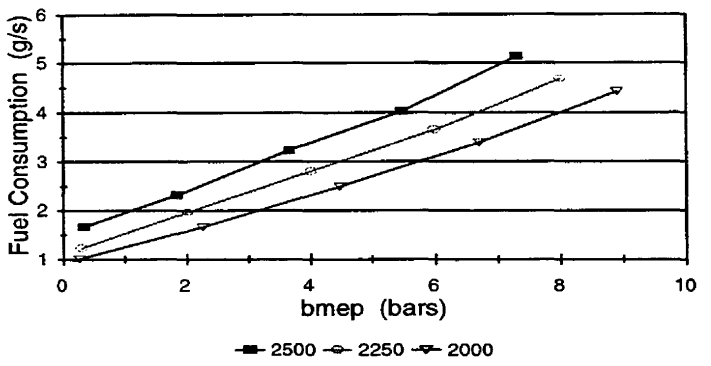
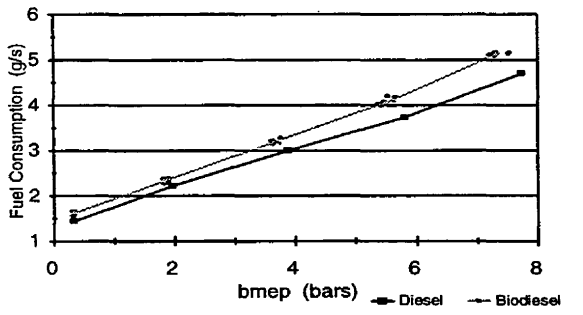


Figure 4. Fuel Consumption versus bmep for Canola Ethyl Ester at 3 RPM's from the Engine Mapping Test. This chart is typical of the 9 Biodiesel Fuels.



Average Biodiesel fuel consumption = 107% of diesel at the same % load

Figure 5. Fuel Consumption versus bmep for the 9 Biodiesel Fuels and D2. Data from mapping test at 2500 RPM.

9. Average thermal efficiencies for Biodiesel fuel in the mapping test was insignificant by difference when compared to D2, Figure 6.

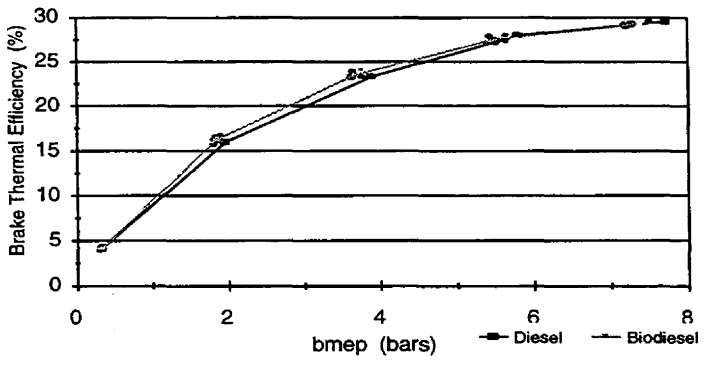


Figure 6. Thermal Efficiency versus bmep for the 9 Biodiesel Fuels and D2. Data is from the Fuel Mapping Test at 2500 RPM.

References

References available on request to the authors.

Table 4

Fuel Characterization

	D2	RME	REE	CME	CEE	TME	TEE	SME	SEE	MWF
Fuel Specific Properties										
Specific Gravity, 60/60	0.8495	0.8802	0.876	0.881	0.878	0.874	0.869	0.886	0.881	0.885
Viscosity CS @ 40°C	2.98	5.65	6.17	4.754	4.892	4.814	5.036	3.891	4.493	3.9
Cloud Point °C	-12	0	-2	1	-1	16	14	3	0	-1
Pour Point °C	-23	-15	-10	-9	-6	16	12	-3	-3	0
Flash Point, PMCC, °C	74	179	124	163	177	160	185	188	171	-18
Boiling Point °C	191	347	273	334	346	313	327	339	357	229
Water and Sediment % Vol.	<0.005	<0.005	<0.005	<.005	<.005	<.005	<.005	<.005	<.005	<0.005
Carbon Residue % mass	0.16	0.08	0.06	0.065	0.07	0.056	0.052	0.068	0.071	0.082
Ash % mass	0.002	0.002	0.002	0.002	0	0.001	0	0	0	0.001
Sulfur Wt%	0.036	0.012	0.014	0.009	0.009	0.01	0.009	0.012	0.008	0.02
Cetane Number	49.2	61.8	64.9	57.9	59.6	72.7	72.4	54.8	52.7	58.4
Heat of Combustion MJ/kg										
Gross	45.42	40.54	40.51	39.90	40.03	39.92	40.09	39.77	39.96	39.61
Net	42.90	37.77	38.00	37.23	37.62	37.25	37.63	37.04	37.44	37.14
Copper Corrosion	1A	1A	1A	1A	1A	1A	1A	1A	1A	1A
Karl Fischer Water, ppm	38	757	761	1087	1119	1142	1005	1062	1200	759
Particulate Matter, mg/L										
Total	0.9	1	1.9	0.9	1.1	1.9	0.8	0.9	1.1	15.65
Non-Combustible	<0.1	<0.1	0.9	0.1	0.1	0.9	<0.1	<0.1	0.1	2.15
Elemental Analysis										
Nitrogen, ppm		6	11	12	12	9	10	1	2	5.7
Carbon, %	86.67	78.7	76.83	77.67	76.71	76.42	76.58	82.44	83.4	77.54
Hydrogen, %	12.98	12.66	11.8	12.57	11.38	12.59	11.57	12.9	11.87	11.64
Oxygen % (by difference)	0.33	9.22	11.36	9.75	11.9	10.98	11.84	4.65	4.72	10.82
Iodine Number	8.6	97.4	96.7	102.8	101.6	49.1	47.2	103.6	43	81.3
Ester Specific Properties										
Percent Esterified		98.02	94.75	96.35	92.31	97.8	95.62	98.17	94.54	97.11
Acid Value		0.128	0.097	0.104	0.141	0.114	0.096	0.111	0.1	0.18
Free Glycerine %wt		0.4	0.72	0.71	0.52	0.2	0.2	0.62	0.7	0.42
Total Glycerine %wt		0.86	0.93	0.87	1.18	0.6	1.42	0.75	1.88	1.25
Free Fatty Acids %wt		0.57	0.58	0.42	0.42	0.37	0.39	0.6	0.21	0.37
Monoglycerides %wt		0	0.58	0.78	1.55	0.22	1.42	Trace	1.85	1.76
Diglycerides %wt		1.35	1.33	1.88	1.54	0.81	1.68	1.41	2.02	0.65
Triglycerides %wt		0.45	2.17	0.76	2.42	1.16	0.99	0.05	1.38	0.05
Alcohol Content % mass		<1	<1	<1	<1	<1	<1	<1	<1	<1
Catalyst		11	12	24	26	30	28	21	36	21
Fatty Acid Composition										
Palmitic (16:0)		2.2	2.6	4.0	4.0	23.3	23.6	9.9	10.0	10.1
Stearic (18:0)		0.9	0.9	2.4	2.4	17.9	18.0	3.8	3.8	3.8
Oleic (18:1)		12.6	12.8	65.0	65.1	38.0	38.5	19.1	18.9	20.5
Linoleic (18:2)		12.1	11.9	17.3	17.4	0.0	0.0	55.6	55.7	56.1
Linolenic (18:3)		8	7.7	7.8	7.6	0.0	0.0	10.2	10.2	8.8
Eicosenoic (20:1)		7.4	7.3	1.3	1.3	0.0	0.0	0.2	0.2	0.0
Behenic (22:0)		0.7	0.7	0.4	0.4	0.0	0.0	0.3	0.3	0.0
Erucic (22:1)		49.8	49.5	0.1	0.2	0.0	0.0	0.0	0.0	0.0

ON-ROAD TESTING OF RAPESEED BIODIESEL

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Abstract

Two on-road diesel pickups were operated on a mixture of 20 percent Biodiesel and 80 percent diesel for 80,500 km (50,000 miles). One pickup, powered by a 5.9 liter direct injected, turbocharged, and intercooled engine was operated on 20 percent RME and 80 percent diesel. The other pickup, powered by a 7.3 liter, naturally aspirated, precombustion chamber engine, was operated on 20 percent raw rapeseed oil and 80 percent diesel. The engines were unmodified, but modifications were made to the vehicles for the convenience of the test. In order to give maximum vehicle range, fuel mixing was done on-board to extend the driving range to over 4,800 km (3,000 miles) between Biodiesel fill ups. Two tanks were added, one for a mixing chamber and one for the Biodiesel fuel tank in the bed of the pickup. Electric fuel pumps supply fuel to the combining chamber for correct proportioning. The Biodiesel fuel tanks were heated through a heat exchanger in the fuel tank with the use of engine coolant.

Chassis dynamometer testing, injector coking, engine compression, injector valve opening pressures, and engine oil analyses were performed at regularly scheduled intervals to monitor the engine performance parameters. RME produced 5 percent less power than D2, 20RME produced 1 percent less than D2, and 20RAW produced 1 percent less power than D2. Opacity was reduced 26 percent with RME, 20RME reduced opacity 10 percent, and 20RAW decreased opacity by 11 percent with the snap idle test compared to D2.

Emissions tests with a chassis transient dynamometer at the Los Angeles Metropolitan Authority Emissions Test Facility resulted in a decrease in HC (20 percent), CO (25 percent), NOx (2.6 percent), PM (10.9 percent), and there was no difference in CO_2 with 20RME compared to D2.

Introduction

Much interest has been generated in the use of alternative fuels for transportation. The Clean Air Act Amendment of 1990 mandates phase-in adoption of clean fuels that are not harmful to the environment. The Energy Policy Act of 1992 also mandates fleet operators to begin purchasing alternative fueled vehicles as a percentage of all new vehicles purchased starting in model year 1996. Increased EPA exhaust emissions requirements for diesel engines have also created much interest in the use of Biodiesel. Such legislation and federal policies will significantly increase the attractiveness of the use and expedite the commercialization of biofuels, including ethanol and vegetable oils. Increased use of these fuels can reduce U.S. dependence on imported oil and help improve air quality by reducing harmful gaseous and particulate emissions.

Emissions from compression ignition engines fueled with vegetable oil contain negligible levels of sulfur dioxide responsible for acid rain. Vegetable oils are also more environmentally friendly in the case of a spill. The fuel is biodegradable and will quickly break down, thus preventing long-term damage to soil or water (Peterson et al., 1994).

Vegetable oil as an alternative to diesel fuel has been under study at the University of Idaho since 1979. Researchers at the UI have pioneered the use of rapeseed oil as a diesel fuel substitute. Through this and other research, it has been demonstrated that raw rapeseed oil is best used for fuel in precombustion chamber type diesel engines as a blend with diesel. Most diesel engines in use in the United States are of the direct injection type. For these engines, it has been found that the rapeseed oil should be transesterified before being used as a diesel fuel substitute. Methyl ester of rapeseed (RME) can be substituted for diesel fuel in unmodified diesel engines without significant reduction in engine performance.

Objectives

Past research has focused on the development and testing of Biodiesel in controlled environments. The objective of this project was to determine if Biodiesel is a viable transportation fuel using two Biodiesel fueled on-the-road pickups. Specific objectives for achieving this goal are:

- Operate two pickups for 80,467 km (50,000 miles) with a blend of 20 percent RME, 80 percent D2 (20RME) in one and a blend of 20 percent raw rapeseed oil 80 percent D2 (20RAW) fuel in the other.
- Design an on-board fuel mixing system to maximize the travel range for each pickup and at the same time keeping the fuel from congealing.
- From chassis steady state dynamometer testing, determine the percent difference in power, opacity, and fuel economy to that of D2.
- Conduct pending ASAE fuel standard tests for 20RME, 20RAW, number two diesel (D2), and 100% RME.
- Compare regulated emissions data including total hydrocarbons (HC), carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NOx), and particulate matter (PM) for RME, 20RME, and diesel control fuel.

Materials and Methods

Two blends of Biodiesel and number two diesel fuel (D2) were studied using two diesel powered pickups at the University of Idaho. During the past decade researchers at the University of Idaho have shown that methyl ester of rapeseed is comparable to D2. This study was to verify the use of blends of Biodiesel in on-road vehicles.

Fuels

The feedstock for both fuels under study is winter rapeseed, Dwarf Essex variety, that was expelled at the University of Idaho's Department of Agricultural Engineering's Farm Scale Processing Facility. One blend of fuel was 20 percent raw rapeseed oil and 80 percent D2. The other was a 20 percent blend of rapeseed methyl ester (RME), produced at the farm scale processing facility, and 80 percent D2. The RME was processed using equipment and techniques scaled up and modified from prior research at the University of Idaho (Mosgrove, 1987). The abbreviations used to denote the different fuels are as follows:

RAW = 100 percent raw rapeseed oil from the oil expeller and filtered
20RAW = 20 percent RAW and 80 percent D2
RME = 100 percent methyl ester of rapeseed
20RME = 20 percent RME and 80 percent D2
D2 = 100 percent number two diesel fuel

The fuels were characterized by evaluating the parameters required in ASAE EP X552. The tests for specific gravity, viscosity, cloud point, pour point, flash point, heat of combustion, total acid value, catalyst, and fatty acid composition were performed at the Analytical Lab, Department of Agricultural Engineering, University of Idaho. The boiling point, water and sediment, carbon residue, ash, sulfur, cetane number, copper corrosion, Karl Fischer water, particulate matter, iodine number, and the elemental analysis were performed at Phoenix Chemical Labs, Chicago, Illinois. The HPLC and titration analysis for total and free glycerol, percent of oil esterified, free fatty acids, and mono-, di-, and trigylicerides were performed by Diversified Labs Inc., Chantilly, Virginia.

On-Road Vehicles

Dodge

The first pickup was a Dodge[1] 3/4-ton powered by a Cummins 5.9 liter turbocharged, intercooled direct injected diesel engine. The engine is an in-line six cylinder and has a bore and stroke of 102.0 x 120.0 mm, respectively; a compression ratio of 17.5:1; produces 119 kW at 2,500 RPM; and a peak torque of 542 N-m at 1750 RPM. It was equipped with a Bosch VE distributor type fuel injection pump. This pickup has been operated on 20RME.

Ford

The second pickup was a Ford, powered by a Navistar 7.3 liter, naturally aspirated, precombustion chambered V-8 diesel engine. The engine has a bore and stroke of 104.38 x 104.44 mm, respectively; a compression ratio of 21.5:1; produces 134 kw at 3,300 RPM; and a peak torque of 467 N-m at 1400 RPM. It was equipped with a Stanadyne rotary type fuel injection pump. A blend of 20 percent raw rapeseed oil and 80 percent diesel was selected for this pickup because of the precombustion chambered engine.

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[1]The use of manufacturer's names or trade products does not represent an endorsement of the product nor discrimination toward similar products which are not named.

Check Vehicles
Three other pickups were used as check vehicles. Two were equipped with the 5.9 liter direct injection engines, and the other used a 7.3 liter engine with a precombustion chamber. These vehicles were privately owned and operated on 100 percent diesel fuel to serve as a comparison. Oil samples and analyses were performed at the owners discretion and analyzed by the same laboratory as the Biodiesel pickups. When possible, these vehicles were dynamometer tested at the same facility as the Biodiesel pickups.

Fuel Mixing System
The fuel delivery systems in the Biodiesel pickups were modified to provide for on-board mixing of the fuel. Providing for on-board mixing greatly extends the range of the vehicles compared to the original equipment manufacturers tanks. A 210 L (55 gal) fuel tank was added to the bed of each vehicle and insulated to store the Biodiesel fuel. A one and one-half gallon mixing chamber was mounted to the frame of each vehicle with the diesel and Biodiesel fuel lines routed to this chamber. Each fuel supply was transferred from the tanks to the combining chamber with 12 volt electric fuel pumps. The combining chamber was constructed from mild steel and designed to incorporate four floats. The bottom float was a normally open, polypropylene float and stem mounted horizontally in the chamber 4.5 cm (1.75 in) from the bottom. It operated a low fuel warning light in the operators cab which makes the operator aware that the fueling circuit is not functioning. The second float was also a normally open polypropylene float and stem mounted horizontally in the chamber. When the fuel drops below this float a relay turns on the diesel fuel pump. Diesel fuel is then transferred into the chamber until the third float deactivates the relay and shuts off the diesel fuel pump. The third float simultaneously activates the Biodiesel fuel pump and fills the chamber until the 20/80 blend is obtained. A fourth float, made of Buna-N and a brass stem, was mounted vertically in the top of the tank and can be adjusted to give the correct blend. The adjustment was preset in the laboratory before being mounted in the frame of the vehicle. Based on a 20 percent blend of Biodiesel / 80 percent diesel and 7.5 km/L (18 mpg) fuel consumption the on-board mixing increased the travel mileage from 965 km (600 miles) to 7,242 km (4,500 miles) before requiring a Biodiesel fill-up.

During the first 32,187 km (20,000 miles) of operation of the Dodge pickup, rust was forming in the Biodiesel tank and transferring to the fuel filter. The fuel filter was being replaced every 4,830 km (3,000 miles) due to plugging and loss of engine power. The mild steel 210 L (55 gal) tank and the combining chamber were replaced with stainless steel tanks of similar design on the Dodge pickup only. New 12-volt positive displacement fuel pumps were installed for the Biodiesel fuel and a 12-volt shut-off solenoid valve was placed in line with the pump on both vehicles.

Fuel Heating System
During cold weather operation the Biodiesel fuels need to be kept above the pour point, which is higher than normal diesel fuel. Engine coolant was used to warm the fuel in the Biodiesel fuel tanks. A stainless steel in-line fuel warmer was installed horizontally into the 210 L (55 gal) Biodiesel fuel tank. A thermostat with an adjustable set point was set at 12.7°C (55°F) and closed on rise to operate the coolant pump. The coolant lines were 1.59 cm (5/8 in) silicon heater hose which were routed along side the fuel supply and return lines and laid beside the fuel combining chamber and Biodiesel fuel pump. They were insulated to help keep the fuel lines and the fuel in the combining chamber above the pour point when the vehicle was not in operation.

When the pickup was sitting idle without the engine running, a 110-volt thermostatically controlled engine pre-heater was used to keep the engine coolant at 38°C (100°F). The thermostat was installed on the inlet side of the heater. It senses the temperature of the coolant at the inlet to the heater, and keeps the coolant at the preset temperature range.

Since the coolant pump operates on 12 volts, a 10 amp DC power supply was used to convert standard 120 volt AC power into regulated 12 volt DC power. A 12 volt, 25 amp DC power relay was used to switch the power source when 120 volts AC was required. A shut off valve was added before the coolant pump for flow control purposes.

Other Modifications

While the engines of the test vehicles were unmodified, the vehicles themselves have been modified for convenience of running the test. For example, it is known that esters will deteriorate rubber components over a period of time, so the rubber fuel lines were replaced with viton hose. A low coolant indicator was installed and a red light in the cab was used to warn the operator of low coolant. An hour meter was also added and operated only when there was engine oil pressure. A Biodiesel fuel tank gauge gave an indication of the level of fuel in the Biodiesel tank. Additional ammeters and indicator lights indicated that the fuel mixing system was working properly. Each pickup was equipped with a log book to keep daily and long-term records. Also, a maintenance record book was kept for each vehicle, which included the oil samples, dynamometer test data sheets, and any other scheduled or unscheduled maintenance.

Dynamometer Testing

Both pickups had a break-in period and were dynamometer tested before the Biodiesel fuel mixing system was incorporated. Each pickup was dynamometer tested every 16,000 km (10,000 miles) at Western States Cat in Spokane, Washington. During each dynamometer test the vehicle was tested with the following: once with the 20/80 mix and again with 100 percent diesel. In addition the Dodge pickup was also dynamometer tested with 100 percent RME. A predetermined set of engine RPM's was programmed into the computer to obtain repetitive data. The Ford pickup was dynamometer tested from 1400 to 3400 RPM in increments of 200 RPM. Engine RPM's for the Dodge were 1600 to 2650 RPM with 150 RPM increments. A computer recorded vehicle power, vehicle speed, fuel economy, engine RPM, opacity, torque, engine oil pressure, fuel pressure and temperature, exhaust temperature, inlet air temperature, and coolant temperature. The Dodge pickup also had the intake manifold pressure and engine blowby measured.

Performance Parameters

After each dynamometer test the injectors were removed from the engine to check for carbon deposits using the procedure described in "A Rapid Engine Test to Measure Injector Fouling in Diesel Engines Using Vegetable Oil Fuels" (Korus et al, 1985). The cylinder compression was tested and the injector valve opening pressure was also checked. The Dodge pickup, Cummins engine, has direct access to the combustion chamber and cylinder walls through the injector bore in the cylinder head. A fiberoptic borescope was used for this engine to visually inspect the amount of carbon build up on the piston crown and valve heads and to check for any abnormal cylinder wear.

Oil samples were taken at each oil change, which was 4,800 km (3,000 miles) for the Biodiesel pickups, and at the convenience of the owners of the control vehicles. The oil

samples were analyzed at a commercial oil analysis laboratory for wear metals, and physical tests were performed, including antifreeze, fuel dilution, water, and viscosity. An infrared analysis for soot, sulfur, nitration, and oxidation of the engine oil were also conducted. The reportable limits for each metal was supplied by the oil analysis lab.

The emissions tests were conducted at the Los Angeles Metropolitan Transit Authority Emissions Testing Facility (ETF) in Los Angeles, California. This facility has instrumentation to measure all regulated emissions: total hydrocarbons (HC), carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NOx), and particulate matter (PM). Peterson and Reece (1994) report on comprehensive emissions testing, materials and methods, procedures, and results from the MTA ETF using methyl and ethyl esters of rapeseed oil.

Two test cycles were utilized for this program. The first was a modified arterial cycle (arterial). The standard form of this test was doubled, creating a 758 second, 8 event cycle. The arterial cycle, as used, had eight repetitions of acceleration to 64 km/h (40 mph) and decelerating to 0 km/h. The second cycle was the EPA Dynamometer Driving Schedule for Heavy-Duty Vehicles (CFR, 1993). The EPA cycle took a total of 1060 seconds.

Results and Discussion

Fuels

A complete summary of the fuel characterization data is avialable in (Reece, 1995.) Important observations on a few of the parameters are listed below.

Viscosity - The RAW fuel had a viscosity 15.7 times greater than D2 at 40°C while RME was only 1.8 times greater than D2. The 20RME had a similar viscosity as did the D2.

Cloud and Pour Point - All the pour points were within 1°C of D2 including the RAW oil. RME had a cloud point of 0°C and D2 was -12°C with the RAW and blends were within 1°C of D2.

Sulfur - D2 (not low sulfur diesel) had 18 times more sulfur than RME and 10.5 times more than RAW.

Heat of Combustion - The gross heat of combustion for D2 is 5.6 percent greater than RME fuel and 11 percent greater than RAW oil on a mass basis.

Flash Point - A flash point of 74°C was measured for D2 while the RME was measured at 179°C and RAW at 274°C. The higher flash points of Biodiesel indicate that it is safer to use, store, and handle based on fire safety concerns.

On-Road Vehicles

Dodge

The Dodge pickup accumulated 89,146 km (55,393 miles) with 85,966 km (53,417 miles) on the 20/80 blend. The fuel economy for the first 3,180 km (1,976 miles) using 100 percent D2 was 8.55 km/L (20.6 mpg). The average fuel economy with the blend was 8.3 km/L (20.0 mpg). It consumed 6,882 L (1818 gal) of diesel and 2,794 L (738 gal) of RME for a blend of 28.8 percent RME and 71.2 percent D2. This was 8.8 percent above the target value of the 20 percent blend of RME.

The rust in the steel tanks may have been due to the heating and cooling of the fuel in the tank during the winter, condensing the moisture in the atmospheric air and/or a very small amount of catalyst is in the RME fuel which is basic and will speed-up the oxidation

reaction. After changing over to the stainless steel tanks there was unusual fuel filter plugging during the winter months. A wax like substance in the fuel filter was analyzed and it was determined to be 50 percent diesel fuel and 50 percent Biodiesel. Fuel filter plugging ceased after winter.

Ford

The Ford pickup accumulated 82,414 km (51,210 miles) with 79,733 km (49,544 miles) on the 20/80 blend. The fuel economy for the first 2,681 km (1,666 miles) using 100 percent D2 was 7.37 km/L (17.76 mpg). The average fuel economy with the blend was 6.93 km/L (16.7 mpg). This truck consumed 8,759 L (2,314 gal) of diesel and 2,438 L (644 gal) of rapeseed oil for a blend of 22.4 percent RAW and 77.6 percent D2. This was 2.4 percent above the initial value of the 20 percent blend.

The mixture of rapeseed oil varied from 14 percent to a high of 41 percent when the pickup would not start. Fuel economy varied from 4.98 km/L (12 mpg) to 8.3 km/L (20 mpg). During the first 48,280 km (30,000 miles) of testing the percent of rapeseed oil was as high as 40. This was higher than the target of 20 percent and caused excessive carbon build-up on the injector tips. The injectors were removed and cleaned at 73,193 km (45,480 miles), after which the performance of the pickup noticeably improved.

Fuel Heating System

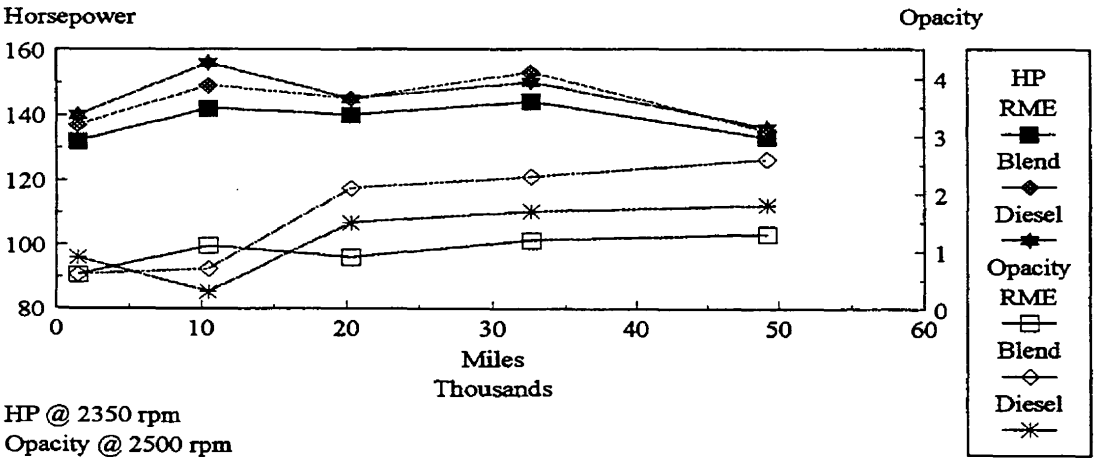
The fuel heating system on both pickups worked very well through the course of testing. After the initial installation of the heating system the pickups were parked outside over a period of three days and nights with temperatures below -9.4°C (15°F). The ambient and Biodiesel fuel temperatures were monitored with thermocouples and a data acquisition system for the three day period. As the ambient temperature dropped below -9.4°C the Biodiesel fuel maintained a temperature of 12.7 to 15.5°C (55 to 60°F).

Dynamometer Testing

Dodge

Figure 1 is a graphical comparison of the horsepower and opacity with each of the three fuels tested over a period of five dynamometer tests. On the average, 100RME produced 5 percent less horsepower than D2 and 20RME produced 1 percent less than D2. Also, opacity was reduced 26 percent with 100RME, while 20RME reduced opacity 10 percent over D2.

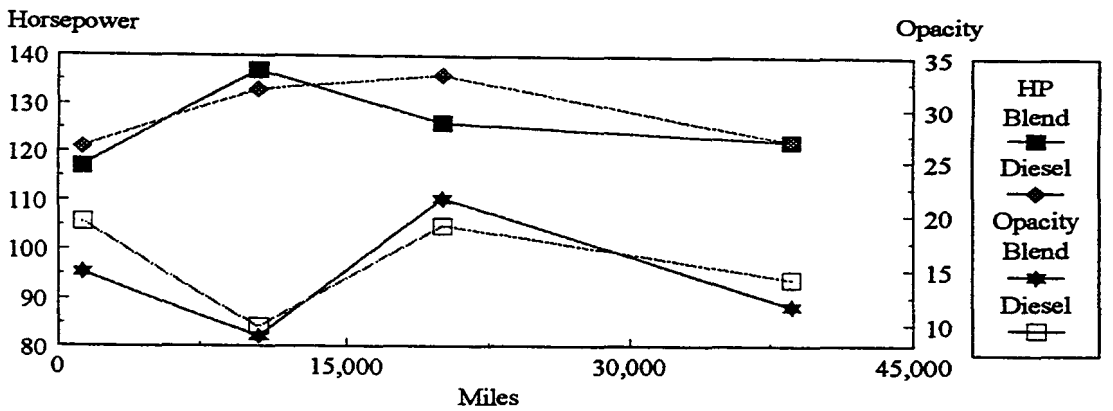
Figure 1. Dodge Horsepower and Opacity at Five Dynamometer Tests.



Ford

Figure 2 is a graphical comparison of the horsepower and opacity for both fuels tested over a period of four dynamometer tests.

Figure 2. Ford Horsepower and Opacity for Four Dynamometer Tests.



HP @ 3000 rpm
Opacity @ 2800 rpm

The 20RAW produced 1 percent less horsepower, and 11 percent less opacity compared to D2 using the snap idle test.

Check Vehicles

The Ford check vehicle was dynamometer tested twice. At 62,235 km (38,671 miles) a horsepower rating of 124 at 3,000 RPM and 11.7 percent opacity for the snap idle test was recorded. The compression was comparable to the Biodiesel and the injector VOP was 1,380 kPa (200 psi) lower. The Dodge check pickups were equipped with automatic transmissions, which are not compatible with the dynamometer.

Engine Oil Analysis

The engine oil was sampled at each oil change interval, which was every 4,800 km (3,000 miles). The engine oil was changed every 4,800 km using Chevron Delo Multigrade SAE 15W-40 heavy duty engine oil. Wear data for the Dodge pickup was at acceptable levels without any significant differences between the sampling reports. The Ford Biodiesel pickup indicated high iron after 45,000 km (28,000 miles). The Ford check vehicle indicated high iron throughout the monitoring period.

Performance Parameters

Injector coking was measured after each dynamometer test but a check vehicle operating on 100 percent D2 was not studied during this testing; therefore, an injector coking index is not available. There was very little carbon build-up on the tip of the fuel injector tips either visually or by calculating the area of the coked injector from one interval to the next for the Dodge.

The Dodge fuel injectors were sticking when tested at the 79,340 km (49,300 mile) engine performance test because of the fuel filter plugging and rusty fuel being introduced in the injectors. The injectors were cleaned and retested, which resulted in a good spray pattern and the specified valve opening pressure.

The Ford fuel injector tips had a significant amount of carbon build-up both visually and by calculating the area of the coked injector from one interval to the next. The fuel injector tips were cleaned at 73,193 km (45,480 miles) due to excess carbon build-up which was distorting the fuel spray pattern.

The engine cylinder compression, on both the Dodge and Ford engines, was checked at each performance interval. The cylinder compression in the Dodge either stayed the same or decreased only as much as 103 kPa (15 psi) from the beginning of the test to the end. The cylinder compression in the Ford increased in each cylinder as much as 276 kPa (40 psi) with the exception of cylinder number 5 which decreased by 103 kPa (15 psi). The average cylinder compression for both pickups was 3,447 kPa (500 psi).

The average beginning valve opening pressure (VOP) for the Dodge was 24.2 MPa (3,510 psi) with a standard deviation of 144 kPa (21 psi) and the average ending VOP was 23.8 MPa (3,450 psi) with a standard deviation of 65 psi. The average beginning VOP for the Ford pickup was 13.8 MPa (2,005 psi) with a standard deviation of 117 kPa (17 psi) and the average ending VOP was 13.4 MPa (1950 psi) with a standard deviation of 220 kPa (32 psi). The Ford check vehicle had the VOP checked at 62,233 km (38,670 miles). The average VOP was 12.7 MPa (1840 psi) and a standard deviation of 317 kPa (46 psi).

The Dodge combustion areas were borescoped at each performance interval. There was no significant visual change from one time to the next. At the end of this study there were a few slight carbon scratches on the thrust side of the cylinder walls of each cylinder, which is normal for the number of accumulated miles. There did not appear to be any excess amount of carbon build-up on the piston crowns or the cylinder head and valves.

Emissions Tests

Since a large amount of data was collected, only summary data from emissions testing is reported. Modal data were archived every 1 second during the test. The data presented is fuel type, cycle, HC, CO, NOx, CO_2, and PM. All the regulated emissions were higher for the EPA cycle than for the modified arterial cycle. This is probably due to the increased idling time and non-repetitive nature of the EPA cycle. The 100RME showed a slight reduction in NOx, a significant reduction in HC and CO, and a slight increase in PM and CO_2 compared to 100D2.

Discussion

The drivers of the vehicles have not noticed any change in vehicle operation or other abnormalities during the course of the test. The Ford averaged 7.35 km/L (17.7 mpg) and the Dodge 8.3 km/L (20.0 mpg) for the 80,467 km (50,000 miles). The Ford check vehicle averaged 5.4 km/L (13 mpg) and the Dodge 7.05 km/L (17 mpg). These two check vehicles were used for utility type applications with heavy loads, while the test vehicles generally were operated empty, which may explain the differences in economy.

On-road performance tests demonstrated that RME and 20RME can be used to successfully fuel a diesel engine. The 20RAW fuel should be limited to pre-combustion chamber engines and may require more frequent fuel injector tip cleaning. The 20RAW fuel has generally not been recommended for general use because of potential engine polymerization and lubrication oil problems.

Conclusions

At the conclusion of 80,467 km (50,000 miles) with two pickups operating on 20 percent Biodiesel (RAW or RME) there is no indication of abnormal wear or performance. The on-board mixing system was essential only for purpose of this experiment. It should be clear, however, that for commercial use the blending would take place at the fuel plant eliminating the on-board mixing system.

Emission tests show that a 20 percent blend of RME and 80 percent diesel produced a reduction in 4 of the 5 regulated emissions (CO_2 being the exception.) Specific conclusions from the results of this testing are presented below.

- Fuel characterization data show some similarities and differences between RME and D2. a) Specific weight is higher for RME, viscosity is 1.9 times that of D2 at 40°C, and the heat of combustion is 5.6% lower than D2. b) Sulfur content for RME is 67% less than D2.
- Visually, all injector coking was low with 20RME especially compared with older tests that included raw vegetable oils. The 20RAW injector tips had accumulated excessive deposits and were cleaned at 73,193 km (45,480 miles) with a noticeable difference in performance. The Dodge injectors were cleaned at 79,340 km (49,300 miles) due to rust.
- The fuel heating systems worked well during the test period. The fuel combining systems were updated two times due to continual adjustments to achieve the targeted 20 percent blend.
- On the average, RME produced 5 percent less power than D2 and 20RME produced 1 percent less than D2. The 20RAW produced 1 percent less power than D2.
- On the average, opacity was reduced 26 percent with RME, while 20RME reduced opacity 10 percent over D2. The 20RAW decreased opacity by 11 percent with the snap idle test.
- The average fuel economy (mpg) for RME was 4 percent higher than that of D2 , 1.8 percent higher for 20RME, and 2.6 percent higher for 20 RAW. The differences in fuel consumption and power reflect the differences in heat of combustion and density between the two fuels.
- Emissions tests with the arterial cycle showed decreases in HC (55 percent), CO (42 percent), NOx (9.1 percent), PM (6.8 percent), and an increase in CO_2 (0.7 percent) when 100 percent RME is compared to D2.
- The 20RME fuel, decreased HC(20 percent), CO (25 percent), NOx (2.6 percent), PM (10.9 percent), and there was no difference in CO_2 compared to D2.
- Statistical analysis showed significant differences with HC, CO, and NOx from diesel ($p<=0.05$), and no significant difference was determined for CO_2 and PM.

References

References available upon request.

ONE-PHASE METHODS FOR ACCELERATING THE PRODUCTION OF BIODIESEL METHYL ESTERS

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Abstract

The base-catalysed (methoxide or hydroxide) methanolysis of vegetable oils (6:1 methanol/oil molar ratio), such as soybean, occurs 15-20 times slower than butanolysis because the former starts out as a two-phase system, in which the solubility of the oil in the methanol phase, where the catalyst is located, is very low. The addition of a cosolvent, such as 1.27 volumes of tetrahydrofuran (THF) per volume of methanol, forms an oil-rich, one phase system in which methanolysis is as fast as butanolysis. Other suitable cosolvents include 1,4-dioxane, diethyl ether and t-butyl methyl ether. THF has a boiling point very close to that of methanol and can be flashed and recycled along with unused alcohol. Glycerol separation usually occurs faster in the presence of cosolvent (4-5 times faster in the case of THF). The sudden and abnormal slowing of both hydroxide and alkoxide transesterifications may be caused by a number of factors including polarity of the mixture, the formation of undesired intermediates and structural differences in the substrates. Simple appropriate measures can dramatically lower 98% conversion times to twenty minutes and less, in which case continuous processes employing centrifuges for glycerol separation become very attractive.

Introduction

Biodiesel, in the form of vegetable oil methyl esters, is already being manufactured and sold in many European countries including Austria, Belgium, Sweden, Denmark, Germany, Italy, the Czech Republic and Hungary. There are 25-30 manufacturing facilities, a few of which operate on a cooperative farm scale. In the U.S.A, 1500 vehicles have been involved in 13 million kilometres of testing. Another 100,000 hours of testing have been carried out in non-moving equipment to measure engine performance in terms other than mileage.[1] The incentives for Governments to encourage the production and use of Biodiesel are environmental concerns, management of the agricultural sector and some perception of self sufficiency. The incentives for farmers and producers are agricultural subsidies and fuel tax relief. The major benefits may well be environmental. The most obvious benefit is that the Biodiesel is made from a renewable crop which takes up carbon dioxide as it grows. Biodiesel is also biodegradeable. The less obvious advantage is the significant reduction in the engine emissions of hydrocarbons, carbon monoxide and particulate matter (nitric oxide emissions increase slightly). In engines in which the timing has been modified, emissions fall even further. Biodiesel can either be run neat or in blends with petrodiesel. The only disadvantages are that engine oil should be changed more frequently and that paint work may be less resistant to spilled fuel. While considerable attention has been placed on fuel performance, relatively little effort has been made on improving the process for Biodiesel production. It is generally assumed that the reaction is slow and must therefore be carried out in a batch mode. Unfortunately, the kinetic data for the reaction has been misinterpreted particularly as mass transfer limitations were ignored.

Background

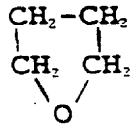
Methanolysis is used to transform vegetable oils to their methyl esters and thus effectively split the vegetable oil molecules into three parts. The product is therefore less viscous than the vegetable oils, and this dramatically improves engine performance. The bas-catalysed reaction is preferred over the acid-catalysed method because it is considerably faster. However, this difference is only relative and it is generally assumed that the methanolysis reaction is inherently slow and also requires considerable time for the separation of the byproduct, glycerol. Although methoxide ion is theoretically the best catalyst, particularly when water or carboxylic acids are absent, hydroxide ion, usually from sodium hydroxide, is the most convenient catalyst. The equilibrium between hydroxide ion and methanol is used to provide methoxide ion. The pKa's of water and methanol are very similar, and if this dissociation comparison can be extended to the methanol rich- system then this is a good way to produce methoxide ions. The presence of hydroxide ion is potentially detrimental because the attack of the hydroxide on the esters leads to the irreversible formation of carboxylic acids. It was determined in 1984[2] that a 6:1 methanol/oil molar ratio is sufficient to give methyl ester yields over 95%. This is a surprisingly low ratio for this type of reaction and strongly suggests that the glyceride anions are inferior nucleophiles compared to methoxide ions. The separation of the glycerol does not appear to be a factor in the phenomenon. It has been reported that glycerol separation does not play a role in the ethanolysis of peanut oil[3]. In addition when glycerol trioctanoate is used as substrate in the presence of a cosolvent, the glycerol does not separate, but methyl ester yields are over 98%. It is also generally concluded[2]

that 1.0 wt.% sodium hydroxide based on the oil is the optimum catalyst concentration.

The kinetics of the methanolysis and butanolysis of soybean oil have been measured in the presence of butoxide and methoxide catalysts[4]. The butanolysis followed second order kinetics whereas the methanolysis did not. In particular the intermediate di- and monoglycerides never built up to the predicted concentrations. The authors very surprisingly, did not point out that the butanolysis reaction was 15-20 times faster than methanolysis even though the latter was carried out at 40°C and the butanolysis at 30°C. The methanolysis also exhibited a lag time of about 4 minutes before significant amounts of methyl esters appeared. This was also ignored by the authors. The observations can be explained on the basis of the physical nature of the initial reaction mixtures in the two cases. Whereas the 6:1 butanol/oil molar mixture is one phase, the equivalent methanolysis mixture has two phases. In addition the solubility of the oil in the upper methanol phase is low. Through the application of some agitation, the oil solubility in the methanol is only 3.7g L^{-1} at 23°C and 5.7g L^{-1} when the mixture is stirred vigorously for 20 minutes Even though the methanolysis reaction mixture is stirred vigorously, the reaction is mass transfer limited. This explains the slow reaction and the lag time. Any di- and monoglycerides formed in the methanol phase, where the catalyst is located, are more likely to react further there rather than passing back to the oil phase, thus explaining the abnormal concentration profiles

One-Phase Methanolysis[5]

Once the explanation for the anomalies became clear it suggested a method for significantly improving the rate of methanolysis. If a suitable cosolvent could be found that would render the mixture one phase without excessive dilution, then the reaction rate should increase greatly. From a consideration of functional groups and their polarities we believed that ethers were prime candidates for this purpose. In addition, ethers are relatively inert, particularly under basic conditions, Several ethers are in fact good cosolvents, including diethyl ether, t-butyl methyl ether, diisopropyl ether and 1,4-dioxane, but the best in terms of the least volume required is tetrahydrofuran (THF, Structure I).



(I)

Only 1.27 volumes of THF per volume of methanol are required to make the 6:1 methanol/soybean oil mixture one phase at 23°C. An even smaller ratio (0.87) is required in the case of coconut oil which has shorter and more saturated side chains. For soybean oil, the total volume of the reaction mixture only increases by 22% because of the high molar volume of the oil. In this one-phase system methanolysis now occurs as fast as butanolysis. Surprisingly, the glycerol separation still occurs, and does so about 4-5 times faster than in the two-phase system. There is yet another advantage to using THF in that

its boiling point is only 2°C different from that of methanol. Therefore, at the end of the reaction the methanol and THF may be flashed off and recycled together. Finally, in the one-phase system no stirring is required, in contrast to the two-phase reaction which requires vigorous stirring. Ternary phase diagrams have been constructed for mixtures of each of the above cosolvents with methanol and four vegetable oils. The results will be published elsewhere.

The reaction in the one phase system is over 95% complete in 20 minutes. It is over 80% complete in one minute and therefore shows the same characteristics as the butanolysis reaction, in being a very fast in the first few seconds but significantly slower thereafter. It has been suggested from a study on the ethanolysis of peanut oil[5] that the depletion of hydroxide is rapid and could therefore cause the slowing of the reaction. However , we believe we have observed this reaction in the study of octanoates (see below) and it is considerably slower than the transmethylation[6]. The phenomenon can also be explained by assuming much smaller rate constants for the conversion of the di- and monoglycerides. We have even suggested cyclic intermediates that would interfere with the transesterification of the mono- and diglycerides. Preliminary experiments with 1,2- and 1,3-glycerol dioctanoates and ethanediol dioctanoate appeared to confirm that the six-membered ring intermediate which is only possible in the case of the 1,3-isomer, was the real problem. However, glycerol trioctanoate (GTO), which should also be capable of forming the intermediate, failed to show the slow phase, the reaction being over 98% complete in three minutes. This is despite the fact that the glycerol does not separate in this reaction. A comparison of the reaction conditions for the one phase methanolysis of soybean oil and GTO is instructive. Compared to the reaction with soybean oil the following are true of the reaction conditions for the methanolysis of GTO: (6:1 methanol /oil molar ratio, 1.0 wt.% sodium hydroxide based on the oil, THF/methanol volume ratio, 1.6, i.e. 28.5% excess).

1. The oil molar concentration increases.
2. The methanol concentration increases.
3. The polarity of the mixture increases because of item 2.
4. The base molar concentration decreases .
5. The glycerol does not separate and therefore decrease the polarity of the mixture.

The only other differences are the shorter and saturated side chains in GTO. There is not much flexibility in changing items 1-3 and 5 independently, particularly in the case of vegtable oils.. However, we have now shown that by increasing the sodium hydroxide concentration into the 1.0-2.0 wt.% range we can accomplish the transesterification of soybean oil in 1-3 minutes and further enhance the glycerol separation. This adjustment is obviously not very effective in the two-phase reaction. The discovery of the one-phase reaction makes continuous processes for the production of vegetable oil methyl esters very attractive. The process is conceptualised as follows. The vegetable oil and methanol/THF mixture (already containing the hydroxide) would be metered into the flow-through reactor. At the appropriate time the reaction would be quenched with carbon dioxide or a small amount of acid. The mixture would pass through a continuous centrifuge to remove most of the glycerol. The methanol and glycerol would be flashed off and returned to a holding tank for readjustment of the methanol/THF ratio and addition of base. A second centrifugation of the crude product would remove more

separated glycerol. Continuous water washing and drying would yield the product. Depending on the purity of the product and the specifications of the required fuel, distillation may or may not be required. The glycerol phase would require its own purification procedure.

Conclusions

Consideration of both chemical and mass transfer concepts has pinpointed that the major reason for the slowness of the base-catalysed methanolysis of vegetable oils is the two-phase nature of the initial reaction mixture. The solution to this problem is the use of an inert cosolvent which produces an oil-rich single phase. A dramatic slowing of the reaction rate towards the end of one -phase methanolyses of vegetable oils under the normal reaction conditions (1.0 wt.% sodium hydroxide based on the oil and 6:1 methanol/oil ratio) does not occur in the case of glycerol trioctanoate. Although the exact reason for this is still being investigated, the transmethylation of vegetable oils can be accomplished in 1-3 minutes by increasing the sodium hydroxide concentration into the 1.0-2.0 wt.% range. This strategy would not work without the formation of the one-phase system. Continuous processes for the production of vegetable oil methyl esters are now feasible. There are obviously subtleties of the transmethylation process that are still not understood, even in a one-phase process, and further work is taking place to define the roles of substrate structure, polarity and base concentration.

References

1. BIODIESEL: A Technology, Performance and Regulatory Overview, National Soybean Development Board.

2. B. Freedman, E. H. Pryde and T. H. Mounts, "Variables Affecting the Yields of Fatty Acid Esters from Transesterified Vegetable Oils", J. Amer.Oil Chem. Soc., 61 (10), 1638-1643, (1984).

3. A. J. Feuge and A. T. Gros, "Modification of Vegetable Oils VII: Base-Catalysed Interesterification of Peanut Oil". J. Amer. Oil Chem. Soc., 26 (3) 91-92 (1949).

4. B. Freedman, R. O. Butterfield and E. H. Pryde, "Transesterification Kinetics of Soybean Oil", J. Amer. Oil Chem. Soc., 63 (10), 1375-1380, (1986).

5. D, G. B. Boocock, S. K. Konar, V. Mao and H. Sidi, "Fast One-Phase Oil-Rich Processes for the Preparation of Vegetable Oil Methyl Esters", Biomass and Bioenergy, (In Press).

6. This Laboratory,Unpublished results.

BIOMASS-DERIVED OXYGENATES FOR TRANSPORTATION FUELS

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Abstract

The transportation sector in the U.S. is the only element that is almost totally dependent on petroleum for its energy supply. With more than half of all petroleum imported, our transportation, which is vital to the U.S. economy, is very vulnerable to economic and strategic disruptions. With about two-thirds of all oil being used for transportation, it also contributes substantially to the large trade deficit for petroleum imports. Transportation fuels contribute about half the urban air pollution and a third of the carbon dioxide accumulation that could result in global climate change. Because lignocellulosic biomass sources such as agricultural and forestry residues, municipal solid waste, and woody and herbaceous crops could be abundant, production of fuels from biomass could address all these problems on a large scale. Biomass can be gasified by thermal processes to produce a mixture of carbon monoxide and hydrogen that can be catalytically combined to form methanol. Alternatively, the cellulose and hemicellulose in biomass can be broken down to their component sugars for fermentation to ethanol. Although ethanol and methanol are currently most favored for use as transportation fuels, other alcohols could also be formed thermally or biologically from biomass. Ethanol and methanol can be used directly as neat or pure fuels. Ethanol is also directly blended with gasoline to displace gasoline use, increase the octane of the blended fuel, and provide oxygen that insures more complete combustion and reduces the contribution to urban air pollution. The alcohols can be converted into ethers such as ethyl tertiary butyl ether (ETBE) and methyl tertiary butyl ether (MTBE) from ethanol and methanol, respectively. These and other ethers are fully compatible with gasoline, reduce oil use, have favorable vapor pressure effects, boost octane, and provide fuel oxygen.

Introduction

The U.S. uses about 84 EJ (about 84×10^{15} BTUs or 84 quads) annually of energy, and the largest fraction, about 34 EJ (34 quads) of that total is derived from petroleum. Furthermore, although all other energy sources such as natural gas and coal are produced domestically (often with some exported), more than half the petroleum that we use is imported. Imported oil accounts for the largest single contribution to the U.S. trade deficit and is equivalent to about 40% of the net deficit. With U.S. oil supplies continually declining, the fraction of imported oil will increase significantly in the near future. This heavy reliance on imported petroleum makes the U.S. extremely vulnerable to interruptions in its energy supply. It also results in the loss of employment.

The transportation sector uses about two-thirds of the petroleum in the U.S. In addition, although all other end use sectors are well diversified in their energy sources, petroleum provides about 97% of the 22 EJ (22 quads) of transportation energy. This severe dependence on petroleum limits the ability of the transportation sector to switch fuel sources and makes it particularly vulnerable to disruptions in the petroleum supply from politically unstable oil exporting countries. It also results in severe economic problems when oil prices rise as a result of such events or because of world political pressure.

The transportation sector is responsible for a large portion of a number of environmental problems. About two-thirds of the carbon monoxide pollution and about 40% of urban smog pollution in our cities is caused by the transportation sector. Through the Clean Air Act Amendments of 1990 (CAAA), 39 cities suffering from severe carbon monoxide pollution are now required to incorporate 2.7% oxygen in gasoline to insure more complete combustion during the winter months, when carbon monoxide formation is most problematic. In addition, 2.0% oxygen is required to be added to gasoline during the smog formation season to combat release of unburned hydrocarbons from vehicle exhaust. Fuel oxygen is now usually provided by adding ethanol or methyl tertiary butyl ether (MTBE) to gasoline.

With its almost total dependence on fossil fuel, the transportation sector is also a major contributor to the potential for global climate change. About one-third of the carbon dioxide released each year by the U.S. is from the transportation sector. Thus, for the U.S. to reduce the release of greenhouse gases, it must seek to reduce the use of fossil sources for transportation. Three such options are available: (1) reduce the number of vehicle miles traveled, (2) improve the efficiency of vehicles to reduce the amount of fuel used, and (3) use alternative fuels that release far less carbon dioxide to the atmosphere. The first strategy is important, but there is concern that the strength of the economy and the number of vehicle miles traveled are so closely intertwined that limited progress is possible in this area without a significant negative impact on the economy. More efficient vehicles can certainly reduce the consumption of fossil fuels substantially if dramatic advances are made in vehicle/engine technology, but this approach will eventually reach a point of diminishing returns. Switching to alternative fuels that release little, if any, net carbon dioxide to the atmosphere will insure virtual elimination of the transportation sector's contribution to the potential for global climate change. These three strategies are mutually supportive to achieving significant reductions in the release of carbon dioxide.

The production of alcohols and ethers from lignocellulosic biomass sources such as waste paper and other components of municipal solid waste (MSW), agricultural and forestry residues, and woody and herbaceous (grassy) crops grown to support large-scale production of transportation fuels, can provide a domestically abundant supply of fuels that will reduce or eliminate oil imports, improve air quality, and reduce the contribution to the potential for global climate change. In this paper, a brief overview of production of alcohols and ethers that have the potential to be economically competitive when produced from cellulosic biomass will be provided.

Lignocellulosic Biomass

Before discussing the production of alcohols and ethers from lignocellulosic biomass, it is instructive to briefly review the availability of this plentiful resource to provide a context as to the importance of considering its conversion to transportation fuels and fuel additives. It has been estimated that from 1.5 to 3.2 Gtonnes (1.7 to 3.5 billion tons) of lignocellulosic biomass could be made available annually in the U.S. from collectable municipal, agricultural, and forestry wastes, together with energy crops grown on available crop and forest lands. This amount of biomass could be converted into between 600 and 1300 GL (160 and 350 billion gal) of ethanol each year (Lynd et al. 1991); similar amounts of fuel could result for methanol and other alcohols on an energy content basis. By comparison, about 510 GL (140 billion gal) of ethanol could displace all gasoline used in this country if the ethanol were employed as a pure fuel (Wyman and Goodman 1993). Although there is some debate about the exact price and quantity for lignocellulosic biomass that can be obtained, we can see that lignocellulosic biomass clearly provides an abundant resource from which to make transportation fuels, and it would take some time before an infrastructure could be developed that would challenge the production of these large quantities.

When transportation fuels such as ethanol are derived from lignocellulosic biomass, very little, if any, net release of carbon dioxide results (Lynd et al. 1991). This is because very limited amounts of fossil fuel inputs are used to grow, harvest, and transport lignocellulosic biomass. Furthermore, it is possible to substitute only renewable resources in these steps in the long run, thereby eliminating all fossil inputs. In addition, the fuel production process is self-sustaining if a portion of the biomass is employed to produce the heat and electricity needed for the process. Excess electricity would generally be left over to export, thereby displacing fossil-based sources of heat and electricity that contribute to the buildup of carbon dioxide in the atmosphere (Hinman et al. 1992, Wyman 1994). Thus, it is estimated that production of alcohols such as ethanol from renewable lignocellulosic biomass resources could reduce net carbon dioxide release by 90% or more, relative to reformulated gasoline (Tyson et al. 1993).

Alcohols

Alcohols can be regarded as either hydroxyl derivatives of alkanes or as alkyl derivatives of water, because similarities exist with both parent groups. The boiling points of the lower alcohols (methanol, ethanol, and propanol) are comparable to that of water, and these lower alcohols are miscible in water in all proportions. The next three higher homologs (n-butyl alcohol, n-amyl alcohol, and n-hexyl alcohol) are progressively less soluble in water. This is because the lower alcohols are like water in that the hydroxyl group composes a

considerable part of the molecule, whereas the higher alcohols are predominately hydrocarbon in character. These factors explain the unique fuel properties of alcohols.

Traditionally, most attention has been focused on methanol and ethanol as fuels. Like all alcohols, both are oxygenated, and they promote more complete combustion of gasoline when used as a fuel additive. However, when methanol is added to gasoline, the vapor pressure increases substantially, causing more evaporative emissions that lead to smog; therefore, methanol is not allowed as a direct gasoline additive in the U.S. (Wyman et al. 1993). Methanol is considered for use as a pure or neat fuel because of its high octane and historically competitive price when made from low-cost, remote natural gas. Historically, the emphasis for ethanol has been for direct blending with gasoline to reduce the use of oil, boost octane, and provide oxygen that promotes more complete combustion, but there is concern about the somewhat higher vapor pressure of ethanol blends contributing to smog formation during the summer months (Wyman and Goodman 1993). Because the fuel properties of pure ethanol are very similar to those of methanol, ethanol is a very good neat fuel as well (Lynd 1989, Wyman and Hinman 1990), although the current cost of ethanol produced from corn is generally considered too high to be viable for large-scale use as a pure fuel.

Methanol

Until 1923, methanol was prepared by the destructive distillation of wood. Wood, as for other forms of lignocellulosic biomass, is composed of about 40% to 50% cellulose, a polymer of glucose sugar; 20% to 35% hemicellulose, a heterogeneous polymer of several sugars typically dominated by xylose; about 20% to 30% lignin, a polymeric substance containing aromatic rings containing methoxyl groups; and minor amounts of other components such as oils and ash. Methanol derived from wood comes from the lignin fraction. When heated in the absence of air above about 250°C (480°F), the lignin decomposes into charcoal and a volatile fraction that partially condenses on cooling to yield methanol, acetic acid, and traces of acetone. However, the yields of methanol from destructive distillation are too low to be attractive as a route to large-scale fuel production.

Currently, methanol is synthesized by generating synthesis gas that contains carbon monoxide and hydrogen from natural gas and then catalytically combining this mixture to methanol. The latter reaction traditionally occurs in the gas phase, but liquid-phase processes are now employed as well. Synthesis gas can also be generated by gasifying wood and other forms of lignocellulosic biomass with a controlled supply of air to generate carbon monoxide and hydrogen. This gas can be catalytically combined (as for natural gas-based processes) to produce methanol. However, a hot gas cleanup step must be employed to remove particulates and tars from the stream that would contaminate the catalysts. It is also necessary to add steam to the gaseous product to shift the gas composition to the hydrogen:carbon monoxide ratio to produce methanol in high yields. Methane and other nonreactive gases must be removed from the product stream prior to catalytic reaction to methanol (Bain 1991; Overend 1991, Wyman et al. 1993).

At this time, it is estimated that methanol from biomass would cost about $0.22/L ($0.84/gal) from biomass feedstocks costing $46/tonne ($42/ton) to cover all costs of production and realize a reasonable return on investment. Targets have been defined to reduce the cost to

be competitive with gasoline from $25/bbl (U.S. DOE 1993). Work is ongoing to operate a 90 tonne/d (100 ton/d) gasifier facility in Hawaii on sugar cane bagasse, to gather information essential to improve the understanding of this technology and evaluate approaches to clean up the gas stream for catalytic conversion into methanol.

Ethanol

Ethyl alcohol or ethanol has been made since antiquity by fermenting sugar with yeast, and beverages such as beer and wine are still made by fermenting various crops such as barley and grapes to ethanol. In Brazil, about 11 GL/yr (3 billion gal/yr) of fuel ethanol is made from cane sugar. This fuel is used both as a 22% blend with gasoline and as a pure hydrous (95% ethanol with 5% water) for dedicated ethanol vehicles. Because the price of cane sugar is controlled at about $0.09/kg ($0.20/lb) in the U.S., which is equivalent to about $0.66/L ($2.50/gal) of ethanol produced just for the sugar, sugar is too expensive to be viable for production of fuels in the U.S. In the U.S., more than 4 GL/yr (1 billion gal/yr) of ethanol is made from corn. However, the cost of ethanol production from corn still exceeds its value for use as a fuel, and the excise tax on 10% blends of ethanol with gasoline is reduced by $0.014/L ($0.054/gal) to promote its use; this translates into an incentive of $0.14/L ($0.54/gal) of ethanol used. Combined with various state incentives, ethanol from corn is economically attractive for blending with gasoline in certain regions (Wyman and Goodman 1993).

Lignocellulosic biomass provides a much lower-cost substrate for producing ethanol. Acids or enzymes can break down or hydrolyze the cellulose to form glucose sugar from which it is derived so that yeast or other organisms can in turn ferment the glucose to ethanol. Similarly, acids or enzymes can hydrolyze the hemicellulosic fraction to form its component sugars, in this case a heterogeneous mixture typically dominated by the five-carbon sugar xylose (glucose is a six-carbon sugar). Thus, typically between 65% and 75% of the biomass material can be converted into ethanol, leaving the lignin and other nonfermentable fractions behind.

Over the years, a number of processes have been investigated for production of ethanol from biomass based on acids and enzymes. Dilute acids rapidly break down the cellulose and hemicellulose in biomass to form sugars, but the harsh conditions required result in substantial degradation of sugars to tars and various by-products. The maximum yields are about 60% or less, and because high yields of ethanol are critical to economic viability, dilute acid technologies are not economically viable. Concentrated acids also produce sugars rapidly but at mild enough conditions to achieve very high yields. However, because of the high price of the acids used, they must be recovered for reuse, and it is challenging to recover the acids at a lower cost than they can be purchased. Concentrated acid technology can be economically viable for near-term applications, particularly for some low-cost waste materials (Wyman and Goodman 1993).

Enzymatic processes can also be employed to produce ethanol from biomass. The biomass is typically milled or processed by other means to reduce the size of the material and promote heat and mass transfer in subsequent steps. Then, a pretreatment step opens up the structure of the biomass to promote more complete and rapid breakdown of the material to sugars; often dilute acids are used in the pretreatment step to hydrolyze the hemicellulose to form

sugars that can be fermented to ethanol. A small fraction of the pretreated biomass is used to grow microorganisms that produce enzymes known as cellulase. The cellulase is added to the bulk of the cellulose-containing material to break down the cellulose to form glucose that organisms ferment to ethanol. The broth containing ethanol is passed to a purification step to be recovered and sold as a fuel or fuel additive. The solid and other materials not converted to ethanol are burned to produce heat and electricity to drive the overall process, and excess electricity is left to export for additional process revenue (Hinman et al. 1992, U.S. DOE 1993).

Through advances in biotechnology, substantial progress has been made in reducing the cost of ethanol production from lignocellulosic biomass via enzymatically catalyzed options. In 1980 the cost of ethanol was estimated at more than $1.20/L ($4.60/gal) to cover all the costs of production and realize a reasonable return on investment, but continued R&D has lowered the cost to about $0.32/L ($1.22/gal) for a feedstock costing $46/tonne ($42/ton) (Hinman et al. 1992); this cost is competitive now with the selling price of ethanol derived from corn in the U.S. Furthermore, advances continue to be made that are dropping the cost. For instance, the bacterium *Zymomonas mobilis,* which could ferment only glucose, sucrose, and fructose in its native state, was recently genetically engineered to ferment both xylose and glucose to ethanol simultaneously (Zhang et al. 1995). This advancement could lower the cost of ethanol production by about 10%. As another example, improvements have been made in pretreatment to enhance the removal of hemicellulose and lignin, resulting in a much more accessible cellulose for conversion into sugars (and therefore ethanol) at much higher rates. Through these and other advancements, the goal is to reduce the cost of ethanol production to less than $0.18/L ($0.67/gal) so it is competitive with gasoline derived from oil at $25/bbl.

Because ethanol from biomass is now competitive with ethanol from corn, several industries are now working to commercialize the technology. To support this, a 0.9 tonne/d (1 ton/d) pilot plant has been recently constructed at the National Renewable Energy Laboratory in Golden, Colorado and is now being operated with industrial partners to gather performance data essential to evaluation and scale up.

Higher Alcohols

In addition to ethanol and methanol, higher alcohols can be derived from biomass via biological and thermal processes. For instance, the sugars derived by enzymatic breakdown of biomass can be fermented to butanol, which could be used as a fuel additive because of its low vapor pressure, compatibility with gasoline, and oxygen content. The synthesis gas derived via gasification processes can be converted into mixtures of higher alcohols by proper selection of reactor design and catalyst. However, the yields and concentrations of these alcohols, coupled with their recovery costs, have not been attractive for commercial use.

Ethers

Ethers are typically regarded as derivatives of alcohols from which they are often prepared. Just as for the alcohols, ethers supply oxygen to the gasoline to which they are added, promoting more complete combustion of gasoline, as required under the CAAA. Ethers boil

at much lower temperatures than the alcohols from which they are derived or than alcohols of similar molecular weight, but their boiling points correspond closely to those of comparable alkanes of similar molecular complexity. Ethers thus provide an effective means to improve the mid range volatility of gasoline, compensating for the increased use of aromatics to replace lead in gasoline. Just as for alcohols, ethers increase the octane of the gasoline to which they are added, reducing the need to add aromatics such as benzene that are often toxic.

MTBE

MTBE is made by reacting isobutylene with methanol. MTBE is essentially vapor pressure neutral so the blended gasoline has nearly the same Reid Vapor Pressure (RVP) as the blend stock to which MTBE is added. MTBE is also fungible; that is, it is fully compatible with gasoline and can be blended, shipped, and stored in mixture with gasoline. Of course, if the methanol is derived from biomass, then the MTBE made from methanol has a renewable component (Piel 1992, 1994).

With a blending octane of 110, MTBE is an effective octane booster. As is typical of ethers, its boiling point is low (55°C [131°F]), and the heat of vaporization of MTBE is quite low at 240 MJ/L (86,000 BTU/gal). Because MTBE has an oxygen content of 18.2 weight % compared to ethanol at 34.8%, almost twice as much MTBE is required as ethanol to achieve the same oxygen level in gasoline. The lower heating value of 26 MJ/L (93,500 BTU/gal) is less than for gasoline (Piel 1992, 1994).

ETBE

Ethyl tertiary butyl ether (ETBE) is formed by reacting ethanol with isobutylene. The reaction is very similar to that of methanol with isobutylene to form MTBE, and with relatively low cost provisions, the etherification process can be made flexible enough to produce either product. ETBE has a very low blending vapor pressure, and addition of ETBE to gasoline actually reduces the RVP considerably. This is a valuable attribute in helping to meet the lower volatility requirements of the CAAA. Like MTBE, ETBE is fungible and can be easily integrated into the existing fuel distribution infrastructure (Piel 1992, 1994). Ethanol derived from biomass provides a renewable feedstock for production of ETBE.

The blending octane of ETBE is 112, slightly higher than for MTBE but somewhat lower than for pure ethanol (115). Its boiling point of 72°C (161°F) is somewhat higher than for MTBE, but its heat of vaporization is somewhat lower at 230 MJ/L (83,000 BTU/gal). The oxygen content of ETBE is 15.7%, even less than for MTBE; thus, considerable displacement of gasoline results when ETBE is added to gasoline to provide a given level of oxygen. The lower heating value of ETBE, like MTBE, is less than for gasoline at 27 MJ/L (96,900 BTU/gal) (Piel 1992, 1994).

Other Ethers

A number of other ethers, including tertiary amyl methyl ether (TAME) from methanol and isoamylenes and tertiary amyl ethyl ether (TAEE) from ethanol and isoamylenes, can be produced from renewable alcohols. These ethers reduce the RVP of gasoline to which they

are added even more than for ETBE. However, they have a somewhat lower blending octane than ETBE or MTBE. Their other properties are quite similar to ETBE and MTBE (Piel 1992, 1994).

A one-step process to produce dimethyl ether (DME) from syngas was recently announced, thereby simplifying the synthesis from the previous two-step approach (Hansen et al. 1995). The plans are to use DME directly as a diesel fuel substitute and not as an additive (Fleisch et al. 1995). Although current practice is to use syngas from natural gas, biomass can also be gasified to syngas as discussed previously for manufacture of methanol. However, the cost of biomass-derived syngas must be compatible with that of syngas from natural gas.

DME has a volumetric energy density somewhat greater than half that of diesel fuel. Its cetane rating is 58 compared to 40 to 55 for diesel. Because DME is a vapor at ambient temperature, pressurized fuel tanks similar to those used for propane are required to contain DME. DME is noncarcinogenic, is virtually nontoxic, and degrades easily in the troposphere. It is noncorrosive to metals, but compatibility with elastomers is a potential problem (Fleisch et al. 1995).

Conclusions

Lignocellulosic biomass provides an abundant resource that can be converted into methanol and ethanol and into higher alcohols. Production of alcohols from biomass contributes 10% or less of the carbon dioxide accumulation to the atmosphere of reformulated gasoline, substantially reducing the potential contribution to global climate change. Biomass can be gasified to a synthesis gas that can in turn be catalytically reacted to form methanol. Alternatively, the cellulose and hemicellulose in biomass can be broken down to form sugars that can be fermented to ethanol. Substantial progress has been made in these technologies, and goals have been set to achieve cost competitiveness with gasoline as a neat fuel without the need for tax incentives. However, ethanol from biomass is now competitive with ethanol from corn for direct blending with gasoline, and a number of companies are now developing technologies for production of ethanol from various waste materials. Methanol and ethanol can be reacted with isobutylene to form MTBE and ETBE, respectively. Both have desirable properties for blending with gasoline to provide fuel oxygen that promotes more complete combustion and boosts octane. MTBE does not affect the vapor pressure of the gasoline blend, and ETBE actually reduces the vapor pressure, thereby lowering the impact of gasoline on smog formation. A new synthesis process for DME could be used with biomass gasification to make a diesel fuel substitute with a number of promising attributes, although the energy density is less than for diesel.

Acknowledgements

The support of the Transportation Sector projects of the Biofuels Energy Systems Program of the U.S. Department of Energy is gratefully acknowledged.

References

Bain, R. (1991). "Methanol from Biomass: Assessment of Production Costs." Presented at the November 1989 Renewable Transportation Alternatives Workshop, Hawaii Natural Energy Institute, Honolulu, HI.

Fleisch, T.; McCarthy, C.; Basu, A.; Udovich, C.; Charbonneau, P.; Slodowske, W.; Mikkelsen, S.-E.; McCandless, J. (1995). "A New Clean Diesel Technology: Demonstration of ULEV Emissions in a Navistar Diesel Engine Fueled with Dimethyl Ether." Presented at the International Congress and Exposition, Society of Automotive Engineers, Detroit, MI, February 27-March 2, 1995, paper 950061.

Hansen, J.B.; Voss, B.; Joensen, F.; Siguroardottir, I.D. (1995). "Large Scale Manufacture of Dimethyl Ether - a New Alternative Diesel Fuel from Natural Gas." Presented at the International Congress and Exposition, Society of Automotive Engineers, Detroit, MI February 27-March 2, 1995, paper 950063.

Hinman, N.D.; Schell, D.J.; Riley, C.J.; Bergeron, P.W.; Walter, P.J. (1992). "Preliminary Estimate of the Cost of Ethanol Production for SSF Technology." *Appl. Biochem. Biotech.*; Vol. 34/35, p. 639.

Lynd, L. (1989). "Production of Ethanol from Lignocellulosic Materials Using Thermophilic Bacteria: Critical Evaluation of Potential and Review." In *Advances in Biochemical Engineering/Biotechnology*. Edited by A. Fiechter, Vol. 38.

Lynd, L.R.; Cushman, J.H.; Nichols, R.J.; Wyman, C.E. (1991). "Fuel Ethanol from Cellulosic Biomass." *Science*; Vol. 251, p. 1318.

Overend, R. (1991). *Proceedings of the Annual Automotive Technology Development Contractor's Coordination Meeting* 1991. Society of Automotive Engineers, Inc. Warrendale, PA, p. 779.

Piel, W.J. (1992). "Expanding Refinery Technology Leads to New Ether Potential." *Fuel Reformulation*; Vol. 34 (November/December).

Piel, W.J. (1994). "Diversify Future Fuel Needs with Ethers." *Fuel Reformulation*; Vol. 28 (March/April).

Tyson, K.S.; Riley, C.J.; Humphreys, K.K. (1993). *Fuel Cycle Evaluations of Biomass-Ethanol and Reformulated Gasoline*. NREL/TP-463-4950. Golden, CO: National Renewable Energy Laboratory.

U.S. Department of Energy (1993). "Assessment of Costs and Benefits of Flexible and Alternative Fuel Use in the US Transportation Sector." *Technical Report Eleven: Wood to Ethanol Process*; DOE/EP-0004. Prepared by Chem Systems for the US Department of Energy, Washington, DC.

Wyman, C.E. (1994). "Alternative Fuels from Biomass and Their Impact on Carbon Dioxide Accumulation." *Appl. Biochem. Biotech.*; Vol. 45/46, p. 897.

Wyman, C.E.; Goodman, B.J. (1993). "Near Term Application of Biotechnology to Fuel Ethanol Production from Lignocellulosic Biomass." In *Opportunities for Innovation in Biotechnology*. Edited by R. Busche. National Institute of Standards and Technology, Gaithersburg, MD (accepted for publication).

Wyman, C.E.; Hinman, N.D.; Bain, R.L.; Stevens, D.J. (1993). "Ethanol and Methanol from Cellulosic Biomass." *Fuels and Electricity from Renewable Resources.* Edited by R.H. Williams, T.B. Johansson, H. Kelly, & A.K.N. Reddy. United Nations Solar Energy Group for Environment and Development (SEGED), 1992, UN Conference on Environment and Development in Brazil, pp. 865-924.

Wyman, C.E.; Hinman, N.D. (1990). "Ethanol: Fundamentals of Production from Renewable Feedstocks and Use as a Transportation Fuel." *Appl. Biochem. Biotech.*; Vol. 24/25, p. 735.

Zhang, M.; Eddy, C.; Deanda, K.; Finkelstein, M.; Picataggio, S. (1995). "Metabolic Engineering of a Pentose Metabolism Pathway in Ethanologenic *Zymomonas mobilis*." *Science*; Vol. 267, p. 240.

ESTIMATING THE NET ENERGY VALUE OF CORN-ETHANOL

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Abstract

Potential air quality benefits and a desire to improve domestic energy security has prompted researchers to investigate the net energy value (NEV) of corn-ethanol. Studies have been conducted in recent years in an attempt to quantify the energy used in growing and converting corn to ethanol. However, variations in data and assumptions among the studies have resulted in a wide range of NEV estimates. The purpose of this study is to identify the factors causing this wide variation and to develop a more consistent NEV estimate. We conclude that the NEV of corn-ethanol is positive when fertilizers are produced by modern processing plants, corn is converted in modern ethanol facilities, farmers achieve normal corn yields and energy credits are allocated to basic coproducts. Our estimate of 16,193 BTU/gal can be considered conservative, since it does not include energy credits for those plants that sell carbon dioxide. Corn ethanol is energy efficient as indicated by an energy ratio of 1.24, i.e., for every BTU dedicated to producing ethanol there is a 24 percent energy gain. Moreover, producing ethanol from domestic corn stocks achieves a net gain in a more desirable form of energy. Ethanol production utilizes abundant domestic feedstocks of coal and natural gas to convert corn into a premium liquid fuel that can replace petroleum imports by a factor of 7 to 1.

Environmental concerns and fears about our Nation's energy security has prompted a number of recent studies that examine the net energy balance of corn-ethanol. However, there was a considerable amount of variation in the findings of these reports. This wide variation relates to various assumptions about farm production, ethanol conversion, fertilizer manufacturing efficiency and energy coproduct evaluation. Furthermore, authors use data from different time periods. Studies using older data may tend to overestimate energy use because ethanol manufacturing and farm production technologies have become increasingly energy efficient over time. The Purpose of this report is to identify the methodological differences creating the inconsistencies among study results and provide a more consistent estimate for the NEV of corn-ethanol.

Table 1 shows the wide variation in the NEV estimates of several recent studies. The midpoint is used when studies report a range of values. Pimentel reports the lowest NEV for corn-ethanol among the studies -- based on a low heating value scale, the total energy input to produce one gallon of ethanol is 131,017 British Thermal Units (BTU). Compared to the LHV of ethanol, 76,000 BTU, this is a net energy loss of 55,017 BTU/gal. Even when coproducts were considered, Pimentel still estimated a net energy loss of around 33,517 BTU/gallon. Keeney and DeLuca also reported a negative NEV for an average farm, but the energy deficit was only 8,431 BTU/gal. Keeney and DeLuca do not consider corn processing byproducts, but they show that a positive energy balance can be attained with low input corn production. Marland and Turhollow reported that it requires 73,934 BTU (HHV basis) to produce a gallon of ethanol assuming conversion takes place in the best ethanol facilities available today. When energy credits from coproducts are included, such as gluten meal, gluten feed, and corn oil, they conclude that the NEV of corn ethanol is 18,324 BTU/gal. The most favorable NEV estimate was derived by Morris and Ahmed. They found a positive net energy balance of 703 BTU/gal for their average case, even without including energy from coproducts. When adding energy coproduct credits, they estimated a net energy gain of 25,653 BTU/gal.

Data Trends

It is important that current data is used to estimate the NEV of ethanol because the efficiency of growing corn and converting it to ethanol has improved significantly over the past 10 years. Total energy used in agriculture including pesticides, fertilizers, other chemicals, liquid fuels, natural gas, and electricity increased from 1,499 trillion BTU in 1965 to 2,155 trillion BTU in 1978, and then declined to 1,550 trillion BTU by 1989. The decline in energy use in agriculture since 1978 is largely attributed to the replacement of gasoline powered farm vehicles with more fuel efficient diesel engines.

While energy use has been declining, there has been a rising trend in corn yields. With the exception of bad weather years, corn yields have been increasing over time. Corn yields ranged between 70 and 110 bushels per acre in the 1970's; they ranged between 80 and 117 bushels per acre in the 1980's; and so far in the 1990's they've ranged between 100 and 140 bushels per acre.

Fertilizer use in grain production rose for many years but lately appears to be on a decline according to the latest data published by USDA (Taylor). Nitrogen use per planted acre of corn declined from 140 pounds per acre in 1985 to 123 pounds per acre in 1993. Phosphate use declined from 60 to 56 pounds per acre and potash use declined from 84

Table 1 -- Energy Input Assumptions of Recent Corn-Ethanol Studies

Study/year	Corn yield	Nitrogen fertilizer application rate	Inputs for nitrogen fertilizer	Corn ethanol conversion rate[1]	Ethanol conversion process	Total energy use	Coproducts energy credits	Net Energy value
	bu/acre	lb/acre	BTU/lb	gal/bu	BTU/gal	BTU/gal	BTU/gal	BTU/gal
Pimentel (1991)	110	136.0	37,551	2.50	73,687 (LHV)	131,017	21,500	-33,517
Keeney and Deluca (1992)	119	135.0	37,958	2.56	48,434 (LHV)	91,127	8,072	-8,431
Marland and Turhollow (1991)	119	127.0	31,135	2.50	50,105 (HHV)	73,934	8,127	18,324
Morris and Ahmed (1992)	120	127.0	31,000	2.55	46,297 (LHV)	75,297	24,950	25,653
Ho (1989)	90	NR	NR	NR	57,000 (HHV)	90,000	10,000	-4,000
This Study (1995)	122	124.5	22,159	2.53	53,277 (HHV)	82,824	15,056	16,193
Average	113	129.9	31,961	NA	NA	NA	NA	2,373

NR: Not reported
NA: Average values are not appropriate in this case because high heat values cannot be directly compared to low heat values.
LHV: Low heat value. A gallon of ethanol has a LHV of 76,000 BTU per gallon.
HHV: High heat value. A gallon of ethanol has a HHV of 83,961 BTU per gallon.

pounds per acre to 79 pounds per acre during the same period. In addition, manufacturing agricultural chemicals has become more energy efficient. For example, the fertilizer industry has undergone a major technological advancement in the last decade and U.S. farmers have gained substantial real energy-saving benefits in terms of nitrogen and phosphorous. Bhat et. al reported that from 1979 to 1987 the energy consumed for producing nitrogen fertilizers declined about 11 percent.

Making ethanol from corn also has become more energy efficient. Hohmann and Rendleman reported that a shift in production to larger plants and the adoption of energy-saving innovations reduced the processing energy required to produce a gallon of ethanol from 120,000 BTU in 1981 to 43,000 BTU in 1991. Modern facilities are conserving energy by utilizing cogeneration facilities that produce steam and electricity simultaneously. Advances in alcohol dehydration have also resulted in considerable energy savings (Hohmann and Rendleman).

Estimating Energy of Farm Inputs

Estimates of farm energy use are based on data from the 1991 Farm Costs and Return Survey (FCRS). We focus on the major corn producing states (table 2). These nine states account for about 82 and 93 percent of U.S. corn and ethanol production respectively. Farm input levels are weighted by corn acreage planted in each state to estimate an average energy input level for corn production. The 1990-92 state average corn yield of 122 bu/ac was used to convert farm inputs from a per acre basis to a per bushel basis.

Table 2 shows the energy used by farm inputs to produce a bushel of corn for each state and a 9-state weighted average. All thermal inputs in this study and outputs are made on a gross high heat value basis. The energy required for hauling these inputs to the farm from local retailers is included in the values in table 2. Electricity used on the farm is adjusted for transmission loss by a factor of 1.203 (EPA).

Estimates of the primary feedstocks used to manufacture farm chemicals are 60 percent for oil, 23 percent as natural gas and 17 percent for electricity. Electricity power was assumed to be produced from coal. It requires about 180,000 BTU to produce a pound of insecticide or herbicide including transportation energy. Energy used for manufacturing nitrogen fertilizer, potash, and phosphate are based on information provided by the Fertilizer Institute. It requires 22,159 BTU, 1,245 BTU, and 4,175 BTU to produce a pound of nitrogen, potash, and phosphate respectively. More than 90 percent of the energy in the applied fertilizer is in the form of nitrogen which is manufactured almost completely from natural gas. The energy embodied in phosphate includes 47.4 percent for electricity, 26.7 percent for diesel and 25.9 percent for natural gas. The energy invested in potash is 42 percent electricity, 31.3 percent diesel fuel, and 26.7 percent natural gas. Energy used for producing lime is 620 BTU/lb.

The total energy required per bushel of corn by state and the weighted average of the nine states are shown on the bottom of table 2. Total BTU of energy per bushel of corn varies from about 41,000 BTU in Minnesota to over 81,000 BTU of energy per bushel in Nebraska. Corn production in Minnesota, Iowa and Ohio require less energy than other states because they can achieve relatively high yields without irrigation. In contrast, direct energy use (gasoline, diesel, electricity, natural gas and LPG) for corn production in

Table 2 -- Energy Requirements for 9 States and 9-State Weighted Average

Item	IL	IN	IA	MN	NE	OH	MI	SD	WI	Weighted average
	States									
	BTU/bu									
Seed	170	189	141	148	271	162	217	290	211	186
Nitrogen	26995	26356	20322	14671	24228	22382	25719	19163	20828	22631
Potash	757	660	452	576	218	609	529	411	693	539
Phosphate	2936	3743	1580	2011	85	3142	2390	588	1635	1992
Lime	2331	1757	1335	208	0	721	3839	0	654	1232
Diesel	4793	5843	4686	5427	18881	5131	8620	10650	9184	7713
Gasoline	3439	3710	3281	3019	4301	2723	3530	4846	2802	3493
LPG	1515	1619	3292	3287	2510	2780	2654	5705	1578	2575
Electricity	1207	2927	511	2907	9270	1011	1209	13627	7537	3432
Natural Gas	479	85	0	0	12632	85	464	0	90	2058
Chemicals	5635	7176	5730	5380	5448	5433	5936	5723	5784	5766
Other	3444	3428	3814	3514	3321	2807	3643	2372	5645	3567
Total energy	53702	57493	45144	41148	81165	46986	58750	63375	56641	55184

Table 3 -- Total Energy Requirments Per Bushel of Corn, 9-State average.

Item	Primary energy requirements	Feedstock share	NG	Diesel	Coal	Gasoline	Oil	Input efficiency factor	Total BTU
	BTU/bu	percent	BTU/bu						BTU/bu
Chemicals	5766	23,60,17	1326		980		3460	1.065	6142
Nitrogen	22631	90,10	20368	2263				1.012	22911
Phosphate	1992	25.9,26.7,47.4	516	532	944			1.088	2168
Potash	539	26.7,31.3,42.0	144	169	226			1.095	590
Lime	1232	26.7,31.3,42.0	329	386	517			1.095	1349
Diesel	10146			10146				1.154	11708
Gasoline	3493					3493		1.349	4712
Natural gas	5767		5767					1.112	6413
Electricity	3432				3432			1.038	3563
Seed	186		97	43		11	11	1.126	209
Total	55184		28547	13539	6125	3504	3460		59765

Nebraska accounts for about 48 thousand BTU per bushel. More than 75 percent of the area planted to corn in Nebraska requires irrigation.

The estimates up to this point do not consider the energy inputs required to mine, extract, and manufacture the raw materials into the final energy product. The sum of these energy values must be added to the values in table 2 to estimate the total energy associated with each farm input required to produce a bushel of corn. Input efficiencies for fossil energy sources which have been developed by EPA were used to calculate these additional energy input values. In addition, the energy content of fertilizer and other farm inputs are adjusted by the energy efficiencies for the fossil fuels used in their production. Since, a number of fuels may be required to manufacture the various farm inputs, the input efficiencies are weighted by each energy source or feedstock. Adjusting all the inputs in table 2 results in a 9-state weighted average of 59,765 BTU/bu (table 3).

Estimating Energy for Transportation

Energy used in transporting production inputs to the farm is based on an average distance of 500 miles by river and 150 miles by truck. This translates into 274 BTU per river-ton-mile, and 2,000 BTU per-highway-ton-mile (DeLuchi). It is assumed that 25 percent of the corn is directly delivered from the farm to ethanol plants. The remaining 75 percent is transported to ethanol plants from grain elevators. The estimated trucking distance from elevator to plant is 100 miles round-trip. The diesel fuel requirement is about 2,000 BTU per ton-mile for a loaded truck and 1,000 BTU per ton-mile to return the empty truck. It requires 3,150 BTU per bushel to haul corn to the plant. On a gallon per ethanol basis, each gallon of ethanol produced in a dry mill uses 1,212 BTU of diesel fuel for hauling corn to the plant. A wet mill uses 1,260 BTU of diesel fuel for each gallon of ethanol.

Estimating Ethanol Conversion

Since both wet and dry milling are used to convert corn to ethanol, our energy conversion estimates are weighted accordingly. Wet milling accounts for about two thirds of U.S. ethanol production and dry milling accounts for about one third. Modern wet milling plants are able to produce one gallon of ethanol with 35,150 BTU of thermal energy and 2.134 KWHs of electricity per gallon of ethanol production based upon azeotropic distillation. If molecular sieves are used, the thermal input falls to 32,150 BTU per gallon. Of the total thermal energy, 7,000 BTU per/gal and 1.16 KWH were related to drying high grade germ, fiber and gluten. On average, wet mills produce 2.5 gallons of ethanol per bushel. A new dry milling plant requires 37,000 BTU of thermal energy and 1.2 KWHs of electricity per gallon of ethanol. The typical dry mill facility produces 2.6 gallons of ethanol per bushel of corn. The total energy used for converting ethanol, weighted by milling process and adjusted by EPA's input efficiency factor for the energy used to mine and transport coal is 51,343 BTU per/gal.

The conversion estimates developed for this analysis represent modern facilities that use cogeneration. The use of cogeneration is absent from most other studies, although it has become common for both modern wet and dry mill ethanol plants. In our analysis, we coupled a modern coal based cogeneration system to wet and dry mill facilities to supply power and steam. The wet mill estimates are based on a plant with a 100 million gallon per year capacity and dry mills have a capacity of 30 million gallons per year.

Ethanol Distribution

Distribution and dispensing energy requirements for ethanol were developed by EPA (1993). Ethanol is shipped to the wholesaler by truck and/or barge. The average trip from a ethanol plant to a terminal requires 2,501 BTU of diesel fuel. Ethanol is blended with gasoline at the terminal and delivered to retailers by truck. It is generally blended with 90 percent gasoline and 10 percent ethanol (E10). The energy used for blending along with the electricity used for dispensing the fuel from the pump is 672 BTU per gallon of ethanol.

Coproduct Credits

The coproducts used in this analysis include distillers' dried grains with solubles (DDGS) from dry milling, and corn oil, corn gluten meal (CGM) and corn gluten feed (CGF) from wet milling. Energy credits are assumed to be equal to the energy value of a substitute product which the ethanol coproduct can replace. For example, in the case of corn gluten meal and corn gluten feed, soybean meal can be used as a substitute, and soybean oil can replace corn oil. Using this method, 19 percent of the energy used to produce ethanol is assigned to coproducts.

Results

Table 4 summarizes the energy requirements by phase of production on a BTU per gallon basis. It includes energy losses from line loss, venting losses at the ethanol plant, and losses associated with mining, refining and transporting raw materials. Also presented is the NEV of corn-ethanol with and without coproduct credits for wet-milling, dry-milling and a weighted average of wet and dry milling. The weighted average is based on production capacity, i.e., two thirds of U.S. ethanol capacity is from wet-milling and one third from dry-milling. The average conversion rate for the two processes is 2.525 gallons per bushel. The NEV for dry-milling was the highest, 5,880 BTU per gallon. The NEV for wet-milling was slightly negative, -1,199 BTU per/gal, but the weighted average of the two processes has a positive net energy balance, 1,137 BTU/gal. The energy ratio, which is the ratio of energy-out to energy-in is close to 1 in all three cases. In other words, the BTU in a gallon of ethanol is about equal to the energy required to produce a gallon of ethanol even when energy coproducts are not considered.

When coproduct energy credits are added to the calculations, the NEV of corn-ethanol is positive regardless of the type of milling used. Dry-milling results in the highest NEV, 19,290 BTU but wet-milling NEV differs only by 4,989 BTU per/gal. The NEV for weighted average case is 16,193 BTU per gallon. Adjusting for coproduct credits also increases the energy ratio significantly. The energy ratio is 1.21, and 1.30 for wet and dry-milling respectively and the weighted average energy ratio is 1.24.

Table 5 shows the energy required for making corn-ethanol by energy feedstock for dry-milling, wet-milling and a weighted average. On a weighted average basis, about 85 percent of the total energy requirement comes from non liquid fuels -- coal accounts for 137,750 BTU per bushel and natural gas and liquid petroleum (LP) account for 28,547 BTU per bushel. The liquid fuels, which include gasoline, diesel and fuel oil account for 29,998 BTU per bushel. Comparing the energy input value of these liquid fuels to the

Table 4 -- Net Energy Value of Corn-Ethanol -- BTU Per Gallon

Production Phase	Dry Mill	Wet Mill	Weighted Average
Corn Production	21,225	22,074	21,793
Corn Transport	1,212	1,260	1,244
Ethanol Conversion	47,425	53,273	51,343
Ethanol Distribution	3,173	3,173	3,173
Energy Losses	5,046	5,380	5,271
Total Energy	78,081	85,160	82,824
Net Energy Value	5,880	-1,199	1,137
Energy Ratio	1.08	0.99	1.01
Coproduct Credits	13,410	15,500	15,056
Net Energy Value with coproducts	19,290	14,301	16,193
Energy Ratio	1.30	1.21	1.24

BTU output value of ethanol indicates a net energy gain of 182,676 BTU for every bushel of corn used in the production of ethanol. Thus, from a liquid fuel utilization perspective, ethanol can extend our domestic crude reserves by a factor of 7.

When comparing this study with the other studies in table 1, we have very similar results to the Marland and Turhollow study. Their NEV estimate was only about 2,000 BTU/gal greater than our estimate. Morris and Ahmed's NEV estimate is 9,460 BTU/gal greater, but much of this difference can be explained by the large value they use for coproduct energy credits. They are the only authors to use carbon dioxide as an energy coproduct which adds 4,460 BTU/gal to their NEV. Information to determine how many modern ethanol facilities are selling carbon dioxide is not readily available, thus it was not included in our analysis. The Keeney and Deluca study reported a negative NEV, but they report a very low value for energy coproducts. They only use a stillage credit and do not include processing coproducts, such as CGF, CGM, and corn oil. Adding these coproduct credits to their NEV estimate would raise their NEV estimate significantly. They also appear to be using an outdated estimate for the energy used for manufacturing nitrogen fertilizer. Adjusting their nitrogen fertilizer estimate to reflect modern technology and adding processing coproducts to their calculations would result in a positive NEV. Ho also reports a negative NEV, but his energy deficit is only 4,000 BTU/gal. Ho uses an unusually low corn yield of 90 bushels per acre. This yield would only represent very poor years such as 1988 when U.S. agriculture experienced a serious drought. If Ho used a yield that reflected a normal year, his NEV estimate would likely be positive.

Table 5 -- Energy Requirements by Feedstock and Petroleum Replacement Value of Ethanol -- BTU Per Bushel

	Dry Mill	Wet Mill	Weighted Average
Coal:			
Ethanol Plant	123,305	133,183	129,923
Ethanol Distribution	1,747	1,680	1,702
Corn Production	6,125	6,125	6,125
Total	131,177	140,987	137,750
Natural Gas and LP:			
Chemicals/Fertilizer	22,780	22,780	22,780
Corn Production	5,767	5,767	5,767
Total	28,547	28,547	28,547
Liquid Fuels:			
Diesel	23,191	22,941	23,023
Gasoline	3,504	3,504	3,504
Fuel Oil	3,471	3,471	3,471
Total	30,167	29,915	29,998
Total BTU Input	189,890	199,449	196,294
Total BTU Output	218,890	209,903	212,674
Replacement Factor	7.24	7.02	7.09

Pimentel reports the lowest NEV by far, -33,500 BTU/gal. There is about a 36,000 BTU difference between Pimentel's NEV and the average estimate of the studies shown in table 1. Many factors contribute to Pimentel's low estimate. For example, with the exception of Ho, Pimentel uses the lowest corn yield among the studies. He uses the highest fertilizer application rate and the lowest ethanol conversion rate. His energy estimate for nitrogen fertilizer processing is extremely high and does not appear to reflect technology used by modern facilities. The amount of energy required for ethanol processing in Pimentel's study also appears outdated. Processing estimates used by the other studies range between 46,000 BTU/gal and 57,000 BTU/gal, while Pimentel reports that it requires almost 74,000 BTU to produce a gallon of ethanol. In addition, he is the only author to include an energy value for steel, cement and other plant materials in the ethanol processing estimate.

Conclusions

We conclude that the NEV of corn-ethanol is positive when fertilizers are produced by modern processing plants, corn is converted in modern ethanol facilities, farmers achieve normal corn yields and energy credits are allocated to coproducts. Our estimate of 16,193

BTU/gal can be considered conservative, since it does not include energy credits for those plants that sell carbon dioxide. Corn ethanol is energy efficient as indicated by an energy ratio of 1.24, i.e., for every BTU dedicated to producing ethanol there is a 24 percent energy gain. Moreover, producing ethanol from domestic corn stocks achieves a net gain in a more desirable form of energy. Ethanol production utilizes abundant domestic feedstocks of coal and natural gas to convert corn into a premium liquid fuel that can replace petroleum imports by a factor of 7 to 1.

References

Bhat, Mahadev, G., Burton C. English, Anthony F. Turhollow and Hezron O. Nyangito. Energy in Synthetic Fertilizers and Pesticides: Revisited. ORNL/Sub/90-99732/2. Oak Ridge National Laboratory, January, 1994.

DeLuchi, M.A., Emissions of Greenhouse Gases from the Use of Transportation Fuels and Electricity, Argonne National Laboratory, 1991.

Environmental Protection Agency (EPA), Regulatory Development and Support Division, Office of Mobile Sources, Office of Air and Radiation. Technical Support Document-Renewable Oxygenate Mandate for Reformulated Gasoline, December, 1993.

Fertilizer Institute, Production Cost Survey, Compiled by TVA. 1992

Ho, S.P. Global Warming Impact of Ethanol Versus Gasoline. Presented at 1989 National Conference, "Clean Air Issues and America's Motor Fuel Business." Washington D.C., October, 1989.

Hohmann, Neil and C. Matthew Rendleman. Emerging Technologies in Ethanol Production. AIB-663. U.S. Dept. Agr., Econ. Res. Serv., January, 1993.

Keeney, D.R., and T.H. DeLuca. "Biomass as an Energy Source for the Midwestern U.S." American Journal of Alternative Agriculture, Vol. 7 (1992), pp. 137-143.

Marland, G., and A.F. Turhollow. "CO_2 Emissions From the Production and Combustion of Fuel Ethanol From Corn." Oak Ridge National Laboratory. Atmospheric and Climate Research Division. Office of Health and Environmental Research. U.S. Department of Energy. February, 1991.

Morris, D, and Irshad Ahmed. How Much Energy Does it Take to Make a Gallon of Ethanol?. Institute for Self Reliance, Washington D.C. December, 1992.

Pimentel, David. "Ethanol Fuels: Energy Security, Economics, and the Environment." *Journal of Agricultural and Environmental Ethics,* Vol. 4 (1991), pp 1-13.

Taylor, Harold, H. *Fertilizer Use and Price Statistics, 1960-93.* SBN 893. U.S. Dept. Agr., Econ. Res. Serv., September, 1994.

Turhollow, A.F. and R.D Perlack. Emissions of CO2 from Energy Crop Production, Biomass and Energy, Vol 1(3), 1991.

AN EXPERIMENTAL COMPARISON OF THE PERFORMANCE, FUEL EFFICIENCY AND EMISSION CHARACTERISTICS OF NEAT ETHANOL VERSUS GASOLINE MOTOR VEHICLE FUELS

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Abstract

The objective of this study was to compare the emissions, fuel economy, power and driveability characteristics of an automobile fueled by E-95, a mixture of 95% ethanol and 5% unleaded regular gasoline, with unleaded premium gasoline. In addition the cost of operation was determined for each fuel.

The vehicle used in the study was powered by a General Motors 2.5 liter 4 cylinder engine equipped with a programmable computer controlled fuel injection system. Fuel and ignition parameters were optimized for each fuel before tests were conducted.

The results of tailpipe emission testing using a 4-gas infra-red exhaust analyzer showed significant reductions in both hydrocarbon and carbon monoxide emissions. When using E-95 the vehicle consumed 31.5% more fuel by volume but 8.7% fewer kilo joules of energy to travel the same distance. The power at the rear wheels increased 5% when the vehicle used E-95. Driveablity with E-95 was noticeably worse during initial start up and during colder conditions, however when fully warmed up there was no difference in driveability. At current fuel prices the cost of operation using E-95 was 91.3% higher at $1.43 per 100 km while the cost on E-95 $2.73 per 100 km.

Introduction

Ethanol has long been used as a fuel in internal combustion engines. Reasons for its use have ranged from a fuel extender during the Arab Oil Embargo, to an octane enhancer and finally most recently as an oxygenate to help reduce carbon monoxide emissions.

This study was funded by the Council of Great Lakes Governors, Inc. and the U.S. Department of Energy. The research was conducted, under the supervision of faculty in the program, by two seniors in the Automotive Engineering Technology program at Mankato State University in partial fulfillment of the requirements of graduation.

The test vehicle was the Mankato State University RAD-Sport project car. The vehicle was designed and constructed by an earlier class of senior design students at MSU. The vehicle has a one piece glass reinforced plastic body which covers a square tube chassis. The vehicle weight is 805 kg (1773 lbs.) without passengers. The RAD-Sport is powered by a General Motors 2.5 liter 4 cylinder engine and a 4 speed manual transmission.

The engine was modified by installing an after market camshaft and increasing the compression ratio. For the purpose of this study the fuel and ignition system of the vehicle was modified to run on either E-95, a mixture of 95% ethanol and 5% unleaded regular gasoline or unleaded premium gasoline. An analysis of the tailpipe emissions, fuel economy, horsepower, driveability, and operational costs was conducted on the vehicle when operated on the two specific fuels.

Conversion Process

The vehicle was equipped with an Offenhauser aluminum intake manifold and a computer controlled Holley Pro-Jection throttle body injection system with an oxygen sensor for closed loop operation. The fuel injection system is fully adjustable allowing the researchers to simply change the fuel enrichment parameters for each fuel used. To aid in the throttle response of the engine on ethanol, a heated base plate (which uses engine coolant to supply the heat) was added between the throttle body and the intake manifold. The system is a commercially available after market component.

Optimization Process

The vehicle was optimized using the same procedure for each fuel. This procedure incorporated the use of three primary pieces of equipment. A Clayton Chassis Dynamometer was used to measure the power produced at the rear wheels. A Bear Ace II engine analyzer was used to measure the engine rpm, oil temperature and ignition timing along with the levels of HC, CO, CO_2, and O_2 present in the exhaust. The final piece used was a Sun distributor machine that allowed the researchers to adjust the ignition timing curve for the most efficient operation.

The first step in the optimization process was to adjust the seven specific parameters controlled by the fuel injection system's electronic control unit (ECU). Light load conditions, at idle and 2500 rpm, were adjusted while monitoring the HC and CO levels

as measured ahead of the catalytic converter. The mixture was adjusted to achieve the lowest CO reading, indicating a lean mixture, without causing a lean misfire indicated by an increased level of HC. The power setting on the ECU provides for the right mixture under hard acceleration. This was optimized by running the vehicle on the chassis dynamometer. The primary adjustment that needed to be made was an increase in fuel pressure from 8 psi on gasoline to 30 psi on ethanol. The increased fuel pressure allowed the system to flow the greater volume of fuel needed because of the lower energy density of E-95.

The second step in the process was the modification of the ignition timing curve. To accomplish this three points of the timing curve were chosen to step the timing; idle, 88.5 kph (55 mph) under normal highway load, and 4700 rpm heavy load. The first point on the timing curve, at idle, was set to provide easy starting.

To identify the second point on the timing curve, the load on the engine at 88.5 kph (55 mph) had to be determined so it could be simulated on the chassis dynamometer. To determine the power needed to propel the RAD-Sport down the road at 88.5 kph (55 MPH) two methods were used, the vacuum method and the throttle position method.

The vacuum method consisted of attaching a vacuum gauge to the intake manifold. The vehicle was then driven on a stretch of road at 88.5 kph (55 mph). The car was driven on a stretch of road at 88.5 kph (55 mph) and the vacuum reading was recorded along with the engine rpm. Another run was made in the opposite direction with the two measurements averaged to account for any wind or unlevel road. Two additional runs were made with the four data points averaged. The average rpm was 2031 and the average vacuum reading was 14.8" hg.

The throttle position method was conducted at the same time as the vacuum method. A digital multimeter was connected to the throttle position sensor (TPS). The TPS voltage ranges from .5 volts to 5 volts depending on how far the throttle plates are open. The voltage reading was taken at the same time as the vacuum readings with an average reading of .94 volts.

The vehicle was then run on the chassis dynamometer to determine the power required at highway speeds. The vehicle was accelerated to 88.5 kph (55 mph) and the dynamometer load was increased until a vacuum reading of 14.8" HG was reached. The power was then recorded. The procedure was repeated using the TPS reading. The dynamometer was loaded until the TPS value was .94 volts at 88.5 kph (55 mph) and the power value recorded.

The researchers found that both methods used to determine the power required to move the RAD-Sport down the road at 88.5 kph (55 mph) yielded the same results, 6.72 kW (9 hp). All subsequent testing that was to be done at highway speeds was simulated by running the vehicle on the chassis dynamometer loaded to 6.71 kW (9 hp) at 88.5 kph (55 mph).

While operating the vehicle on the dynamometer at highway speeds small adjustments were made to the ignition timing until vacuum and hp readings were optimized with the throttle held steady. The timing point was measured using a timing light and recorded.

The final point on the timing curve was set with the vehicle driven on the dynamometer at 4700 rpm at wide open throttle (WOT). The rpm and power readings were measured with adjustments made to the ignition timing until the maximum power was achieved. Again the timing point was measured and recorded.

Once the ignition timing points were identified, the distributor was removed from the vehicle and installed on the Sun Distributor Machine. The distributor was then recurved by installing different weights and springs to bring the timing curve into the desired parameters. Table 1 below contains the ignition system parameters for each fuel.

Table 1. Optimized Ignition Timing Specifications

Crankshaft RPM	Total Crankshaft Timing (Gasoline)	Total Crankshaft Timing (E-95)
600	12° btdc	6°btdc
2050	38° btdc	26° btdc
4700	36° btdc	29° btdc

Testing Process

Emission Testing

Tailpipe emissions, fuel economy and road horsepower tests were conducted to compare the engine performance on both fuels. The procedure for both fuels was identical to allow for accurate comparison of the two fuels.

Emission testing was conducted at three specific conditions: idle with no load, 2500 rpm with no load, and with a 6.71 kW (9 hp) at 88.5 kph (55 mph) on the chassis dynamometer. Carbon monoxide (CO), hydrocarbon (HC), carbon dioxide (CO_2), and oxygen (O_2) levels were measured both before and after the catalytic converter with a 4-gas infra-red exhaust analyzer.

Before each test was begun, the date, room temperature, and barometric pressure were recorded. Each of the tests were started after an initial warm-up procedure was conducted to raise the oil temperature to 93° C (200° F).

The tailpipe emission levels, measured before the catalytic converter, were considerably less when the vehicle ran on E-95. In addition, the levels of CO measured after the catalytic converter were significantly lower. However, the HC readings were higher after the catalytic converter when the vehicle ran on E-95. The study did not specifically look at catalytic converter efficiency, however exhaust temperature was measured both ahead and behind the catalytic converter during all testing. The temperature after the catalytic

converter averaged 65° C (150° F) hotter than the inlet temperature when running on gasoline. The increase in temperature on E-95 averaged 54° C (130° F) hotter when running on E-95. This observation might lead one to suspect that the catalytic converter efficiency was different for the two fuels. Table 2 displays the results of the idle emission testing, Table 3 displays the results of the 2500 RPM no-load emissions, and Table 4 displays the results of the simulated highway emissions.

Table 2. Idle Emissions

Before Catalytic Converter

	Gasoline	E-95	% Change
CO	1.37%	0.92%	32.8%
HC	82 PPM	29 PPM	64.5%
CO_2	10.1%	7.7%	23.8%
0_2	6.4%	9.6%	33.3%

After Catalytic Converter

CO	0.26%	0.00%	100%
HC	6.0 PPM	8.0 PPM	25%
CO_2	13.5%	14.0%	3.5%
0_2	2.6%	2.5%	3.8%

Table 3. 2500 RPM No-Load Emissions

Before Catalytic Converter

	Gasoline	E-95	% Change
CO	0.47%	.25%	46.8%
HC	7 PPM	0 PPM	100.0%
CO_2	14.5%	14.6%	0.7%
0_2	0.7%	1.3%	3.5%

After Catalytic Converter

CO	0.10%	0.00%	100%
HC	0 PPM	0 PPM	--
CO_2	15.3%	14.4%	5.8%
0_2	0.3%	1.4%	78.6%

Table 4. Simulated Highway Emissions
6.71 kW (9 HP) at 88.5 KPH (55 MPH)

Before Catalytic Converter

	Gasoline	E-95	% Change
CO	0.33%	0.20%	39%
HC	65 PPM	31 PPM	52%
CO_2	14.1%	14.4%	2%
0_2	2.4%	1.7%	29%

After Catalytic Converter

CO	0.05%	0.02%	60%
HC	3 PPM	9 PPM	66%
CO_2	15.4%	14.5%	6%
0_2	0.6%	1.7%	65%

Fuel Economy Testing

The fuel economy testing was conducted using the chassis dynamometer, engine analyzer and a digital scale that measured to the mass of the fuel consumed. In addition an apparatus was designed and constructed that suspended the fuel supply and return lines from the vehicle into a small fuel tank that rested on the scale.

Before the test was begun the date, time, fuel specific gravity, air temperature and pressure were recorded. The vehicle was warmed up on the dynamometer until the oil temperature reached 93° C (200° F). Once the operating temperature was reached the vehicle was accelerated to the highway simulation parameters. When the test conditions were reached, the stopwatch was started and the weight of the fuel was recorded simultaneously. Each test run lasted for 20 minutes with fuel readings recorded at regular intervals along with a final reading at the end of the test.

Using the specific gravity of the fuel and the weight of fuel consumed, the amount used per run was calculated to the nearest .001 of a gallon. The following is an explanation of the fuel economy calculations used:

Distance Traveled	speed in kph (mph) x elapsed time in hours
Energy Consumption	[kj/kg of fuel x kg of fuel used] / km traveled [BTU/lb of fuel x lb of fuel used] / miles traveled

Fuel Economy Gas Equivalent

$$\frac{\text{km traveled x kj/liter gasoline}}{\text{kg of fuel x kj/kg E-95}}$$

$$\frac{\text{miles traveled x BTU/gal gasoline}}{\text{lbs of fuel x BTU/lb E-95}}$$

Cost of Operation

cost of fuel per liter / kilometers per liter
(cost of fuel per gallon / miles per gallon)

The fuel economy of the test vehicle can be analyzed several ways. The results are presented in Table 5. The first and most common being liters per 100 kilometer (miles per gallon). As indicated in Table 8 the fuel economy decreased from 6.39 l/100km (36.8 mpg) on gasoline to 9.33 l/100km (25.2 mpg) on E-95, a decrease of 31.5%. This reduction can be attributed the lower energy density of E-95.

Table 5. Fuel Economy Results

	Gasoline	E-95	% Change
Fuel Economy	6.03 km/l (36.8 MPG)	4.15 km/l (25.2 MPG)	31.5% Worse
Fuel Economy (Gasoline Equivalent)	6.03 km/l (36.8 MPG)	6.60 km/l (40.3 MPG)	9.5% Better
Energy Consumption*	2237 kj/km (3413 BTU/m)	2034 kj/km (3101 BTU/m)	9.1% Better
Cost Per Liter* (Gallons)	$0.23/liter ($0.87/gal)**	$0.30/liter ($1.12/gal)***	28.7% Worse
Cost of Operation	$1.43/100km ($0.023/Mile)	$2.73/100km ($0.044/Mile)	91% Worse

* Gasoline Energy Density 34,313 KJ/l (125,093 BTU/GAL)
* E-95 Energy Density 20,608 KJ/l (78,829 BTU/GAL)
** Price of unleaded premium gas minus Federal ($.18) and State ($.20) taxes
*** Price of E-95 from Minnesota Corn Processors. No tax included.

If the fuel economy comparison is made in gasoline equivalent kilometers per liter the results are quite different. The gasoline data would remain at 6.39 l/100km (36.8 mpg). The E-95 would now have a gasoline equivalent mpg of 5.84 l/100km (40.3 mpg) yielding a 17% increase in energy efficiency. This illustration shows that the vehicle converted the energy in the E-95 to usable power more efficiently.

A comparison of the cost per liter of the fuels shows that E-95 is more expensive at $ 0.30 per liter ($1.12 per gallon). The cost does not include any of the fuel taxes. The cost of a liter of gasoline with tax removed is $0.23 per liter ($0.87 per gallon). Using the cost per liter figures the cost per km of operation can be calculated. That cost for E-95 is $2.73 per 100 km ($0.44 per mile) and $1.43 per 100 km ($0.23 per mile) for gasoline.

Power Output

The power test, as measured at the rear wheels, was conducted on the chassis dynamometer. As in the earlier tests for emissions and fuel economy tests, environmental conditions were measured and recorded before testing. The measurements were used to determine the horsepower correction factor (HPCF).

All power tests were conducted after the oil pressure reached 93° C (200° F). The power and torque was measured at 500 rpm increments starting at 2500 rpm and ending at 5000 rpm. All tests were run with the transmission in the same gear. Results of the power testing are found in Table 6.

Table 6. Power Output Results

RPM	Gasoline Torque NM (lb-ft)	E-95 Torque NM (lb-ft)	Gasoline Corrected Power kW (HP)	E-95 Corrected Power kW (HP)	% Change
2500	174 (128)	158 (116)	46 (61)	41 (55)	8.8% -
3000	159 (117)	158 (116)	50 (67)	49 (66)	2.0% -
3500	163 (120)	166 (122)	59 (80)	60 (81)	3.4% +
4000	159 (117)	166 (122)	66 (89)	69 (93)	4.5% +
4500	141 (104)	150 (110)	66 (89)	70 (94)	6.1% +
5000	117 (86)	127 (93)	61 (82)	66 (89)	8.2% +

Conclusions

Emissions

It can be concluded from this study that the test vehicle produced significantly less CO and HC emissions at most points when measured both before and after the catalytic converter. In the two cases where there was an increase in HC emissions the difference fell outside the range of measurement accuracy.

Temperature measurements taken before and after the catalytic converter indicated a lower exit temperature when run on E-95. This could indicate a drop in converter conversion efficiency causing the increased HC emissions. More research should be conducted on different converter designs for high concentration ethanol fueled vehicles.

The current Minnesota Inspection Maintenance Program uses an exhaust analyzer similar to the one used in this study. It should be noted that the test vehicle met the current standards for 1979 cars , for which it is legally required to meet, and also easily met the latest model standards for 1995 model vehicles.

Fuel Economy

It can be concluded from this study that the test vehicle converted the energy in the E-95 to usable power at the rear wheels more efficiently than when using gasoline. The gasoline equivalent fuel economy and energy consumed per unit distance increased by 8.1% and 9.1% respectively.

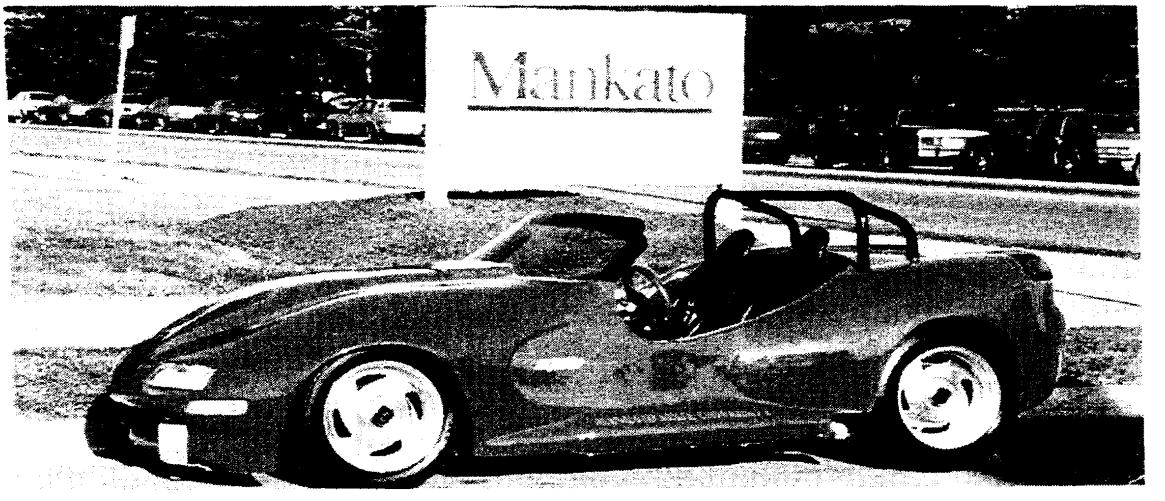
However, based on the lower energy density of the E-95 and its cost per unit volume, the vehicle range would be limited at the same time the cost of operation would be increasing. This represents an increase in the cost of operation of 91% if State and Federal taxes are not figured into the equation.

Power Output

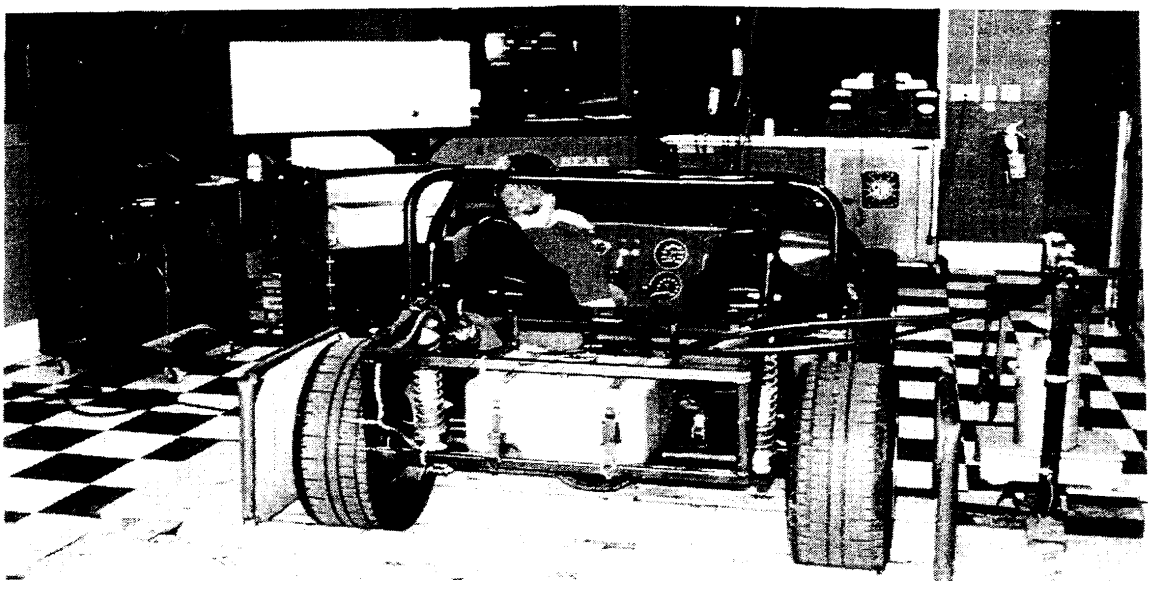
In general, both the power and torque were slightly lower for the E-95 fuel at low rpm. At the middle and higher rpm the E-95 allowed the engine to produce more torque and power. When the engine ran on E-95 the peak power output was 5% higher than the peak power output on gasoline.

Driveability

Driveability using the E-95 fuel was significantly worse during cold operation and initial startup. When fully warmed up, there was no difference in throttle response or any other driveability characteristics. It is believed that variations in the volatility of the E-95 along with heat storage devices could easily remedy any cold operation driveability problems encountered.



The Mankato State University RAD-Sport Project Car



The Mankato State University RAD Sport During Final Testing

A LABORATORY AND PILOT PLANT SCALED CONTINUOUS STIRRED REACTOR SEPARATOR FOR THE PRODUCTION OF ETHANOL FROM SUGARS, CORN GRITS/STARCH OR BIOMASS STREAMS

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Abstract

An improved bio-reactor has been developed to allow the high speed, continuos, low energy conversion of various substrates to ethanol. The Continuous Stirred Reactor Separator (CSRS) incorporates gas stripping of the ethanol using a recalculating gas stream between cascading stirred reactors in series. We have operated a 4 liter lab scale unit, and built and operated a 24,000 liter pilot scale version of the bioreactor.. High rates of fermentation are maintained in the reactor stages using a highly flocculant yeast strain. Ethanol is recovered from the stripping gas using a hydrophobic solvent absorber (isothermal), after which the gas is returned to the bioreactor. Ethanol can then be removed from the solvent to recover a highly concentrated ethanol product. We have applied the lab scale CSRS to sugars (glucose/sucrose), molasses, and raw starch with simultaneous saccharification and fermentation of the starch granules (SSF). The pilot scale CSRS has been operated as a cascade reactor using dextrins as a feed. Operating data from both the lab and pilot scale CSRS are presented. Details of how the system might be applied to cellulosics, with some preliminary data are also given.

Introduction

Ethanol production in the USA can offer a renewable source of liquid fuel produced within the borders of our own nation as well as providing a market for excess grain production capacity of the midwestern states. However, in order for the ethanol fuel industry to be able to expand without governmental subsidies, ethanol production costs must be reduced closer to the level of refined unleaded gasoline ($0.55-$0.75 per gallon). Ethanol production costs can be reduced via: 1) reducing costs of substrate, 2) increasing the efficiency of substrate conversion to ethanol, 3) reducing the energy costs for purifying and dehydrating the ethanol, 4) reducing the amount of effluent 'bottoms' waters which must be treated, 5) reducing the capital costs for the ethanol processing plant, 6) reducing the labor for operating the ethanol plant.

A Continuous Stirred Reactor Separator (CSRS) consisting of stirred tank type reactors operated in series, with the liquid streams moving from tank to tank contacted with a stripping gas to remove the ethanol product has been designed and tested. A patent (#5,141,861) has been issued which describes this reactor technology. Capital costs for the CSRS system have been estimated to be about $1.40/annual gal. at the 500,000 gal/yr scale, which compares to a cost of $2.70 for a batch plant at this scale. This CSRS is a new type reactor which allows simultaneous saccharification, fermentation, and ethanol separation in a combined process. Combining these reactions allows significant improvements in each operation. Combining reaction with separation allows the fermentation of highly concentrated streams of up to 50% solids. Simultaneous saccharification and fermentation of polysaccharides such as starch and cellulose can be quickly completed in this bio-reactor/separator. Saccharification (of both starch and cellulose)is sped by the reduction of sugar concentration as the sugar is fermented to ethanol. Fermentation is sped by the removal of the toxic ethanol product, and ethanol purification and concentration costs are reduced by the enrichment of the ethanol in the vapor phase. The gas stream is co-current to the tank to tank liquid flow in the enriching section, and counter-current in the stripping section. The final effluent from the CSRS is characterized by complete saccharification of all polysaccharides, complete fermentation of sugars to ethanol and complete removal or separation of the ethanol into the gas phase. A schematic of the CSRS process is shown in Figure 1 for a system incorporating complete recycle of the thin stillage.

The CSRS can be coupled with a solvent ethanol recovery system to give a low energy continuous process for the production of ethanol from starch or biomass. Energy savings are attained by combining the CSRS reactor concept with solvent absorption of the ethanol from the gas stream exiting the CSRS as shown in Figure 1. The ideal solvent for absorption of ethanol from a gas stream would have the following properties: 1) low vapor pressure of the solvent, 2) solvent miscible with ethanol, 3)solvent vapor carry-over non-toxic to fermenting microbes in CSRS, 4)low solubility of water in the solvent, and 5) low solubility of solvent in water. The ideal solvent would absorb only ethanol allowing an anhydrous ethanol product to be stripped off from the solvent/ethanol stream from the absorber. However, all solvents having the ability to solvate ethanol also dissolve some

water. Tedder et al. (1986) state that the solvents they tested for direct solvent extraction of ethanol have a 3 to 5% water weight fraction in the solvent phase when contacted with an aqueous phase. Each solvent can be characterized by an equilibrium distribution coefficient, K_{dc}, for ethanol between the water and solvent phase, as well as a distribution coefficient for water, K_{dw} between the aqueous and solvent phases. Dividing the ethanol distribution coefficient by the water distribution coefficient (K_{dc}/ K_{dw}) gives a separation factor, a, which describes the relative affinity of the solvent for ethanol compared to water. Dodecanol, found by Minier and Goma (1982) to be non-toxic in direct solvent extraction in-situ separation, has an ethanol distribution coefficient of .21, and an ethanol/water separation, a, factor of 21. Work by Kollerup and Daugulis, (1985) indicated that dodecanol was somewhat toxic to microbes. Research in our labs has shown that dodecanol in direct contact with immobilized cells was toxic to yeast, but when used as vapor ethanol absorber, the dodecanol vapors carried over to an immobilized cell type reactor were not toxic, with fermentation rates of immobilized cells stable over 4 to 6 days (Lee and Dale, 1991 unpublished data). By not actually contacting the cells with an organic phase, toxicity problems and solvent loss into the water phase are both minimized. An anhydrous ethanol product may be recovered from the solvent using a simple extractive distillation procedure using the same solvent used for the ethanol absorption. This process has been designed, tested, and modeled by hand calculations and using the Aspen II library using solvents with a separation factors of 50-90, which would give the energy usages shown in Table 1 for steam energy requirements to recover an anhydrous ethanol product.

Table 1. Distillation Steam Energy Requirements for Anhydrous Ethanol (MBTU/gal)

% Ethanol	Conv. Distillation/PS Dehydr.	Sol. Abs. Extr. Distillation
2.5	44	22
5.0	21	13.3
7.5	15	8.4
10.0	13	6.7
12.5	11.5	5.9

It can be seen that as the ethanol concentration in the stage from which the gas exits is allowed to increase, energy costs for ethanol recovery drop. The selection of solvents and testing of the SAED system was described in a paper given by Dale (1993).

No-cook conversion of starch to sugars-

If the cook process can be completely eliminated from the process of converting starch/grits to ethanol, energy, capital, and labor costs could be significantly reduced. This conversion, when coupled with ethanol separation may allow the simple starch to ethanol process shown in Figure 1. Glucose inhibition of enzymatic action has been noted to increase at lower temperatures. These results are similar to the kinetics determined by Matsumura et al (1987,1989) for raw starch saccharification using a glucoamylase with sweet potato starch. The use of *Aspergillus niger* on wet corn as a source of amylase

enzymes was reported by several researchers as giving good results with this type of process (Han and Steinberg, 1986; Fujio et al, 1984; Ueda et al, 1981).

Bottoms water recycle

It is a common practice in the fermentation industry to recycle 20-50% of the stillage to help reduce and control the pH of the initial fermentation broth. Nofsinger et al. (1982) showed good performance with 100% recycle of stillage. However, in a recycle scheme, there will be recycling of any non-volatile fermentation products or non-fermentables in the feed. Thus for molasses (which is characterized by about 40-50% fermentable solids) a maximum stillage recycle ratio of 30% has been determined, while for high-test molasses with 85% fermentable solids, 1a 50% recycle can be used (Hodge and Hildebrandt, 1954). The major fermentation by-products that will tend to build up over time are glycerol (3.3% yield) and lactic/succinic acid (0.5-1.0% yield).

Conversion of cellulose and hemicellulose to ethanol-

Biomass in the form of corn stalks, wood chips, waste paper, and grass clippings offers an enormous and low cost source of sugars for ethanol production. Xylose fermentation techniques, and the simultaneous saccharification and fermentation of cellulose are being studied as an application for the CSRS reactor system. The two stage fermentation of biomass, following a basic extrusion solubiliziaton of lignin and hemicellulose (the Xylan delignification process (Tyson et al, 1995)) is being developed. We are hoping to demonstrate a 5 stage CSRS system with a two stage xylose fermentation followed by a 3 stage SSF of cellulose (Dale, 1994).

Methods and Materials

A four liter, four stage lab scale CSRS was constructed using rectangular stages as per Figure 2.The ethanol vapors were absorbed into an isothermal water stream flowing 4 times faster than the feed to the reactor. Stage 1 has a liquid volume of 1,100 ml and stages 2-4 have a hold up of 900 ml. A single trough type bubble cap contactor was used as the gas-liquid contacting device after stages 2,3 and 4. This reactor was used for starch, sucrose, and molasses fermentations. Batch fermentations were performed in 250 to 500 ml Er. flasks using a magnetic stirrer placed in an environmental temperature controlled cabinet. Organisms used included strains of *S. pombe, S. cerevisae, K. marxianus,* and *A. niger* obtained from the NCAUR and CBS culture collections. Standard nutrients used in these fermentations were a YEP supplementation, with yeast extract, malt extract, and peptone added at 3 g/l each unless otherwise noted. A mix of 8% malt and 200 to 300 DU/# starch L-200 glucoamylase from Solvay was used in our no-cook fermentation studies. In the continuous reactor experiments, pH was maintained at between 3.5 and 4.2 via addition of ammonium hydroxide. Degree of starch conversion was determined by mass balance in the CSRS experments, and by glucose release from the fermentation broth in a post experiment cook with alpha-amylase followed by glucoamylase at 60 C (Solvay, 1991).

Results

Batch 'No-cook' fermentations.

12 and 20% starch concentrations were fermented using a flocculant yeast strain. Comparisons of the fermentation of cooked starch treated with alpha-amylase were run versus a raw starch fermentation. Figure 3 show the results of this comparison with a 12% raw starch feed. It can be seen that ethanol generation is slightly quicker with the cooked medium as compared with the raw starch medium. Glucose levels in the raw starch feed were maintained at near zero levels. The release of glucose was rate limiting. At a 20% starch feed, the cooked medium showed a faster fermentation again during the first 20 hours, after which the ethanol levels in the no-cook medium reached the same level at 25 hours of 82 g/l. Conversion efficiency (based on residual starch) was determined to be 96% and 86% for the cooked medium at 12 and 20% starch as compared to 92% and 84% for the raw starch medium at 12 and 20% starch mediums respectively. The possibility of generating amylase enzymes insitu was investigated using *Aspergillus niger* co-cultured with yeast. Good, but somewhat slower starch breakdown was noted when compared to commercial gluco-amylase added to the same raw starch medium (12%) as shown in Figure 4. A lower final starch conversion rate with the co-culture broth was noted after 100 hours (92 vs 96%).

Continuous 'No-cook' fermentation of starch in the lab CSRS

The lab scale CSRS was operated on raw starch for a period of 37 days using concentrations of 10%, 15%, 20% and 30% TS sequentially. Enzymes for starch granule hydrolysis were a commercial gluco-amylase and ground malt at an 8% level (Dale et al, 1991). The CSRS was operated at 38C using an adapted temperature tolerant strain of yeast (*K. marxianus*, NRRL 2415). Profiles of glucose and ethanol on the stages are given in Table 1 for a 20% starch feed. It is difficult to determine starch concentration directly due to the starch and yeast granules being mixed together, however, the conversion efficiency can be determined based on average ethanol and glucose yields (1 g starch ->1.0 g glucose-> .46 g ethanol). Using these conversions, a conversion efficiency of 79% was determined for the data shown in Table 2 at a residence time of 40 hours. Yeast density of 1.5 e 9 was measured on this day. When it was attempted to feed 30% starch, clogging of the bubble troughs caused pressure drop of the gas phase through the reactor to increase and the reactor was shut down for cleaning.

Table 2. Compositions (g/l) in the CSRS with Raw Starch Feed (Day 10)

Stage	Glucose	Ethanol
1	22	17.8
2	2.8	31.1
3	2.1	33.3
4	0.1	26.7
Abs. effl.	0	8.9

Continuous fermentation of sucrose in the lab CSRS with 80% bottoms water recycle

The effects of bottoms water recycle were studied in the CSRS. An adapted flocculant S. cerevisae strain (NRRL Y265) was added to the CSRS. 4 liters of bottoms water was used to reconstitute 1,200 g of sucrose, after which nutrients were added and the volume adjusted to 6 liters with deionized water. The reactor was operated on a continuous basis for 120 days. at a feed rate of 100 ml/hr. Settled yeast from the effluent was also recycled. A steady state cell density of 14 to 18 g/l was maintained over this period. High rate conversion of the sucrose was noted as shown in Table 3. Sugar utilization rates of 10 to 19 g/l hr were routinely achieved in stage 1. Glycerol levels of between 17-54 g/l. were noted over the test period. The average glycerol levels were 22-28 g/l. Even at the highest glycerol levels, high rates of fermentation were noted.

Table 3 CSRS Compositions (g/l) on Day 32-Sucrose Feed

Stage	Glucose	Fructose	Lactic A.	Glycerol	Eth.	Brix
1	117	96	2.5	22.5	21.9	20
2	51	66	2.7	24.1	56.2	16.2
3	4.8	16	2.5	22.5	53.7	10.2
4	0	0.5	2.6	23.1	33.7	7.1
Recycle	0	0	3.1	27.9	5.0	7.0

Continuous fermentation of cane molasses in the lab CSRS with bottoms water recycle

Cane molasses from the Savannah Sugar company was fermented in the CSRS . The molasses was diluted to the desired brix using a mix of 80% bottoms water and 20% fresh DI water. Feed to the system was maintained at 100 ml/hr. Good conversion was noted on day 1 with a 34 brix feed reduced to 13 brix in stage 4. By day 11, however, brix in stage 4 had increased to 21. Brix drop in stage 1 dropped from 6 to 2 over the 17 day test, stage 2 showed a drop from 5 to3 brix drop, while stage 3 stayed relatively constant at 4-5 brix drop. After 17 days operation a lower brix feed of 17% was next fed for 5 days. Cell density was observed to drop from an average density of 6.5 g/l on day 3 with low brix feed to under 2 g/l on day 5 even though it was attempted to recycle the yeast. The molasses substrate seemed to have some inhibitors which caused floc breakdown and loss of fermentation activity over time, so that either continuous addition of yeast, recycle of yeast or further research is needed to apply the use of the floc yeast to molasses.

Construction of a 24,000 Liter pilot scale CSRS system.

A 24,000 liter CSRS bioreactor was constructed during 1994 and installed at Permeate Refining Inc's ethanol plant site in Hopkinton, IA. This system will be similar to the diagram shown in Figure 1, and a photograph of the installed reactor/solvent absorber system is shown in Figure 5. This system has been operated as a continuous cascade reactor during the first quarter of 1996. Feed rates have been varied between 2 and 5 GPM (18 -40 hour residence time) with near complete utilization of a 20% feed sugar stream. Some trouble shooting during this period of time has been accomplished including; 1) redesigning and replacing seals around the stirring shaft, 2) continuous addition system and

formulation of nutrients/enzymes , and 3) introduction and maintenance of an adapted flocculant yeast strain in the bioreactor has been a. A feed of dextrins (Amaizo, AMP, Hammond IN) is being fed with simultaneous saccharificiation of the dextrins to glucose using glucoamylase and fermentation of the glucose occurring in the bioreactor. The Solvent Absorption Extractive Distillation system is scheduled for installation during June of 1995 to allow in-situ removal of ethanol from the bio-reactor.

Conclusions

Our basic objective in this work has been to demonstrate feasibility a process as outlined in Figure 1. This includes 1) maintenance of a high cell density yeast in the bioreactor, 2) the no-cook conversion of starch granules to sugars and ethanol, and 3) the inclusion of a high amount of recycle waters from the bottom of the reactor. Each of these objectives were met as described in our experimental section. Use of a flocculant yeast strain in the bioreactor allows continuous high rate fermentations without the cost and complexity of a cell recycle system. Cell densities of 20-40 g/l have been regularly observed in our long term tests. This will allow residence times to be reduced to as low as 6 to 12 hours in the CSRS system. Raw starch can be converted to ethanol with a high conversion efficiency (>95%) in batch fermentations of 30 to 48 hours, but current results show less efficient (80%) yields in the CSRS when residence times are under 20 hours. Enzymatic breakdown of the starch granule is rate limiting, with glucose levels held low in both batch and continuous fermentations. The use of the no-cook technology will have to be economically compared to starch cooking technology on a site by site basis, with either a longer reactor hold time or incomplete starch utilization being factored into the comparison of the no-cook technology with conventional cooking of the starch/grits. The lab scale conversion of sucrose with an 80% recycle of bottoms water showed some build-up of glycerol over time, but no significant inhibition of fermentation rates. The use of up to 80% recycle of bottoms water as per Figure 1 can thus be confidently implemented and will have the further benefit of recycling of some nutrients and enzymes remaining in the broth.

We thus see no obstacles to implementations of the CSRS technology as outlined in Figure 1 on grains or to any other fermentable substrates, and are in the process of demonstrating the technology using the 24,000 L pilot plant (design capacity of 0.3-0.5 million gal/r scale) in Hopkinton IA presently. It is our goal to develop and demonstrate technology to allow the economical production of ethanol on a smaller scale (0.5 -10 million gal/yr) for on-site production of ethanol at 1)cow or chicken feeding operations, 2) cheese making facilities, 3) corn refining operations, 4) food/candy processing operations.

Acknowledgments

This work was supported by the DOE Energy Related Inventions Program, The Great Lakes Biomass Regional Biomass Energy Program, Permeate Refining Inc., DOE Industrial Wastes Program, Xylan Inc, and Bio-Process Innovation Inc.

Bibliography

Arenson, D. S. Kertes, and J. King. 1990. Extraction of Ethanol from Aqueous Solution with Phenolic Extractants. IEC Res. 29:607.

Dale, M.C., A. Eagger and M. Okos. 1990. Osmolality Effects on Free and Immobilized K. fragilis. AICHE. Nov.

Dale,M., N. Perrin and M. Okos. 1994 Fermentation of Concentrated Sucrose and Molasses streams use Free and Immobilized S. pombe. AICHE Symp Series

Dale, M.C., 1992. A Continuous Multi-Stage Stirred Reactor-Separator for Production of Volatile Fermentation Products. Patent # 5,141,861.

Dale, M.C., S. Michel, and M. Okos. 1993. Conversion of raw milled corn to sugars as a function of temperature and ensyme use. COFE Chicago, Feb.

Dale, M.C., 1993. "A Solvent Absorption-Extractive Distillation (SAED) Process for the Recovery of Ethanol from Vapor or Gas Streams." AICHE COFE. Chicago, Feb.

Dale, M.C., 1994 A Pilot Scale Reactor Separator for Biomass Conversion to Ethanol. Accepted Proposal to the GL Biomass Energy Program

Downs, H., B. Clary, and J. O'Neal. 1982. Ensyme Function and Control during Conversion of Grain Starches to Fermentable Sugars. ASAE Dec.

Fujio, Y., P Suyanadona, and S. Ueda. 1984. Alcoholic Fermentation of Raw Cassava by Rhiz. koji without Cooking. Biotech Bioeng 24:315

Han, I, and M. Steinberg. 1986. Solid State Fermentation of Raw Corn with Koji Hydrolysis.Biotech Bioeng Symp. 17:449.

Kollerup, F. and A. Daugulis. 1985. Mathamatical Model for Extractive Fermentation. Biotech Bioeng. 27:1335

Matsumura, M. and J. Hirata. 1989. Cont. SSF of Raw Starch in a Membrane Reactor. J. Chem. Biotech. 46:313.

Matsumura, M., J. Hirata, and S. Ishii. 1987. Kinetics of Saccharification of Raw Starch by Glucoamylase. J.Chem Biotech. 42:51.

Minier, M. and G. Goma. 1982. Ethanol Production by Extractive Fermentation. Biotech and Bioeng. 25:1565

Munson, C. and C. King. 1984. Factors influencing Solvent Selection for Extraction of Ethanol from Aqeous Solutions. IEC Proc. Des. 23:115

Nofsinger, G.W., R. Bothast, and J. Wall. 1982. Fermentation Byproducts-Recycling Soluble Solution, and Chemical Preservation, NRAES Cooperative Extension Publication.

Roddy, J., 1980. Distribution of Ethanol-Water Mixtrues to Organic Liquids. IEC Proc. Des. Dev. 20:104.

Tedder, D., W. Tawfic, and S. Poelheim. 1987. Ethanol Recovery by Solvent Extraction and Extractive Distillation- the SEED Process. Chem. Sep. Vol

Ueda, S., C. Zenin, D. Monteiro, and Y. Park. 1981. Production of Ethanol from Raw Cassava Starch. Biotech Bioeng. 23:291

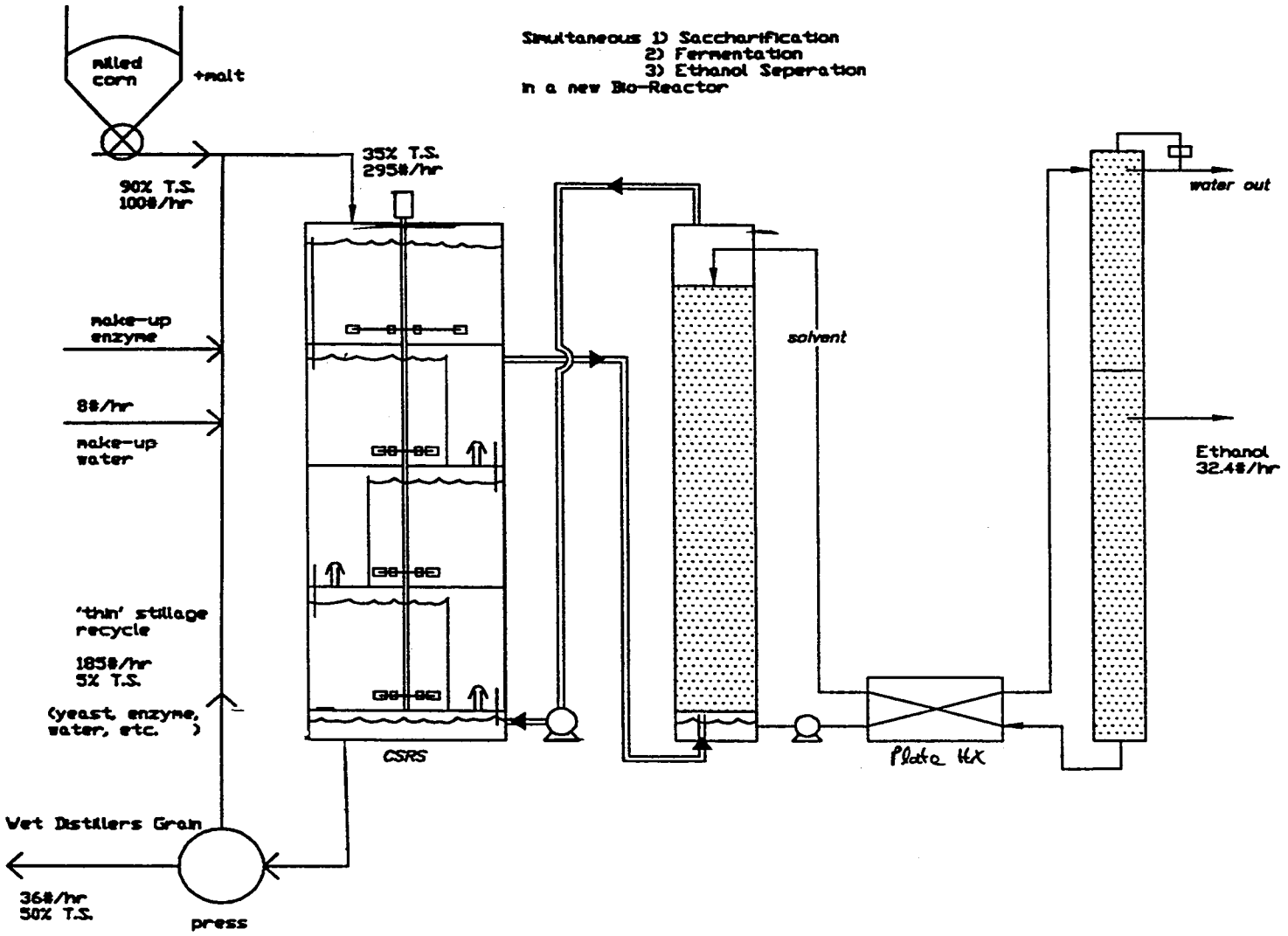

Figure 1. The Proposed CSRS No-cook Conversion of Milled Corn to Ethanol

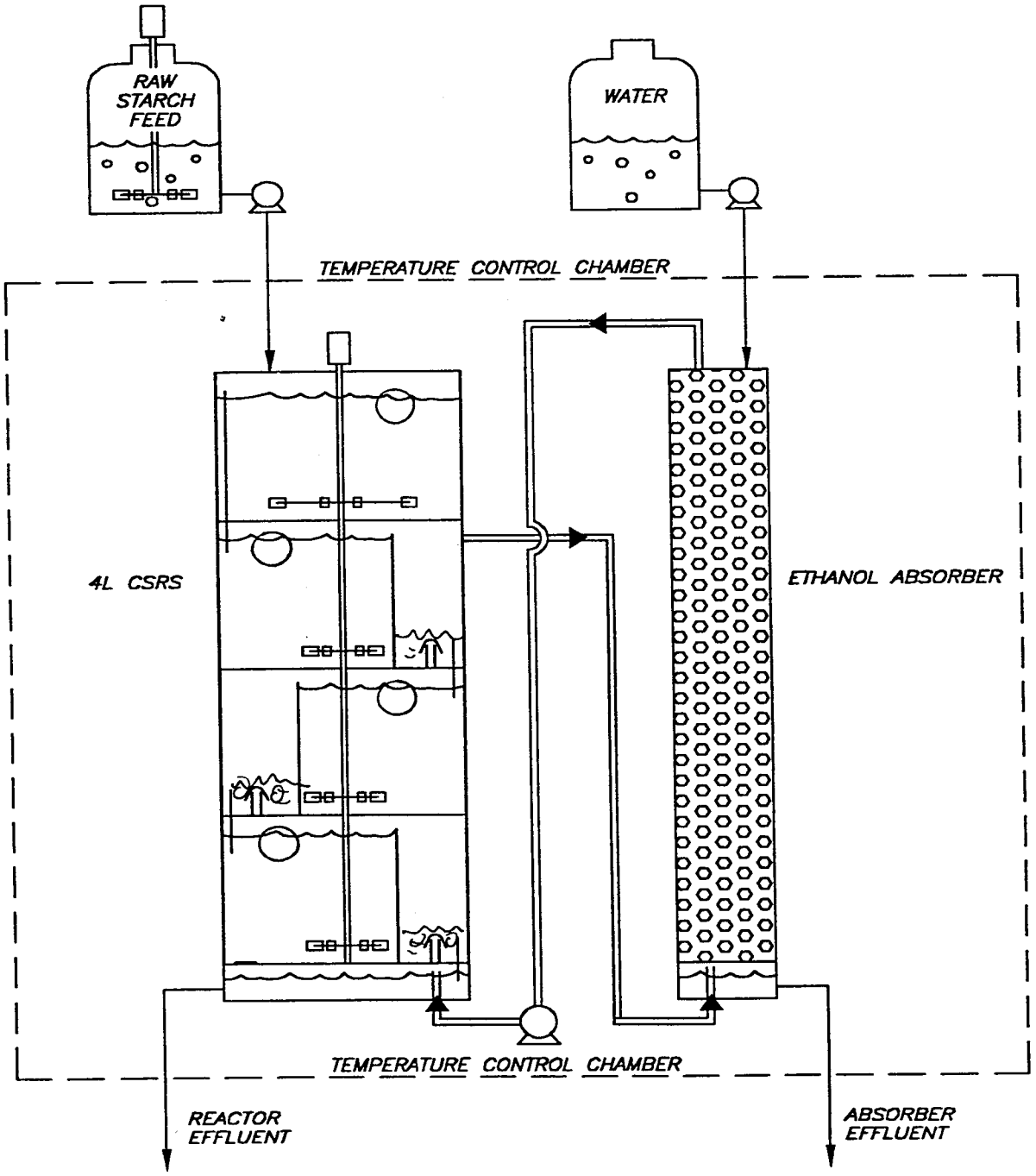

Figure 2. The 4 L. Lab Scale CSRS

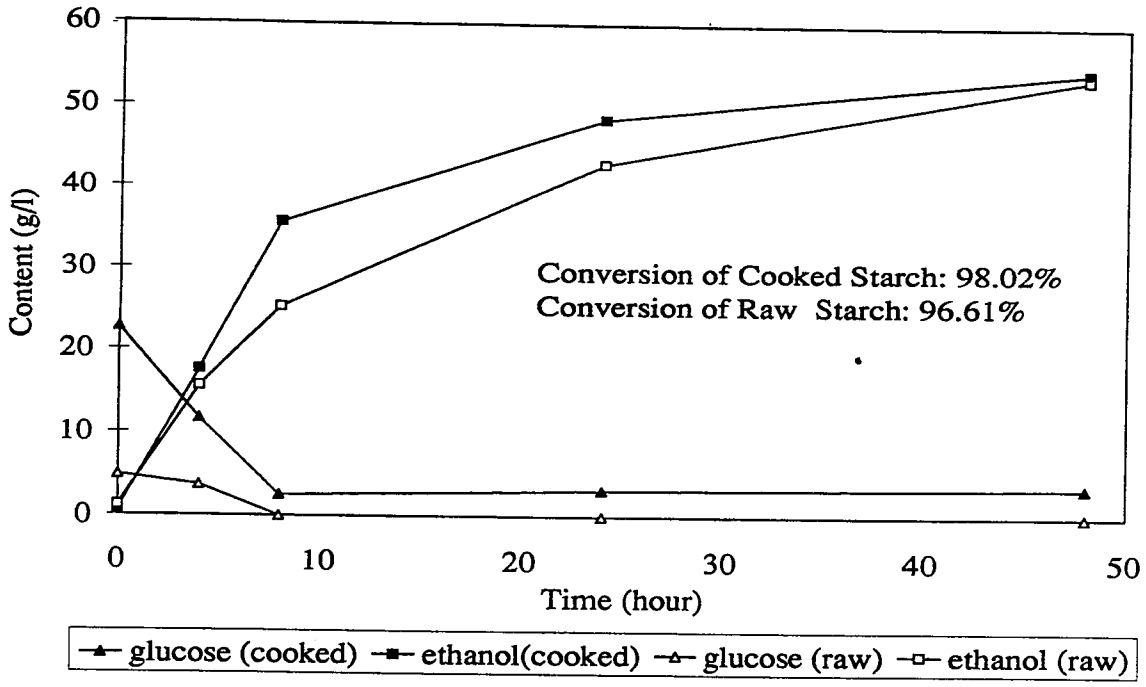

Figure 3. Batch Fermentation Comparison of Cooked versus Raw Starch

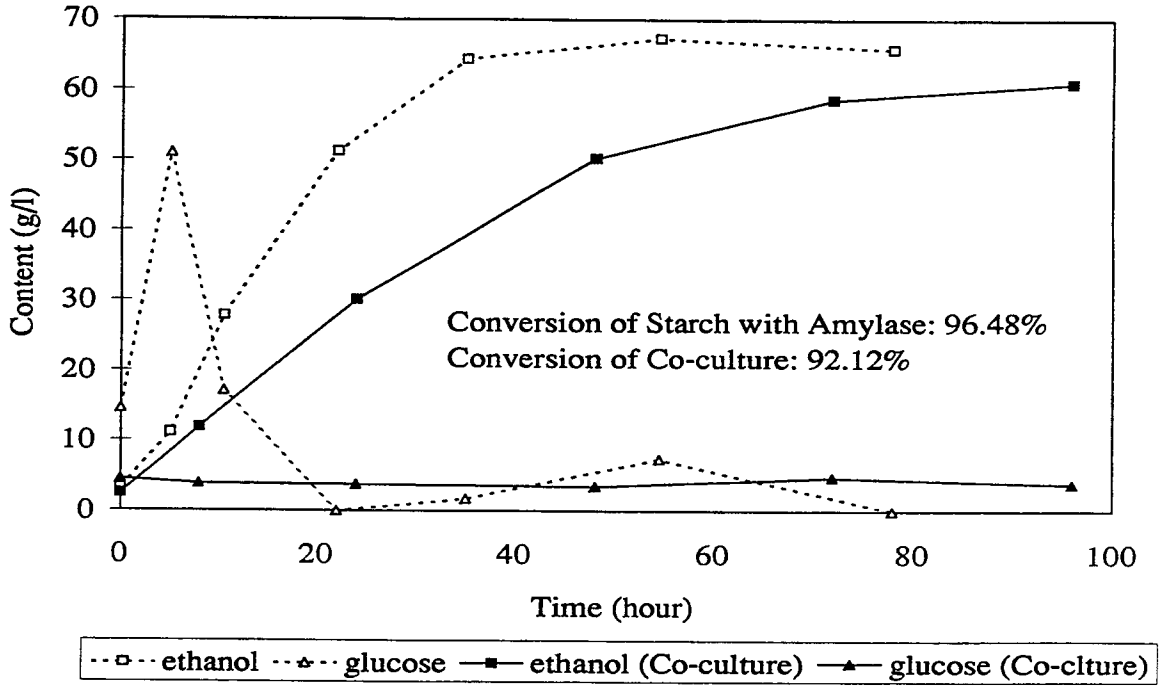

Figure 4. Batch Co-culture of S. Cerevisiae & A. Niger for Ethanol from Raw Starch

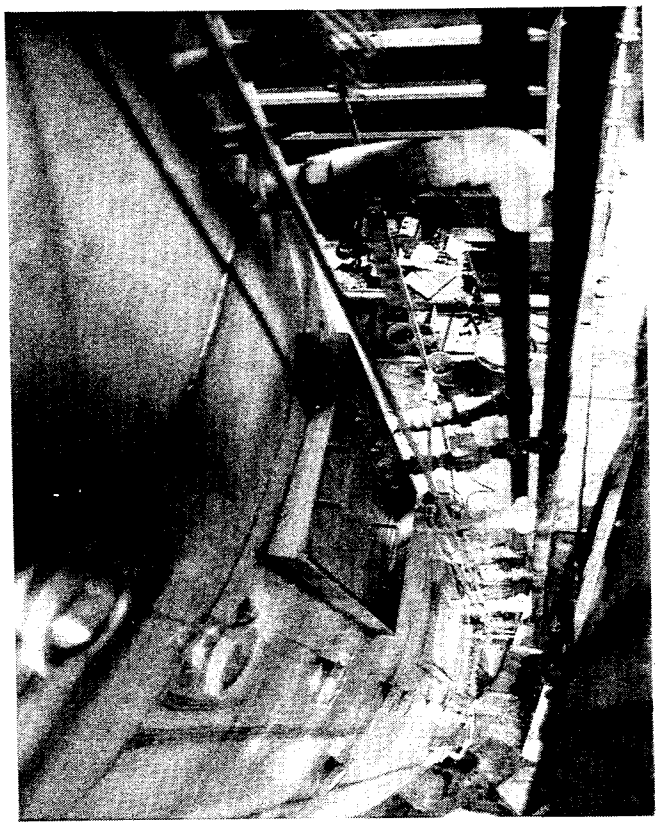

Figure 5 A Vertical View Down from the 24,000 L Pilot Scale CSRS

CELLS ON FOAM AND FIBER

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Abstract

Cells grow on high area foam and when a screen is put around the foam, it is made heavier so it can be fluidized. When foam is rotated in a half full RBC, drops are formed and mass transfer of oxygen to drops is much faster. Most fungi and some mammalian cells need oxygen. Corrugated fibers with holes in the valleys also produce drops. White rot fungus needs oxygen and it degrades many chlorine compounds, azo dyes, and TNT. Old cardboard boxes are readily available and when buried in soil, oxygen is entrapped. In a lake, the boxes expose high area.

Fibers have high surface area for immobilizing cells and when the fibers are rotated, fast reactions occur,converting one chemical to another. Sugar has been fermented to alcohol in 10-15 minutes. Ethanol has high octane and does not need lead. Old cars and trucks still use lead and high levels have been found in the drinking water of several large cities. Bacteria on fibers can remove lead in a few seconds. When an RBC of plain fiber discs is rotated and a light shone in the top the light hits a thin moving film to degrade chlorine compounds. Microbes and light remove sulfur from oil. Calcium magnesium acetate is a non corrosive road deicer. Salt on roads causes millions of dollars damage to bridges and cars. An inexpensive reactor has been made for optimization studies of mammalian and plant cells. A magnet is near the bottom but not touching and oxygen is put in the top where there is no seal that can leak.

INTRODUCTION

In a recent article (1) Kargi removed COD and nitrogen from wastewater with wire mesh sponge, in a fluidized bed bioreactor.This design is covered in Clyde patent (2). Wire mesh sponge can also be used in a half full RBC where drops are formed. Mass transfer of oxygen to drops is much faster than to a flat surface.(3). Macaskie (44) removes uranium with sponge.

Two designs have been developed for rotating cells on fibers.These designs have many applications for environmental and energy purposes. They can assist in degrading toxic metals, such as lead in drinking water, mercury, and cyanide. They can degrade jet fuel, chlorinated compounds, and TNT in soil. Cells on fibers can be used to degrade toxic azo dyes, and they can assist in removing sulfur from oil and burning coal. In addition to eliminating or reducing toxins, cells on fibers can also help create products and procedures that are better for the environment and save energy. They can ferment sugar to alcohol for the production of gasohol, a lesser pollutant than current automobile fuel. Fibers have high surface area but to produce even more, Celite® can be entrapped. Photos of Celite® in fiber and yeast growing on the Celite® are shown by Clyde(4) Cells on rotating discs can help make lactic acid , which is used to make biodegradable polymers for the manufacture of fast food cups. They can make calcium magnesium acetate (CMA), a non-corrosive road de-icer. For applications where a gas is evolved, as in sugar to alcohol, a horizontal unit is used for easy exit of the gas, but when the gas is evolved and then reacted, as in CMA, a vertical unit is better. Plain flat discs are used in the above applications.

In the second design, corrugated fibers with holes in the valleys are used so that oxygen can be added quickly to fungi and some mammalian cells. Polyurethane foam can also be cut to produce drops when rotated.

TOXIC METALS

Lead has been found in the drinking water of several large cities. Millions of people in 100 large cities are drinking water that is over the limit of 10 ppb. It has been found in parking lot runoff so it probably comes from old cars and trucks that use leaded gasoline. In my design of cells on rotating fibers, lead can be removed in a few seconds.

Tyvek® fiber is not expensive and it has small pores and many fibers. When the bacterium *Zymomonas mobilis* was immobilized on a piece of white Tyvek® fiber about two inches long, and dipped into a colored solution of lead and six valent chromium, the metals got on the fiber immediately, not only on the part immersed, but the color climbed right up the fiber and got on the fingers of the holder. It was not just the wicking effect, because a control showed nothing. In the control, the same procedure was used, including nutrients for Zymomonas, except no Zymomonas was used. In another experiment 21 ppb of lead was stirred for 3 seconds with 100 Tyvek® discs 45 mm in diameter and the 100 ml of lead was reduced to 3 ppb. This experiment was repeated two more times on the same discs with the same result. The popular

conception of bacteria is that they are poisonous, but Morais found that Zymomonas is therapeutic (21) . Several doctors in the Recife (Brazil) area treated their patients with intestinal disturbances and they showed great mending with disappearance of their symptoms.

Lead was analyzed with a Hitachi Z-8100 Polarized Zeeman automatic absorption spectrometer with a graphite furnace. Presence of the metals was confirmed with a spectrometer at Tulane University, and photos made. The Zymomonas was NRRL 14023 and the Tyvek ® 1085B. It took about 30 hours for the Zymomonas to grow on the fiber. Nutrients were 100 g/l glucose, 10 g/l yeast extract and 1 g/l of three salts, $(NH_4)_2SO_4$, $MgSO_4$ and KH_2PO_4. (4) . If the pH was below 6, half the amount of K_2HPO_4 was used because it has a higher pH. Instead of yeast extract, inexpensive corn steep liquor can be used.

A patent by Clyde-Whipple(7) covers removing metals with bacteria. Example 6 in this patent also mentions *Pseudomonas putida* and *cepacia*. Chapatwala (9) degrades cyanides with Ps.putida. Cadmium and trichloroethylene can be removed with these. Example 2 in the patent describes uranium and contamination from old fuel rods.

Steinberg (33) shows a photo of uranium and Zymomonas on fiber. Lovley (19) reduces uranium to an insoluble form with bacteria. Wang (37) reduces chromium in a similar manner. If the bacteria were put on fibers, the process could be run continuously. Macaskie (44) removes uranium with a bacterium. Faison(11) removes strontium with a bacterium. Gas meters are leaking mercury. *Pseudomonas putida* removes mercury (12) and degrades cyanides (39) also (9). These scientists did not immobilize on fibers, but we have tried so many organisms successfully that we believe the chances are good that other bacteria could be immobilized and the reaction run faster when the fibers are rotated.

ETHANOL

Ethanol is less pollluting than regular gasoline and the EPA has recently suggested we need more ethanol. High rates of mass transfer result when yeast is put on a single fiberglas disc at 90 rpm, say Bringi and Dale(45). We have found that 30 rpm works well too. With the bacterium Zymomonas, sugar can be fermented to ethanol in 15 minutes(38). Wayman rotated at 40 rpm. We have a 30 cm diameter reactor and we rotate at 22 rpm because the tip speed is greater in the larger diameter. A turbine agitator rotating at 200 rpm uses much more energy.We have found, when you don't rotate, you get a bubble here and there, about 2 per second, but when you rotate, the CO_2 which comes off sometimes blows the cotton right out of the vent.With polyester discs 9.5 cm in diameter, and rotated 40 rpm, Wayman got 96% yield starting with 50 g/l glucose and termed the results "remarkable". Using almost identical equipment except starting with 100 g/l glucose, we got an 80% yield in 10-15 minutes in two runs.Continuous runs have been made for up to two weeks, using the same residence times as in a batch run. . Nutrients were the same as those used to take lead out of wastewater. Several runs were also made in a smaller unit, 4.5 cm. in diameter.

Alcohol was determined by HPLC. Higher concentrations of glucose can be fermented and end product inhibition avoided by stripping off some alcohol and recycling the sugar as in Fig. 6 of a patent (8). Another method to eliminate end product inhibition is to extract the ethanol with a higher alcohol such as oleyl (15).Daugulis has a similar method (10).

E.coli also grows on fibers. The Zymomonas gene can be put into *E. coli* to ferment other sugars(14). The *E. coli* gene can also be put into Zymomonas (24).

SOIL AND SEDIMENT

Soil has been contaminated in many parts of the world by jet fuel. White rot fungus degrades this( ), as well as chlorinated compounds and TNT, but the fungus needs air to grow. A fast way of getting oxygen into cells is described in a recent patent (5). Corrugated fibers are rotated in a half full rotary biological contactor. Liquid is carried up into the vapor space and falls through holes in the valleys. Mass transfer of a gas to drops is much faster than to a flat surface (3). When a liquid is carried up into the vapor space with corrugated fiber or polyurethane foam, drops are formed. With a vertical reactor, oxygen is depleted after passing through the column but in a long horizontal reactor, oxygen can be added in the middle.When a small unit of corrugted fibers was rotated, it took three days to grow white rot fungus, but when holes were put in the valleys, it took a day and a half. The tube was 12 cm long and 4.5 cm in diameter. Holes in the valleys were about 3mm in diameter and rotation was 6 rpm. The horizontal tube was half full of nutrient. Formula for nutrient is described in the American-Type Culture Collection book.

Some people use pellets or microspheres but it's hard for oxygen to diffuse into the interior of a pellet. At a distance of less than 0.4 mm inside the pellet there was no oxygen says Reddy(25). When the corrugations are buried in contaminated soil, air is entrapped for further growth of the fungus. Sawdust was used in Brookhaven, Mississippi, but not very successfully, probably because there was not enough oxygen even though soil was tilled once a week.

Spiker (32) says that white rot fungus is sensitive to large amounts of TNT and needs a matrix to protect it. The fungus on the inside of the corrugations will protect it from the TNT.Instead of filling up landfills with old cardboard boxes, fungus could be coated on the weighted boxes and then lowered slowly (so as to not spread the contamination) into sediment in the bottom of a river. The Hudson River below Schenectady is heavily contaminated.

A reactor for immobilizing the fungus is shown in patent 5,256,570 Fig. 7. If there are problems with contamination from seals, it is rotated half way and then back in the opposite direction so as to not entangle flexible hoses for inlets and outlets. A laboratory corrugator has been made from an old washing machine wringer, so other fibers can be corrugated. Scale up will be easy because companies that make cardboard boxes have machines 87 inches wide and paper is fed in at 600 feet per minute.

LACTIC ACID

Landfills are also full of fast food cups. Lactic acid polymers are biodegradable. Iyer (16) makes lactic acid with a fungus on plastic discs, but fibers have more area and corrugated fibers supply oxygen faster. Tsai (36) makes lactic acid from potato waste. Fermentation is better than chemical synthesis because the biologically active L-form is produced.We feel confident that if these systems were used with rotating fibers, it would be an improvement.

CITRIC ACID

When rotating discs are used with a fungus, there is less energy and no foaming, says Imai(13), and the limiting step is oxygen transfer. In an air lift reactor, it takes energy to compress the air and bursting bubbles damage shear sensitive cells.A yeast can also be used says Sims (31) and productivity is increased sharply with an increase in dissolved oxygen.

AZO DYES

In a recent article, Suominen (34) degrades toxic azo dyes and nine other dyes with white rot fungus on nylon. These dyes are released into the water supply by the textile industry and require energy to remove them by conventional means.Many people in this area (including this author) drink only distilled water but this is a very energy intensive process.

CALCIUM MAGNESIUM ACETATE

Salt on roads causes millions of dollars damage to bridges and cars. People on low salt diets are effected, because the salt gets into drinking water and damages crops. . In the future, when electronic devices are implanted in roads, salt will corrode them. CMA is a non-corrosive deicer which can be made with cells on rotating fibers says Ljungdahl(18). For this application Ljungdahl used a vertical unit because he wanted to save the carbon dioxide. They used Reemay polyester discs 48 mm in diameter separated by teflon washers 0.8 mm thick and rotated at 80 rpm. A Figure is shown on page 412 of the book, and on page 365 he says "the basic idea is that of Clyde". Their conclusion was very positive. Raw material was hydrolyzed corn starch, and they stated that the process could be more economical if corn steep liquor were used instead of yeast extract. In a recent talk by Shah(29) this is done and satisfactory results obtained. Cells on cotton also make CMA from cheese whey says Yang(40). If Tyvek and Celite® were used, the reaction would probably be faster.

Cells on rotating fibers is covered in a patent by Clyde(8). Another one (2) describes cells on polyurethane foam, cut so drops are formed. When a screen is put around foam, it is made heavier so it can be fluidized.

COAL AND OIL

Spraying CMA into burning coal removes most of the sulfur. Sulfur in oil is removed by microbes. These operations could be carried out using cells on rotating fibers. Polycyclic aromatic hydrocarbons (PAHs) are degraded by fungi in a manufactured gas plant (46). There are over 1500 of these in the United States. We have developed a way to dramatically increase the surface area of cardboard boxes so more cells can be immobilized.

PHOTO REACTOR

When an RBC is run half full and a light shone in the top, the light hits a thin moving film as in a patent (6). In other photo reactors, colored solution blocks the light. Titania can also be entrapped in the fibers to promote a faster reaction. Light has been found to degrade some chlorinated compounds, including dioxin, says Sawyer (28).
The RBC can be run outside, saving energy by using the sun.

OTHER APPLICATIONS - MAMMALIAN, PLANT CELLS, AND TAXOL

It takes a lot of energy to compress air and bubble it up from the bottom of a tall vertical reactor and bursting bubbles cause foam and damage to shear sensitive cells. To avoid damage to the cells, air can be put up the middle and the oxygenated water overflowed and put down the side to contact cells on fibers, but in this method, oxygen becomes depleted as it reaches the bottom.
In our design oxygen can be put in one end and also the middle of the horizontal reactor. Mitsuda (43) makes t-PA faster with cells on rotating fibers.

Scientists at Tufts University have found that polyester fibers are "much less costly and provide a much higher surface/volume ratio than current matrices." (23),. They (and also a well known company in New Jersey) put nutrient down through small discs in a zig zag fashion, but we have found that when larger discs are rotated, nutrient makes a large circle before dropping through holes to the next lower disc. Rubeai (27) has found that rotation removes cell debris. In our design, there is a magnet near (but not touching) the bottom and oxygen is put in the top where there is no seal that can leak. The raw material for a small unit cost only $10. Larger units have been made also.

Kompala (17) puts bone marrow cells on fiberglass and gets a glucose consumption rate more than 250-fold relative to monolayer. Yarmush (41) finds that a critical design factor in liver cells is to deliver enough oxygen. The December '94 issue of In Vitro, Animal, has several articles on hepatocytes, also a recent meeting of In Vitro in Denver. Taxol for cancer can be made from a fungus; fungi need air which can be supplied from corrugations. Professor Demain at MIT states that a problem might be to supply enough oxygen for the fungus. Yoo (42)emphasizes the importance of low stress and high oxygen for hairy roots. Langer (30) has developed a biodegradable fiber so organ cells can be grown on it and implanted in the body. Lin grows hepatocytes on sponge (34).

DISCUSSION AND CONCLUSION

Bench scale tests look very promising and scale up tests would appear to be justified. In fermenting sugar to alcohol, Wayman used a condensor on top but we didn't so we probably lost some alcohol. According to the literature, this is supposed to be an exothermic reaction, but we had to supply heat to the water bath with two fish tank heaters. This could be because the carbon dioxide came off so fast it carried some water with it. Evaporation is a cooling process. We also have a 20 cm diameter reactor which we run at about 23 rpm because the tip speed is faster. We also plan to try Tyvek [R] fiber with Celite [R] entrapped and feel quite confident that the fermentation will be faster. Inexpensive cheese whey has been fermented with *Kluyveromyces fragilis*. For toxic metals we plan to investigate the effect of other metals at different pH values. In soil degradation, we have made a box about 2/3 of a meter on a side and will check to see if soil venting is effective with the corrugated fibers, and to see how far the fungus will travel in search of food, in different types of soil.

REFERENCES

1. Kargi, F. and Eyiisleyen.S. Batch biological treatment of synthetic wastewater in a fluidized bed containing wire mesh sponge particles. Enz.Micro.Tech. 17,119-123,"95.
2. US Patent, Clyde, 4,333,893.
3. Perry's Chem. Eng. Handbook 6th ed. 18-41.
4. Clyde, R.,1991, Methanol dissociation and cells on fibres for ethanol production and pollution control. Fuel Magazine vol. 70 page 1225-6.
5. Clyde, R.,1993, US Patent 5,256,570.
6. Clyde, R.,1984, US Patent 4,446,236.
7. Clyde and Whipple, 1985,US Patent 4,530,763.
8. Clyde, R. 1983. US Patent 4,407,954.
9. Chapatwala,K,et.al. Screening of encapsulated microbial cells for the degradation of inorganic cyanides,J.Ind.Micro. 11,69-72,1993.
10. Daugulis,A. et al. 1991,Extractive Fermentation by *Zymomonas mobilis* and the Control of Oscillatory Behavior, Biot.Letters, 13,291-296.
11. Faison, B. et. al.,1990, Binding of Dissolved Strontium by *Micrococcus luteus*. App. Env. Micro. pg.3649-3656.
12. Horn, J. 1992, Development of Bacterial Strains for the Detoxification of Mercury-Containing Pollutants. Talk 131, GEOC section, ACS meeting, San Francisco.
13. Imai,H. 1992, Effect of Operational Conditions on the Rate of Citric Acid Production by Rotating Disk Contactor Using *Aspergillus niger*, J. Ferm.and Bioeng. 73,251-254
14. Ingram, L. US Patent 5,000,000 ,1991,also Genetic Improvement of *E. coli* for Ethanol Production; Chromosomal Integration of *Zymomonas mobilis* Genes Encoding Pyruvate Decarboxylase and Alcohol Dehyrogenase II. App. & Env. Micro 893-900
15. Ishii,S. et al.1985, Monitoring and Control for Extractive Fermentation of *Clostridium acetobutylicum*. , J. Ferm.Tech. 63,181-187.

16. Iyer, C. 1992, Immobilized whole cell Reactor for Fermentation of Glucose into Lactic Acid. Talk 100, Biot. Section, ACS meeting, SanFrancisco.
17. Kompala,D. et al. 1993, A Three Dimensional culture system for Murine Bone Marrow. Talk 134, BIOT section, ACS meeting, Denver.
18. Ljungdahl L. and Wiegel J.,1991, Ch. 16 in book, Calcium Magnesium Acetate, Elsevier, ed. D. Wise
19. Lovley, D. et.al. 1993, Reduction of uranium by Cytochrome c3 of *Desulfovibrio vulgaris*. App Env. Micro. 59,3572-3576c.
20. Macaskie,L. 1990, An Immobilized Cell Bioprocess for the Removal of Heavy Metals from Aqueous Flows. J. Chem. Tech.Biotech. 49,357-379. See also Science 257,782-784 (1992)
21. Morais, J.,et. al.1993, *Zymomonas mobilis* research in the Pernambuco Federal University, J. of Biot.,31,75-91
22. Perry's Chemical Engineers Handbook, 1984, 6th ed., 18-38
23. Petti,S. et al. 1992, Nonwoven polyester fabric as a matrix for three dimensional mammalian cell growth. Talk 151c, AIChE meeting, Miami,also Biot.Progress,10,548-550.
24. Picataggio,S. et.al. Metabolic Engineering of a Pentose Metabolism Pathway in Ethanologenic Zymomonas mobilis.
Science 267,240.1995.
25. Reddy,C.et al. 1992, Determination of the Respiration Kinetics for Mycelial Pellets of *Phanerochaete chrysosporium* ,App.Env. Micro. 1740-1745
26. Reddy,C. and Yadav.J. 1993,Degradation of Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX)by the Lignin-Degrading Basidiomycete *Phanerochaete chrysosporium*. App. Env. Micro. 756-762
27. Rubeai,M. 1993, Use of a spin filter can reduce disruption of hybridoma cells in a bioreactor. Biot.Tech. 7,351-356.
28. Sawyer,C. 1983, Talk presented at ACS meeting, Washington D.C. Environmental Health, Safety, and Legal Considerations for the Successful Excavation of a Dioxin-Contaminated Hazardous Waste Site.
29. Shah, M. et. al.,1993, Optimization & Scale-up of CMA Production by Fermentation,AIChE meeting, St. Louis talk 116g
30. Langer, R. Chem. Eng. News, Nov.22, '93 pg. 4.
31. Sims,K. 1994,Oxygen Uptake and Citric Acid Production by *Candida lipolytica* Y 1095. Biot. and Bioeng. 43,131-137
32. Spiker,J. et al. (1992) et al. Influence of 2,4,6-Trinitrotoluene (TNT) Concentration on the Degradation of TNT in Explosive-Contaminated soils by the White Rot Fungus *Phanerochaete chrysosporium*. App.Env. Micro 3199-3202
33. Steinberg, S. 1983, In a Ferment, Science News, 124,234-235.
34. Lin,K. et.al. Long term maintenance of liver-specific functions in three-dimensional culture of adult rat hepatocytes with a porous gelatin sponge support. Biotech.Appl. Biochem.21,19-27.1995.
35. Suominen,I. et al. 1993, Decolorization of Azo,Triphenyl methane,Heterocyclic, and polymeric dyes by Lignin Peroxidase Isoenzymes from *Phanerochaete chrysosporium*. App. Env. Micro. 59,4010-4016.

36. Tsai,S. et.al. 1992, Strain Screening and Development for Industrial Lactic Acid Fermentation. Paper 16, Gatlinburg conf.
37. Wang,Y. and Shen,H. (1993) Characterization of Emzymatic Reduction of Hexavalent chromium by *Escherichia coli* ATCC 33456. App. Env. Micro. 59,3771-3777
38. Wayman, M. et. al.,1989, Ethanolic Fermentation of Wood-derived Cellulose Hydrolysates by *Zymomonas mobilis* in a Continuous Dynamic Immobilized Biocatalyst Bioreactor, Process Bioch. June 88-91
39. Wolfram, 1993, Screening of encapsulated microbial cells for the degradation of inorganic cyanides. J.Ind.Micro.11,69-72.
40. Yang, S.,1991, Biomass based Calcium Magnesium Acetate May Prove Economical and Harmless Road Deicer. Biopr. Tech. Mar, pg. 6-7
41. Yarmush M. et al. 1993, Oxygen Uptake Rate of Hepatocytes;Importance in Bioartificial Liver Design. AIChE meeting, St. Louis, talk 121b.
42. Yoo,Y. et al. 1993, Development of a Bioreactor for High Density Culture of Hairy Roots. Biotech. Techniques 7,859-862.
43. Mitsuda,S. et.al. Non Woven Fabrics as New Cell Matrices for IMR-90 Human Embryonic Lung Diploid Fibroblast Cells. J.Ferm.and Bioeng. 70,289-291.1990
44. Macaskie, L. et.al. Enzymatically-Mediated Uranium Accumulation and Uranium Recovery using a Citrobacter sp. Immobolized as a Biofilm Within a Plug-Flow Reactor. J.Chem.Tech.Biot.63,1-16,1995.
45. Bringi,V. and Dale,B. Experimental and Theoretical Evidence for Convective Nutrient Transport in an Immobilized Cell Support. Biot.Progress 6,205-209,1990.
46. Cerniglia, C. et.al. Enantiomeric Composition of the transDihydrodiols Produced from Phenanthrene by Fungi. App. Env.Micro.59, 2145-2149, '93

CONTINUOUS ETHANOL PRODUCTION IN BIOFILM REACTORS CONTAINING PLASTIC COMPOSITE RINGS AND DISCS

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Abstract

Biofilms are natural forms of cell immobilization in which microorganisms attach to solid supports. At ISU we have developed plastic composite-supports (50% agricultural material, and 50% ploypropylene) which stimulate biofilm formation and which can supply micronutrients to the attached microorganism. These plastic supports are produced by twin-screw high temperature extrusion producing ring or discs. For continuous ethanol fermentations with *Saccharomyces cerevisiae* (ATCC 24859), each packed-bed bioreactors (50 ml) contained plastic composite-rings and -discs, or polypropylene rings (control) with support surface areas of 160 cm^2, and operated at 30°C. For polypropylene rings, cell-washout occurred at dilution rates of 1.9 h^{-1} in 0.6% yeast extract medium, and at 0.48 h^{-1} in $\geq$0.4 % ammonium sulfate medium. With plastic composite-support bioreactors, however, *S. cerevisiae* at a dilution rate of 1.92 h^{-1} produced 50 g/l/h with 100% expected theoretical conversions of glucose to ethanol. Also, repeated batch fermentations were performed for 11 different composite-supports in medium with varying concentration of yeast extract to 0% nitrogen. *S. cerevisiae* demonstrated no significant reduction in ethanol production even in 0% nitrogen medium with plastic composite-supports whereas with polypropylene supports, ethanol production was reduced significantly. The plastic composite-support blend selected for best performance contained 40% ground soybean hulls, 5% soybean flour, 5% yeast extract, mineral salts, and 50% polypropylene. Therefore, increased productivity in low cost medium can be achieved beyond conventional fermentations by using this novel bioreactor design.

Introduction

Ethanol, methanol, and ETBE (ethyl tertiary-butyl ether) are blended with gasoline as fuel extenders, and as octane enhancers. Ethanol is produced commercially by microbial batch or continuous fermentation, and recovered by distillation. However, it is necessary to increase productivity and ethanol concentration in the fermentation medium in order to decrease ethanol production costs, which were $1.25 per gallon in 1992 (Hohmann and Rendleman, 1993). Fermentation medium costs represent 70% of the final ethanol costs (Maiorella, 1984).

Some fermentation techniques have been developed to improve ethanol fermentation to decrease cost. End-product inhibition can be overcome by employing a vacuum fermentor which removes ethanol continuously from the fermentation medium. (Cysewski, and Wilke, 1977). Another method for continuous removal of ethanol from fermentation medium is extractive fermentation which utilizes suitable solvent and/or membrane (Christen et al., 1990). Other commonly studied fermentor types focus to increase biomass concentration in the fermentor which also increases productivity, and ethanol concentration. Cell recycle (Tin et al., 1993), hollow fiber membrane fermentors (Cheryan, and Mehaia, 1984), and cell immobilization (Nguyen, 1992) are continuously being improved. However, these systems have found little application commercially, because of mass transfer limitation, and other limitations in long term fermentations.

Biofilms are a natural form of cell immobilization that results from microbial attachment to solid supports (Characklis, and Marshall, 1990). Biofilms have been used in waste water treatments (Kurt et al. 1987), production of vinegar by the "quick vinegar process", mineral ore treatment (Crueger, and Crueger), and lactic acid production (Demirci et al., 1993). In this paper, ethanol fermentation by *S. cerevisiae* in biofilm reactors containing plastic composite-supports is described in the medium with varying nitrogen concentration. Continuous and repeated batch ethanol fermentation with plastic composite-supports stimulated biofilm formation, provided essential nutrients to *Saccharomyces cerevisiae*, and significantly reduced the medium composition and cost.

Materials and Methods

Microorganism and Media

Saccharomyces cerevisiae (ATCC 24859) was maintained in a medium containing 2% (w/v) glucose, 0.6% yeast extract (Ardamine-Z, Champlain Industries, Inc., Clifton, NJ), 0.023% $CaCl_2 \bullet 2H_2O$, 0.4% $(NH_4)_2SO_4$, 0.1% $MgSO_4 \bullet 7H_2O$, 0.15% KH_2PO_4. All fermentations inoculum were prepared from 24-h static culture at 30°C. For culture-tube fermentation medium, ingredients were kept the same except glucose was 5%, and the concentration of yeast extract and/or ammonium sulfate were varied. For continuous fermentation, glucose concentration was 7.5% with varying concentration of nitrogen,

and medium was sterilized in a B.B. Braun fermentor U-50 (Allentown, PA) with constant agitation (220 rpm) at 121°C for 20 min. A KH_2PO_4 solution was autoclaved separately then added to the medium aseptically for all culture medium. Sixty-liter of sterile medium was aseptically transferred into sterile carboy.

Support Materials

Various plastic composite-rings and -discs were produced from blends of 50% (w/w) agricultural materials and 50% polypropylene (Table 1). The plastic composite-supports were prepared by high-temperature extrusion in a Brabender PL2000 co-rotating twin-screw extruder (Model CTSE-V, C. W. Brabender Instruments, Inc., South Hackensack, N.J) through a tubing assembly onto a metal rod, collected as 10-15 cm length then removed from the rod and air cooled. The barrel temperatures were 200, 220 and 200°C, the die temperature was set at 165°C, and the screw speed was 11 rpm. The agricultural products used were 20-mesh soybean hulls (Cargill Soy processing Plant, Iowa Falls, IA), soybean flour (Archer Daniel Midland Co., Decatur, IL), yeast extract (Ardamine-Z, Champlain Industries, Inc., Clifton, NJ), and bovine globulin, bovine albumin, and dried red blood cells (American Meat Protein Corporation, Inc., Ames, IA). Soybean hulls and soybean flour were vacuum dried for 48 h at 110°C. Polypropylene pellets (Quantum USI Division, Columbus, OH), specific agricultural blends and salts (0.46 g of $CaCl_2 \bullet 2H_2O$, 8 g of $(NH_4)_2SO_4$, 2 g of $MgSO_4 \bullet 7H_2O$ per kg of mixture) were mixed in a container by shaking and then added to the extruder hopper. The melted polypropylene was uniformly mixed with agricultural product by the co-rotating movement of the twin-screws and extruded through a large pipe die with 9.5 mm ID, 12.7 mm OD for rings or with 3.2 mm ID, 12.7 mm OD for discs, and then cut into approximately 3 mm slices. Polypropylene-alone rings were cut manually out of a sheet of polypropylene by using cork bores, 7 mm ID, 11 mm OD.

Repeated Batch Fermentation

The selected plastic composite-discs (bulk density : 0.19 g/ml), or polypropylene rings (bulk density : 0.2 g/cm^3) with a total surface area of 60 cm^2 were placed in 25x150 mm screw-cap culture tubes, and autoclaved dry for 30 min. After cooling, 10 ml of sterile medium was added to each tube. The tubes were stored at 30°C for 24 hr, then aseptically decanted to remove excessive particles. After adding 10 ml of fresh medium, the tubes were inoculated with 0.1 ml of a 24-hr suspension culture of *S. cerevisiae*. Every other day, the fermentation culture medium was aseptically decanted and 10 ml of fresh sterile medium was added for seven transfers. These repeated batch fermentations were performed in duplicate including suspension-culture fermentation with no support. At the end of seven transfer, medium nitrogen composition was decreased to 0.3, 0.1, and 0.05% yeast extract, then all yeast extract was removed (0.4% ammonium sulfate medium) and finally all ammonium sulfate was removed (0% N medium). The spent culture medium from each transfer was analyzed for change in absorbance (620 nm), ethanol and glucose concentration. After the 7 transfers were completed for 0.4% ammonium sulfate medium, four discs were aseptically removed from each culture-tube for biofilm determination. The repeated batch fermentation

continued by adding 7.8 ml of 0% N medium. Upon completion of 7 transfers in 0% N medium, four discs were removed and analyzed for biofilm.

Analysis of Biofilm

The four discs removed from each culture-tube were washed in 100 ml of sterile 0.1% peptone by turning the bottle upside down ten times, then transferred into 25x150 mm screw-cap tube containing 5 g of sterile sand and 9 ml of sterile 0.1% peptone. After vortexing the tube three times for 30 seconds, the sample was serially diluted and, 10^{-2} to 10^{-6} dilutions were spread plated onto potato dextrose agar plates. After incubating at 30°C for 48 hours, colony-forming units were counted.

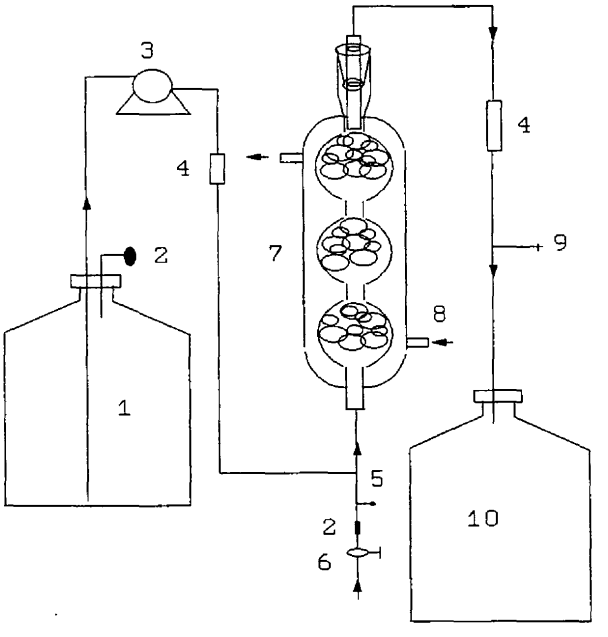
Table 1. Composition of plastic composite-rings and -discs.

PC[a]	SH (%)	Minor Ag. Material(s)	Salt	Weight[b] (g)	Abs. V[b]. (cm^3)
SH-SF	40%	10% Soybean Flour	-	3.422	5.5
SH-SF-S	40%	10% Soybean Flour	+	4.242	6
SH-YE	40%	10% Yeast Extract	-	2.910	5
SH-YE-S	40%	10% Yeast Extract	+	3.743	5
SH-SF-YE	40%	5% Soybean Flour 5% Yeast Extract	-	3.784	5
SH-SF-YE-S	40%	5% Soybean Flour-5% Yeast Extract	+	4.107	4
30%SH-SF-YE-S	30%	10% Soybean Flour-10% Yeast Extract	+	2.960	5
30%SH-YE-RBC-S	30%	10% S. Flour-10% Red Blood Cell	+	3.450	5
SH-SF-BG	40%	5% Soybean Flour-5% Bovine Globulin	-	4.080	6
SH-YE-BG	40%	5% Yeast Extract-5% Bovine Globulin	-	3.607	6
SH-SF-BA	40%	5% Soybean Flour-5% Bovine Albumin	-	4.084	6
SH-YE-BA	40%	5% Yeast Extract-5% Bovine Albumin	-	3.667	5.5
SH-RBC	40%	10% R. Blood Cells	-	4.040	6.5

[a] Fifty percent of plastic composite consisted of polypropylene (w/w)
[b] Nineteen PC-discs were used for weight and absolute volume (Abs. V.)

Continuous Ethanol Fermentation

With select plastic composite-supports, continuous ethanol production was performed in a custom-made semi packed reactor. The reactor consisted of 400 mm long cylindrical-bulb condenser with three bulbs (Figure 1). Each bulb was packed with a mixture of equal number of selected discs and rings or ploypropylene-alone rings to give a total surface area of 160 cm^2, and bulk volume of 60 ml. The reactor was aerated with sterile air, and had a working volume of 50 ml. Liquid breaks were placed in both medium feed and exit lines to prevent contamination. A rubber septum was placed in the air line for bioreactor inoculation. Feeding medium and air entered the reactor from the bottom, and exited from the top. Dilution rates varied from 0.48 to 6.4 h^{-1}. Reactor was operated at each dilution rate until steady state was achieved. Samples were taken daily and analyzed for changes in cell density, ethanol and glucose concentration. Culture purity was frequently monitored microscopically to ensure bioreactor purity.



1. Feed reservoir
2. Air filter
3. Pump
4. Liquid break
5. Inoculation septum
6. Manifold
7. Bioreactor 8. Water in
9. Sampling port
10. Effluent collector.

Figure 1. Schematic diagram of biofilm reactor.

Analysis of culture broth

The suspended cell density in the reactors was measured by absorbance at 620 nm by using a Bausch and Lomb Spectronic 20 spectrophotometer (Milton Roy, Rochester, NY). Glucose and ethanol concentrations were measured by using a Waters High Pressure Liquid Chromatograph (Millipore Corporation, Milford, MA) equipped with a Waters Model 401 refractive index detector, column heater, autosampler and computer controller. The separation of ethanol, glucose and other broth ingredients were done on

a Bio-Rad Aminex HPX-8711 column (300 x 7.8 mm) (Bio-Rad Chemical Division, Richmond, CA) using 0.012 N Sulfuric acid as a mobile phase at a flow rate of 0.8 ml/min with a 20 μl injection volume and a 65°C column temperature.

Results and Discussion

Continuous Ethanol Fermentation with Rich Medium

Plastic composite-supports (PC-supports) of soybean hull, and soybean flour (20% soybean hulls, 5% soybean flour, and 75% polypropylene) were used in continuous ethanol fermentation as suggested by Kunduru, M.R. (1995). However, rings and discs supports were employed instead of chips, and higher total agricultural material-composition (40% soybean hulls, 10% soybean flour, and 50% polypropylene) was used. Increase in agricultural material could help biofilm formation on the PC-supports. In Kunduru's initial study (1995) with chips, reactors slowly plugged with growing and flocculating *S. cerevisiae* cells. Therefore, to avoid reactor plugging the support shape was changed to rings and discs, and dilution rates 0.48, 0.96, 1.92, 3.84, and 7.68 h^{-1} were employed. Reactors containing PC-supports of SH-SF constantly produced more ethanol especially at dilution rates of ≥ 0.96 h^{-1} than other PC-supports (Figure 2). Also, PC-supports of SH-SF reactors produced 26, 8.6, and 4.8 g/l ethanol, whereas the polypropylene-alone reactor produced no ethanol at dilution rates of ≥ 1.92 h^{-1}, with 3.2 g/l ethanol on day 26 at 3.84 h^{-1}. This sudden spike in ethanol production in control might be the result of cell deposition in fermentor lines and junctions. Ethanol yields at the dilution rates of 0.48, 0.96, and 1.92 h^{-1} were about 50%, with a decrease to about 30% at higher dilution rates. The highest productivities for PC-supports of SH-SF and polypropylene-alone were 50.2 and 20.8 g/l/h at the dilution rates 1.92 h^{-1}, and 0.96 h^{-1}, respectively. To reduce the level of *S. cerevisiae* flocculation each reactor started as a batch culture for 24 hr, than changed to continuous fermentation at a higher dilution rate (1.92 h^{-1}) than previously used. The benefit of yeast extract addition to PC-supports SH-YE, SH-YE-S, SH-SF-YE, and SH-SF-YE-S (Table 1) were evaluated. All four PC-support bioreactors produced 4 to 6 g/l ethanol at the dilution rate of 1.92 h^{-1} (Figure 3). At a slower dilution rate of 0.96 h^{-1} bioreactors with PC-supports of SH-SF-YE, SH-SF-YE-S, and SH-YE-S produced 24 to 27 g/l ethanol. At a dilution rate of 0.96 h^{-1}, reactor with PC-supports of SH-YE-S, and SH-YE demonstrated a significant reduction in ethanol production to 12 to 22 g/l, and 10 to 12 g/l, respectively. These findings suggested that PC-supports with both soybean flour, and yeast extract and mineral salts addition were beneficial to *S. cerevisiae*.

Repeated Batch Fermentation

In repeated batch fermentations, all the PC-supports, polypropylene-alone, and suspension culture in 0.6, 0.3, 0.1, 0.05% yeast extract media demonstrated no differences, consuming all the glucose (50 g/l), and producing 25 g/l ethanol. However, in 0.4% $(NH_4)_2SO_4$ medium and in 0% N medium, ethanol production decreased to 5 to 0 g/l, respectively, in polypropylene-alone culture tubes. Whereas, all culture tubes

containing PC-supports produced about 25 g/l ethanol. This nutritional benefit of PC-supports was attributed to the yeast extract, to biofilm formation on the supports. Furthermore, in 0.4% $(NH_4)_2SO_4$ medium, polypropylene-alone had $<10^5$ CFU/cm^2, whereas all PC-supports had $>10^6$ CFU/cm^2. This confirms biofilm formation on all supports. For 0% N medium, CFU/cm^2 was slightly less, but not significantly different for 0.4% $(NH_4)_2SO_4$ medium.

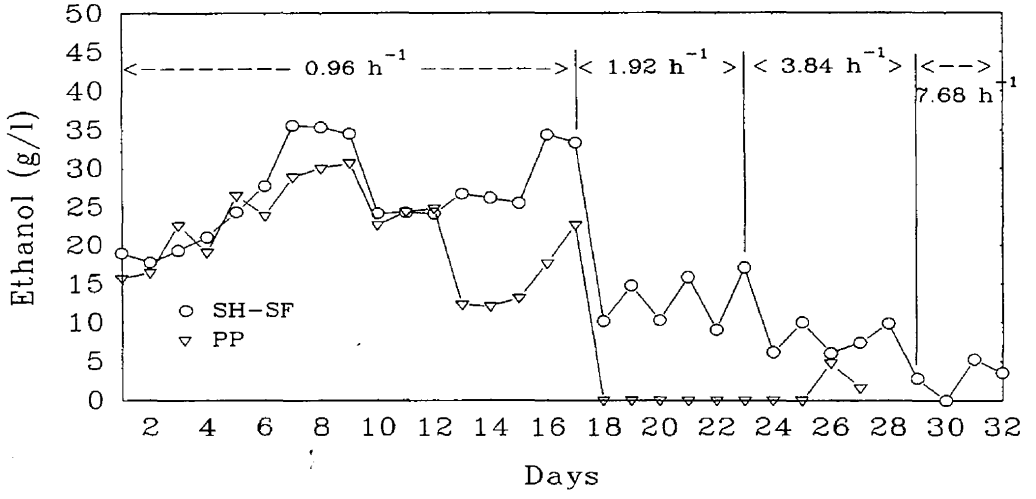


Figure 2. Continuous ethanol fermentation in 0.6% yeast extract medium at different dilution rates by using SH-SF supports, or ploypropylene-alone (pp). Each data point is average of two replicates.

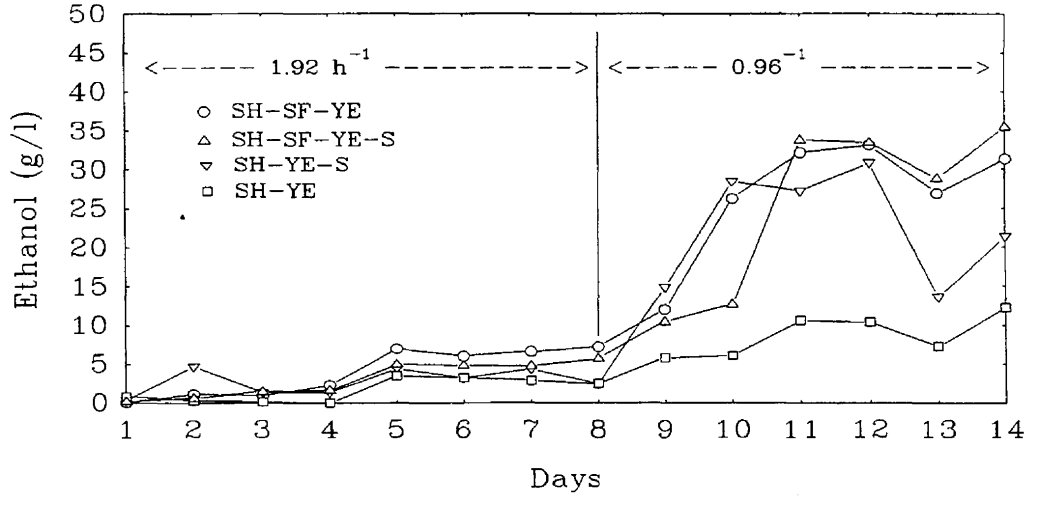


Figure 3. Continuous ethanol fermentation in 0.6% yeast extract medium at different dilution rates by using PC-supports of SH-YE, SH-YE-S, SH-SF-YE, or SH-SF-YE-S.

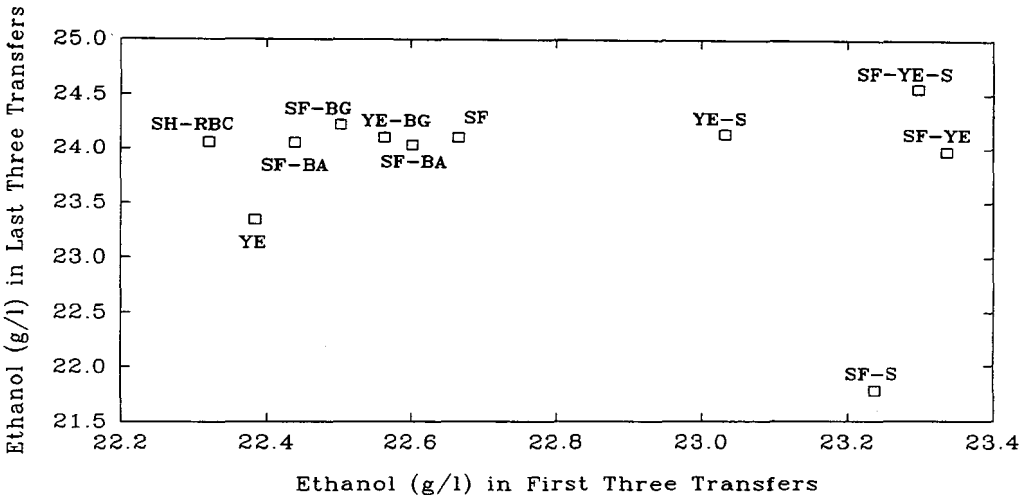


Figure 4. Comparison of each supports performance in repeated batch fermentations with 0% nitrogen medium. Each supports have 40% soybean hulls. Each data point is average of two replicates, and three transfers.

Selection of the best performing PC-supports was determined by plotting the average ethanol concentration of the first three repeated batch culture-tube transfers to the last three in 0% N medium (Figure 4). SH-SF-YE-S supports demonstrated the best performance by illustrating the highest ethanol productions for both cases. These results also suggested that a significant reduction in organic nutrients in the culture medium is possible for continuous ethanol production with these supports.

Continuous Ethanol Fermentation with Low or No Nitrogen Medium

In continuous ethanol fermentations, the effect of doubling the concentration of minor nutrient was evaluated by using PC-supports of SH-SF-YE-S, 30%SH-SF-YE-S, and 30%SH-YE-RBC-S (Table 1). For biofilm development, reactors were operated with 0.6% yeast extract medium. Visible biofilm was observed in 9 days for the reactors containing SH-SF-YE-S supports, and flocculation was observed in the polypropylene-alone reactors in the 7 to 9th days (Figure 5). However, no biofilm formation was observed for the reactors containing PC-supports of 30%SH-SF-YE-S, and 30%SH-YE-RBC-S in 15 days. Overall, the bioreactors with SH-SF-YE-S supports performed significantly better than supports with twofold more micronutrients by faster biofilm development, and by higher ethanol production in 0.6% yeast extract medium. In the 0% nitrogen medium all the supports performances were similar, again emphasizing no benefit from the twofold increase in micronutrients. The other difference between the 5 and 10% blended PC-supports was in the concentration of soybean hulls which was 40 and 30%, respectively. The results suggest that the higher soybean hull concentration benefitted ethanol production and biofilm formation and/or protected heat sensitive micronutrients during extrusion. When medium was changed to 0% N medium, in the

polypropylene-alone reactors *S. cerevisiae* washed out. Whereas, ethanol production was 3 g/l for SH-SF-YE-S, 2 g/l for 30%SH-SF-YE-S, and 1.5 g/l for 30%SH-YE-RBC-S at a dilution rate of 0.48 h^{-1}. When aeration was stopped, there was a slight change in bioreactors working volume due to the loss of air bubbles in the reactor which reduced the dilution rate. Overall, ethanol production was not changed with or without aeration. When medium was changed to 0.4% ammonium sulfate medium, there was no ethanol production for polypropylene-alone support reactor, whereas ethanol production was 9.1 for SH-SF-YE-S, 5.0 g/l for 30%SH-SF-YE-S, and 3.5 for g/l for 30%SH-YE-RBC-S at a dilution rate of 0.48 h^{-1}.

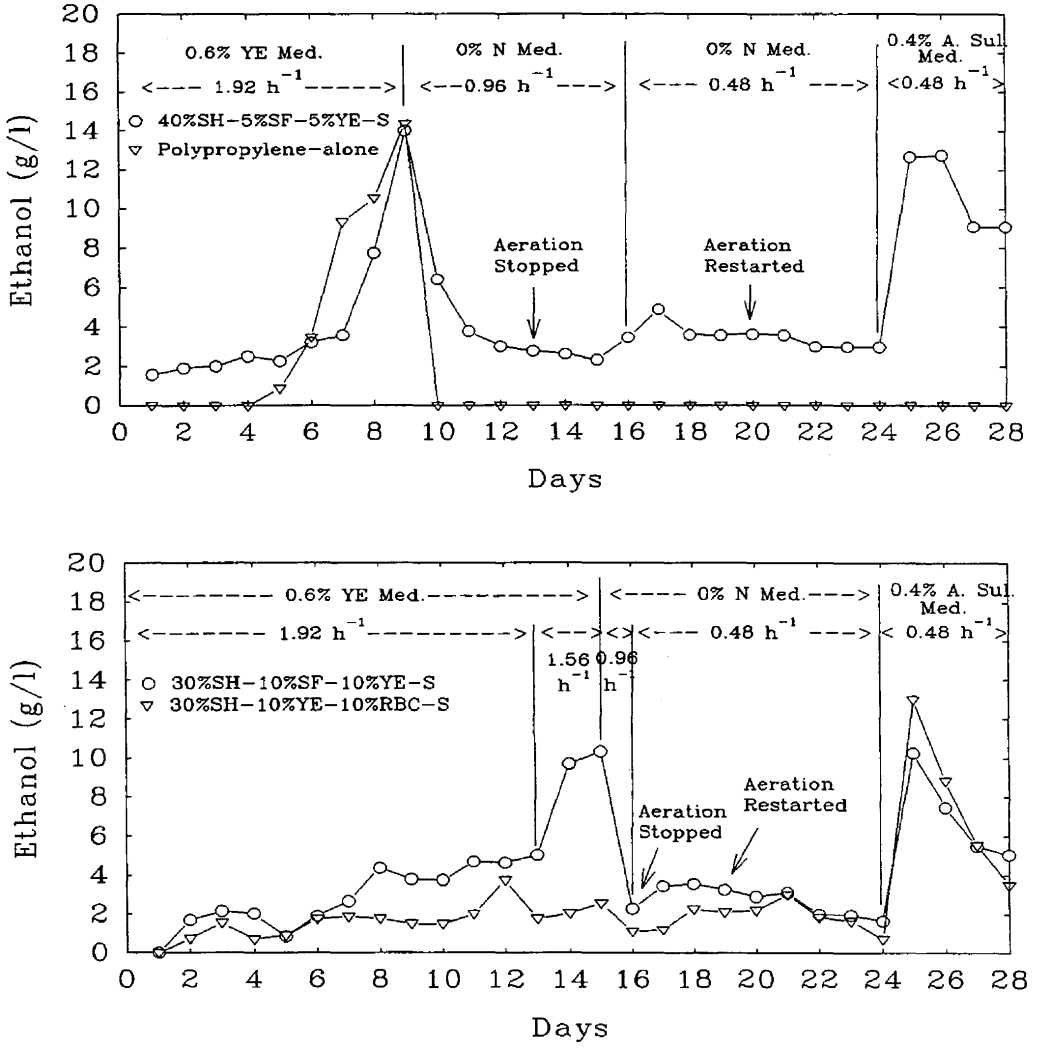


Figure 5. Continuous biofilm ethanol fermentation in various fermentation media with different plastic composite-supports. Each data point is average of two replicates.

Conclusion

Biofilm reactors containing plastic composite-rings and -discs potentially can benefit continuous ethanol production. Under conditions with limited organic nitrogen available, plastic composite-supports can act as a slow release material of an expensive micronutrient like yeast extract. The result is high productivities, and decreasing the medium cost.

Acknowledgements

This research was supported by the Council of Great Lakes Governors, by the Illinois Corn Promotion Board, by the Iowa Corn Promotion Board, and the ISU Center for Crops Utilization Research, and by the Iowa Agriculture and Home Economics Experiment Station. We also acknowledge Dr. John Strohl for technical assistance and the use of the ISU Fermentation Facility.

References

Characklis, W.G., and K.C. Marshall. 1990. Biofilms. John Willey and Sons, Inc. New York, NY.

Christen, P., M. Minier, and H. Renon. 1990. Ethanol extraction by supported liquid membrane fermentation. Biotech. Bioeng. 36:116-123.

Crueger, W., and C. Crueger. 1989. A textbook of industrial microbiology. Sinauer Associates, Inc., Sunderland, Mass.

Cysewski, G.R., and C.R. Wilke. 1977. Rapid ethanol fermentation using vacuum and cell recycle. Biotech. Bioeng. 19:1125-1143.

Demirci, A., A.L. Pometto III, K.E. Johnson. 1993. Lactic acid production in a mixed-culture biofilm reactor. Appl. Environ. Microbiol. 59:203-207.

Hohmann, N., and C.M. Rendleman. 1993. Emerging technologies in ethanol production. Agric. Inform. Bull. 663.

Kunduru, M.R. 1995. Development of a biofilm bioreactor for enhanced ethanol production. Dissertation. Iowa State University. Ames, IA.

Kurt, M., I.J. Dunn, and J.R. Bourne. 1987. Biological denitrification of drinking water using autotrophic organisms weigh hydrogen in a fluidized bed biofilm reactor. Biotechnol. Bioeng. 26:493-501.

Maiorella, B.L., H.W. Blanch, C.R. Wilke. 1984. Feed compound inhibition in ethanolic fermentation by *Saccharomyces cerevisiae*. Biotechnol. Bioeng. 26:1155-1166.

Nyguyen, V.T., and W.K. Shieh. 1992. Continuous ethanol fermentation using immobilized yeast in a fluidized bed reactor. Chem. Tech. Biotechnol. 55:339-346.

Tin, C.S.F., and A.J. Mawson. 1993. Ethanol production from whey in a membrane recycle bioreactor. Process Biochem. 28:217-221.

SUNSPUDS™: A NEW SUGAR CROP FOR PRODUCING ETHANOL FUEL

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Abstract

A new proprietary sugar crop called *Sunspuds*™ has been developed by JMCA, Inc. and is being grown and tested to provide a new commercial energy crop for ethanol production. The question of potential crop superiority has never been answered. Previous technical assessments have shown the crop is easy to grow using planting and harvesting practice with typical potato machine farming. As an ethanol feedstock, the sugar tubers can be broken down easily to solution for a value-added liquid product at the farm gate for export to existing typical refineries. The crop has additional product potential markets for sugar and food, and co-product as feed for cattle.

Sunspuds™ grow with little or no fertilization, irrigation, and pest damage. Study results indicate yields of ethanol twice that of corn at similar cost using simple preparation and fermentation processes adaptable to farm operations. Research continues on prototype scale to expand seedstock and establish developing country markets. Objectives of the energy crop development include establishing costs involved in production of ethanol utilizing various options of fermentation for expanded recovery.

JMCA, Inc. funding for the development research was provided through the Southeastern Regional Biomass Energy Program (SERBEP) which is administered by the Tennessee Valley Authority (TVA) for the U.S. Department of Energy (DOE); and by the Western Area Power Administration (WAPA) which administers the Western Regional Biomass Energy Program (WRBEP) for U.S. DOE.

Introduction

In recent years, efforts to produce ethanol from biomass have been initiated with scattered economic success. There are many anticipated benefits for providing new resources to make ethanol. If a superior crop can be developed, and if the cost of energy supply required for pretreatment and conversion of wine into vehicle grade ethanol can be reduced to a nominal sum, then production economics will be radically improved.

JMCA, Inc. is involved in renewable energy, and especially in biomass research leading to alcohol fuel use for power, transport, heating, lighting and cooking. JMCA has developed a viable energy crop alternative to starch and cellulose that can result in the economical operation of the small farm units and the small refining and processing operations. This new crop is a hybrid of the sunflower, researched and grown on a seed farm by JMCA, is called *Sunspuds*™. This sugar crop consists of tubers which are of a farinaceous nature, and can be planted and harvested with standard potato machinery. The tubers can be grown and marketed as ethanol feedstock with minor retrofit to farm and ethanol plant equipment. As an ethanol feedstock, the sugar tubers easily reduce to solution for fermentation, thus creating a potential value-added product at the farm gate for export to ethanol plants.
The resulting new crop (*Sunspuds*™) and new products (i.e., fructose and ethanol) can provide an adequate return on investment without subsidies or price supports.

The *Sunspuds*™ have characteristics more attractive for the production of ethanol. Agricultural planning/analysis and the planting and harvesting practices developed in Colorado will be applied in other regions. Tuber growth, and sugar levels are currently being monitored to determine maximum ethanol conversion potential.

The approach proposed by JMCA is a departure from cellulosic biomass projects which require the development and construction of new processing facilities and the development of a new set of farming practices and farming equipment, all of these in a very large scale. The development of *Sunspuds*™ as a sugar energy crop can be achieved on a smaller scale and provide economic ethanol fuel feedstock alternatives for standard farming and processing operations. Activities required for achieving commercial business agreements are currently being pursued. Licensing activities for contracting grower-farmers will focus on economic justification for adopting the *Sunspuds*™ crop to produce ethanol. Minimum alteration of agricultural potato practices and limited retrofit of existing ethanol plants will be emphasized.

The *Sunspuds*™ are being expanded to a scale required for pilot farms and commercial sales. JMCA plans for continuous availability of "seed" tubers beginning in the 1995-96 growing period. The objective is to continue propagation of the crop for supplying the potential market. In Fall 1995, JMCA will begin a market program by developing *Sunspuds*™ license agreements for grower-farmers to start crops for harvest and sale in 1996 (see Market Approach below). JMCA also plans to negotiate contract sales for sunspuds feedstock supply to ethanol plants. Negotiations with investor groups for the construction of new ethanol plant facilities dedicated to *Sunspuds*™ feedstock will be conducted.

Additional activities are focusing on the demonstration of optimum preparation and fermentation facilities to provide *Sunspuds*™ feedstock supply or fermented "broth" to ethanol plants and coproducts for evaluation by industries and commercial users. Fermentation system design will be flexible and will allow for data to be obtained by ethanol refiners so any alterations to existing product flow can be considered. Research has included farming practices which has lead to adaptation of the *Sunspuds*™ to typical planting, cultivating, and harvesting with conventional potato machinery. Replication plots were established for testing cultivation, irrigation, soil conditioning (fertilizer), and possible stalk harvesting for animal silage.

Discussion

Planting and Cultivating

Sample plants from each of the research plots, i.e., irrigated and fertilized, and non-irrigated and non-fertilized have been pulled for laboratory analysis. Depth of the tubers, number of tubers, radius of growth, and the ease of removal from the stalk were recorded and photographed. Average depth was 5-6 inches, average radius from the stalk was 30 inches and average number of tubers was 128. Tubers were generally not attached to the crown of the plant or to stringers. Tubers still attached to the stalk were easy to shake off. In the sandy loam soil, very little dirt remained on the tubers. Tuber growth was evaluated through the growing season to determine the differences between fall and spring harvesting and the timing for maximum harvest yield for fermentation and conversion to ethanol and for optimum ease of farming.

Using an average of 125 tubers and .0635 lb/tuber, an acre of 7176 plants (3 foot rows and 2 feet in-row) yielded 28.5 tons/acre, or from fermentation tests, 713.5 gallons of ethanol. From the samples taken, it appears that the tuber yield of about 40 plants is needed to seed an acre of *Sunspuds*™. Overall farm production results are shown in Table 1 and results of fermentation tests are shown in Table 2.

TABLE 1.

SUNSPUDS™ FARM PRODUCTION

PLANTING CONDITIONS:

Plot of 208 ft. x 208 ft. (one acre)
Planting 3 ft. rows, 2 ft. in row
Required 7,176 plants (69 x 104)

DATA:

Average Number of Tubers per Plant:
From first set of samples: 128 tubers per plant
From second set of samples: 122 tubers per plant
Average: **125 tubers per plant**

Average Weight per Tuber:
From first set of samples: 0.0675 lbs. per tuber
From second set of samples: 0.0595 lbs. per tuber
Average: **0.0635 lbs. per tuber**

YIELD OF *SUNSPUDS*™ PER ACRE:

From first set of samples: 31 tons per acre
(7,176 plants x 128 tub./plant x 0.0675 lbs./tub. = 62,000 lbs/acre)
From second set of samples: 26.1 tons per acre
(7,176 plants x 122 tub./plant x 0.0595 lbs./tub. = 52,090 lbs/acre)
Average from both sets of samples: **28.5 tons per acre**

A significant conclusion is that fertilized plants tend to grow taller stalks, but not necessarily larger tubers. This meant that with the 1994 crop planting, fertilizer was eliminated for extreme dry land conditions. Our continuing research focuses on plant development and yield as a dry land crop versus irrigation.

Converting the *Sunspuds*™ to Ethanol

Preparation

For fuel alcohol production, direct fermentation is required. *Sunspuds*™ sugar is inulin, with about 75% water content. Testing of the fall sample *Sunspuds*™ yielded a sugar content of about 21%. (Future testing of Spring samples, after storage over winter, may yield higher sugar concentrations.) The sugar concentration was measured as 21.0°B. The °B are Baume degrees. This unit is used in the sugar industry to measure the concentration of sugar solutions. This technique measures density of a solution as the equivalent density of a sucrose solution and reports the concentration of the equivalent sucrose solution.

The tubers are approximately 21% sugar and the solution was about 7% sugar. Fat, protein and ash were not measured. It is assumed that only carbohydrates and water are present. *Sunspuds*™ are a source of levulose for use in natural sweetening used by diabetics. The carbohydrates are mostly several polysaccharides, chiefly synanthrine, which when hydrolyzed by acids or enzymes produce the very sweet sugar of levulose, fructose or fruit sugar.

Thus, *Sunspuds*™ will not require starch or cellulosic pretreatment, such as prehydrolysis, acid or enzymatic hydrolysis, xylose fermentation or lignin processing. Typically, the cost of feedstock pretreatment is a factor which increases the overall production cost of ethanol. For example, most ethanol plants are designed to receive grain and especially corn with wet or dry milling plant equipment needed prior to fermentation.

Simplicity of preparation allows the Sunspud to be considered for on-farm processing to a beer, thus also reducing the cost of bulk transport and creating a general value-added product acceptable to most ethanol plants. As an alternative approach, a grower cooperative could be created for the preparation and fermentation stages of ethanol production. Such an approach recognizes the need for reducing individual farm capital investment for equipment and may optimize the scale of operations while controlling the quality and source of feedstock for sales to ethanol plants. Ethanol plants would more likely accept purchase of prepared "broth" for distillation, reducing the cost of pretreatment.

Fermentation

Fermentation of *Sunspuds*™ was conducted in several stages from November 1993 to February 1994. The first fermentations were performed by chopping the samples in a blender with some water and adding the simplest "bakers" yeast to the slurry and fermenting in flasks with air-locks at room temperature as a baseline approach. The alcohol content was determined by gas chromatography by comparison to known alcohol-water mixtures. The yields varied from 8.2-18.8 gal/ton. Hence, the initial data showed an average yield of 13.5 gal/ton with a standard deviation of 3.5 gal/ton.

A second set of fermentations was started. These samples were obtained by grating the tubers with Mouli, squeezing out the juice by twisting the gratings in a square of cloth, collecting the juice, using Saccharomyces cerevisiae, Red Star Distillers active dry yeast, rather than bakers yeast and fermenting at 90°F for five days. The results of the second set of fermentation were variable, indicating that not enough time might have been allowed for the fermentation to finish or a problem with competing organisms. The highest percentage alcohol obtained from juices was 11.97%. This corresponds to about 21 gal/ton.

For one sample, the pressed pulp was mixed with water and then re-pressed and this rinse was then fermented. This rinsing process produces a lower alcohol content fermentate but this process would increase the yield to about 25.2 gal/ton (25 gallons per ton will be used for yield calculation purposes--see Table 2).

A third set of fermentations was done to determine if the Distillers yeast could be used at room temperature. These samples were fermented at 90 and 70°F from ten days. The 70°F samples gave slightly higher values. It is possible that some alcohol was lost by evaporation and this loss would be more for the hotter samples. At any rate, there does not seem to be a problem in doing the fermentation at a lower than optimum temperature, although it will take longer. In production, it might be possible to heat the juice to close to 90°F and then dump it into underground tanks and add the yeast. In this manner fermentation would start fast, which would be an advantage if there are competing organisms (a quick increase in alcohol would discourage other organisms).

Fermentations were performed at both 70° to 90°F. The temperature difference does not seem to affect yield with the current yeast, but does affect the time for fermentation. With 70% juice, 12% alcohol fermentation yields 21.0 gallons per ton. A 20% boost is achieved by rinsing the pulp, yielding 25.2 gallons per ton. These numbers appear to be at least conservative, since the yield per acre and the yield for fermentation can be improved with greater sophistication of harvesting and preparation.

The best procedure seems to be to ferment the neat juice since this will give the highest alcohol concentration. The pulp can be rinsed and fermented to give a lower alcohol fermentate to increase the overall yield. JMCA is continuing research on optimum yeast or bacteria strains to reduce fermentation time and reduce contamination risk. From the fermentation experiments, it was determined that the yield can be increased by at least 25% if the pulp is rinsed and the rinse fermented. However, this rinse will produce a lower alcohol content fermentate so it will be somewhat more "expensive" to recover the alcohol. Also, alcohol can be obtained from the residue by acid or enzymatic hydrolysis or heating but this would be more energy expensive. The residue instead has value as a co-product for feed or soil conditioner. The following are the estimates of ethanol per acre based on previous fermentation tests performed under the JMCA/SERBEP contract:

TABLE 2.

SUNSPUDS™ ETHANOL PRODUCTION

Calculated average gallons of ethanol per ton yield : **25 gal/ton**

YIELD OF ETHANOL PER ACRE:
From first set of samples: 31 tons/acre x 25 gal/ton = 775 gal/ac.
From second set of samples: 26.1 ton/ac x 25 gal/ton = 652 gal/ac.
Average from both sets of samples: **713.5 gallons per acre**

Based on the samples collected and the fermentation data produced under the JMCA/SERBEP work, our estimates are that the yield of ethanol per acre of *Sunspuds*™ is about twice the average yield obtained from corn. It appears that with additional primary data from the 1994-1995 season on the production cost of *Sunspuds*™, cost per gallon of ethanol will be equal or better than the cost of corn. Also, since *Sunspuds*™ are a sugar crop, pretreatment and distillation costs will be lower, with an overall reduction in ethanol price.

Crop Yield Comparisons
Sunspuds™, which have a high content of easily fermented inulin sugar, may have a technical and yield advantage over other sugar and starch feedstocks. For example, sugar cane offers an average production of 470 gal/acre of ethanol; sweet sorghum produces 280 gal/acre of ethanol; manioc has an output of 510 to 560 gal/acre of pure ethanol.

Using average data about corn from the USDA/CSRS "New Industrial Uses, New Market for US Crops", August, 1993, the yield of corn is estimated at 119 bushels/acre which can be converted to 2.5 to 2.65 gal of ethanol/bushel, for a total of 315.35 gal/acre.

In comparison, from the analysis done in prior months on the fermentation and the crop yields per acre using typical potato farming practice, the *Sunspuds*™ can yield an average of 713 gal/acre, based on samples of 775 gal and 652 gal (see table 2). For cellulose feedstocks, similar to the perennial switchgrass crop now being developed, the Sunspud advantage of reduced pretreatment processing is obvious.

Competing Technology

Sugar cane is the conventional sugar crop for fuel production purposes, but it is grown only in a few states in the U.S., whereas the *Sunspuds*™ can be grown in every state. Similarly, the sugar beet is grown only in the western and northern midwest U.S. and has little farm base east of the Mississippi. A DOE report has stated that, for example, the primary reason to reject the sugar beet from further consideration as an energy crop was the "necessity to practice crop rotation with sugar beets to control hematodes and other organisms, usually on a four-year cycle...". No such restriction applies to the *Sunspuds*™.

Corn is currently a major starch crop used for conversion to ethanol. The National Corn Growers Association and the Governor's Ethanol Coalition have joined to promote and expand the use of corn as a feedstock for ethanol. This is a logical rationale since corn is widely grown and is used for production of high fructose sweetener. The refining process is well developed. However, corn, as a starch crop needs extensive pretreatment in order to prepare and ferment sugars prior to distillation. *Sunspuds*™ are already a sugar crop and therefore the additional steps required for corn are not necessary with the *Sunspuds*™.

Many other feedstocks have been proposed for ethanol production, especially cellulosic types. However, the various pyrolytic conversion methods for cellulosic feedstock have high processing cost, and the ethanol output for per acre for cellulosic crops is generally less than the ethanol output obtained with the *Sunspuds*™.

Co-product Uses
Stillage from sugar fermentation and separation is the main co-product. Research on the processing of Sunspud stillage is beginning in the coming season with plans for installation and testing of a pilot fermentation plant. This stillage is both a problem and opportunity, depending on how it is managed and utilized. Use of stillage as high protein feed is considered as a co-product credit in most analyses of large industrial conversion plants.

By comparison, however, the small farm is penalized, since the required drying and processing equipment is costly, or animals to feed wet stillage may not be available. Therefore, stillage as fertilizer will be considered and evaluated as an alternate co-product use, since both large and small farms may claim a valuable credit.

The *Sunspuds*™ Ethanol Market Potential

Potential Domestic Market
Total annual demand in 1995 (reported by the Renewable Fuels Association) could be as much as 430 million gallons. By 1996, the industry expansion is expected to reach a total of over a billion gallons production annually.

Many ethanol plants are organized to receive feedstock and process grains through pretreatment stages which preclude the use of alternative inputs. JMCA intends to pursue the development of Sunspud preparation so that fermented beer can be delivered to ethanol plants for distillation. This procedure will reduce the volume of feedstock to be delivered and therefore reduce transportation costs. This would enable farmers or farmer cooperatives the option of delivering a value-added product for ethanol production.

***Sunspuds*™ and the International Market**
JMCA is beginning seed farms for Sunspud development and ethanol production in Puerto Rico, France, Ethiopia, India and Peru. It has been recognized that developing nations must consider and develop a wide variety of alternative fuel sources.

At the present state-of-the-art, ethanol burned straight(not as an additive) seems the most suitable choice for general uses. Ethanol is widely accepted as a logical substitute for oil and gas and has environmental benefits in addition to the potential for fuel supply differing greatly from current availability and distribution of oil. Ethanol can be marketed as a substitute for use in cooking, lighting and heating (kerosene), stationary power (diesel) or vehicles (gasoline). High protein feed is a co-product credit of the conversion process and a highly valued product. Because of high nitrogen and protein content, it is favored for soil conditioning or for animal feed.

While most production technologies envision the main end use for fuel ethanol in its anhydrous state, there are fuel applications which do not require anhydrous (100%) ethanol. Using ethanol in the 150-190 proof range is well suited for many rural and urban uses currently being supplied by wood or wood products. Ethanol is a potential substitute for cooking with kerosene, which is a preferred fuel. Therefore, ethanol acts as a "demand management" tool to relieve pressure on fuelwood use, allowing long-term tree planting greater possibility for success.

Because of its flexibility and efficiency, kerosene is a highly desirable cooking and heating fuel, but in many countries kerosene is also an oil-based import and very expensive. If ethanol, processed to over 50% ethanol/water ratio (over 100 proof) can be produced on-farm at the lower-end equivalent cost for kerosene or coal used in a traditional stove, then ethanol becomes a possible direct substitute for coal and kerosene. Where fuelwood is scarce and high labor or cash cost is incurred, locally produced ethanol may be price competitive as cooking fuel, given at least farmer-contributed labor and self-produced ethanol fuel for plant operations.

Ethanol can be utilized in a kerosene cooker with minor modification. The air-to-fuel mixture is different than kerosene, which is 18:1. Ethanol (100 proof) has an air-to-fuel ratio of 5:1. This means that for the same heat value, the rate of flow would be faster for ethanol and requires more fuel to combust. Therefore, the fuelport of a kerosene-cooker would need to be enlarged.

The purchase cost of durable mass-produced, light weight and portable liquid fuel cookers and lighting lanterns, suitable for kerosene or ethanol, is affordable to many subsistence level rural or urban people--if local ethanol fuel supply was being produced. Clearly, the option of supplying a liquid biofuel must assume simultaneous capacity to produce the ethanol at low cost locally. Such cookers and lanterns are already market available--designed, engineered, and fabricated for consumer sales at the equivalent cost of similar kerosene equipment.

For ethanol production, output of fuel at 150-190 proof would appear to broaden the potential market opportunities and range of applications for rural use. A gross breakdown of various quality outputs from ethanol conversion plants, shows the overall potential use for liquid biofuels:

- 200-proof ethanol --substitute for gasoline (anhydrous) fueled vehicles.
- 190-proof ethanol --direct use in gas (hydrous) modified spark engine, or in ethanol designed engines.
- 150-190-proof ethanol --direct use for kerosene-modified cook-stoves, lighting and heating, or in similar ethanol designed products, such as fuel cells for electricity.

Potential to Economically Produce Energy from Biomass

The *Sunspuds*™ can be an effective new energy crop based on these market advantages:

1. The anticipated average yield of ethanol obtained from *Sunspuds*™ is about <u>double</u> the average yield of ethanol obtained with corn.
2. The yield of fodder may be as much as 3 to 4 tons an acre and the yield of tubers ranges from 20 to 35 tons.
3. The stems and leaves are very palatable, digestible and nourishing to cattle and horses, increase the yield of cow milk, and are equal to or better than sunflower for ensilage, and is preferred by animals.
4. The co-product residue is specially useful for fattening cattle, sheep and hogs and is a serviceable poultry feed.

For ethanol production that can be derived from perennial dedicated feedstock supply systems, the *Sunspuds*™, have an advantage in terms of conversion economics and higher ethanol yield over other feedstocks. In terms of conversion, the *Sunspuds*™, which have high content of easily hydrolyzed inulin, require lower energy input and simpler pretreatment process as a sugar crop, as compared to cellulose or starch type of crops. This factor, combined with the high ethanol yield per acre obtained from the *Sunspuds*™ will improve conversion system production economics as compared to existing ethanol crops. Hence, it is our expectation that the *Sunspuds*™ can be a competitive crop in the ethanol market.

Many ethanol plants are organized to receive feedstock and process grains through pretreatment stages which preclude the use of alternative inputs. JMCA intends to pursue the development of *Sunspuds*™ preparation so that fermented "broth" can be delivered to ethanol plants for distillation. This procedure, demonstrated in this project at the University of Idaho, will reduce the volume of feedstock to be delivered and therefore reduce transportation costs. In commercial practice, this procedure would enable farmers or farmer cooperatives the option of delivering a value-added product for ethanol production.

Advantages Over Competing Technologies in the Market
These growing characteristics of the *Sunspuds*™ also have advantages over other crops:

1. They will grow on most soils, poor as well as rich, if not too wet. It responds to moderate amounts of irrigation. Hence, reclamation land can be used.
2. The growing season extends further into the winter than other root crops.
3. They will grow in any climate where staple crops are grown, and will withstand frosts that are ruinous to corn, beets, and potatoes.
4. Periods of drought may lessen the yield of forage or tubers but do not injure the plant.
5. The plant and tubers are impervious to injury by insects, except perhaps the grasshopper. Herbicides and pesticides are not needed.
6. Storage and keeping present little difficulty if the tubers are left in the ground or covered with a layer of earth immediately after being dug.
7. The period of cultivation is shortened because abundant growth kills the weeds and prevents the soil from baking.

In addition to the advantageous growing characteristics listed, the *Sunspuds*™ can be a competitive crop for ethanol because of the combination of these two previously mentioned factors: the *Sunspuds*™ are a high yield crop for ethanol feedstock, and the *Sunspuds*™ sugar tubers have the capability to be broken down easily to solution for fermentation, thereby reducing preparation costs creating a potential value-added product at the farm.

Conclusions

Based on information and data obtained, the following conclusions can be established:

From the Planting and Harvesting:
Sunspuds™ grow rapidly and can get between six and ten feet tall. They store well in the ground during the winter months. However, the sugar content also changes during storage. Future analysis of spring harvest is required.

Periods of drought may lessen the yield of forage or tubers but do not appear to injure the plant. Hardiness of the plant is important for future growing seasons as a dryland crop, since irrigation and water consumption is a major issue. Next years crop will fully test the ability of the plant to survive. Yield under these conditions will be monitored in detail.

Herbicides and pesticides were not used. It appears that such precautions are not needed, since there was no infestation. However, weed control is still an issue, requiring either carefully scheduled cultivation until the plants can gain control, or using weed prevention techniques. Future seasons will test both approaches from cost, time and pollution perspectives.

Typical potato farming machinery can be used for planting and harvesting. For future harvesting, multi-row harvesters will be modified to use smaller gap chains to capture the smaller tubers.

Fertilized and irrigated plants tended to grow taller stalks, but not necessarily greater volume or larger tubers. With the 1994 crop planting, fertilizer was deleted to further test this preliminary result. JMCA continuing research also focuses on plant development and yield as a dryland crop versus irrigation.

From the Fermentation Experiments:
As a result of fermentation experiments, we were able to obtain an ethanol yield of approximately 25 gal/ton.

Temperature does not seem to affect alcohol yield, although the time of fermentation is probably increased with lower temperatures.

The alcohol yield can be increased by at least 25% if the pulp is rinsed and the rinse fermented. This rinse will produce a lower alcohol content fermentate so it will be somewhat more "expensive" to recover the fuel alcohol.

Alcohol can be obtained from the residue by acid or enzymatic hydrolysis or heating but this would be more energy expensive. Instead, the residue may be used as a co-product for feed or as a substitute for chemical fertilizer.

General Conclusion:
The *Sunspuds*™ produced between 26.1 to 31 tons per acre which, based on our fermentation tests (See Table 1 and Table 2), provide an equivalent estimated yield of between 652 to 775 gallons of ethanol per acre. Therefore, the yield of ethanol obtained with *Sunspuds*™ is about twice the average yield per acre obtained from corn.

Selected References

The following is a selected list of references related to the research work:

The Clean Fuels Report, J. E. Sinor Consultants Inc., Vol. 5, No. 4, September, 1993, pages 126-136.

New Industrial Uses, New Markets for U.S. Crops: Status of Technology and Commercial Adoption, USDA Cooperative Research Service, August, 1993.

Gerald J. Seiler, "Forage and Tuber Yields and Digestibility of Selected Wild and Cultivated Genotypes of Jerusalem Artichoke", Agron. J., 85:29-33 (1993).

General Report: Biomass for Energy (Economic and Policy Issues), Working Party No.1 of the Committee for Agriculture, Organization for Economic Operation and Development (OECD), AGR/WP1(83)5, June, 1983.

Vukov, K.; Erdelyi, M.; Pichler-Magyar, E. Preparation of pure inulin and various inulin-containing products from Jerusalem Artichoke for human consumption and for diagnostic use. Studies in Plant Science, 1993. (3) p. 341-345.

Barta, J. Jerusalem artichoke as a multipurpose raw material for food products of high fructose or inulin content. Studies in Plant Science, 1993. (3) p. 323-339.

Meijer, W.J.M.; Mathijssen, E.W.J.M.; Borm, G.E.L. Crop characteristics and inulin production of Jerusalem Artichoke and chicory. Studies in Plant Science. 1993. (3) p. 29-38.

Hans E. Grethlein and Thomas B. Nelson, "Projected Process Economics for Ethanol Production from Corn", Michigan Biotechnology Institute, Final Report to USDA/Agricultural Research Service, July 12, 1992.

Inulin and inulin-containing crops. A. Fuchs. International Congress on Food and Non-Food Applications of Inulin and Inulin Containing Crops. (1991: Wageningen, Netherlands).

Yokota, A. (Hokkaido Univ. Sapporo (Japan). Faculty of Agriculture); Enomoto, K. Tomita, F. Purification and properties of an inulin fructotransferase. Journal of Fermentation and Bioengineering, Oct. 1991, v. 72(4) p. 262-265.

BIOMASS FAST PYROLYSIS

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Abstract

Fast pyrolysis of biomass for liquid fuels is of rapidly growing interest in Europe while in North America, interest seems to have peaked a few years ago. This paper summarises the current status of fast pyrolysis activities in both regions and reviews the problems faced by the developers of fast pyrolysis, upgrading and utilisation processes which require resolution if the technologies are to be implemented. Aspects of design of a fast pyrolysis system include feed drying; particle size; pretreatment; reactor configuration; heat supply and transfer; heating rates; reaction temperature; vapour residence time; secondary cracking; char separation; ash separation; liquids collection. Each of these aspects is reviewed and discussed.

Introduction

Interest in fast pyrolysis of biomass is currently growing rapidly in Europe. Approximately US$ 12 million per year are being spent by the European Commission (EC) on thermal biomass conversion research, development and demonstration which has been estimated to increase to around US$ 25 million/y in the next few years. Most installations there are small laboratory units where number of units is the dominant effect rather than scale. In North America a number of units are operating commercially and RD&D is being maintained in a number of organisations but with few new activities.

Pyrolysis concepts

Biomass is a mixture of hemicellulose, cellulose, lignin and minor amounts of other organics which each pyrolyse or degrade at different rates and by different mechanisms and pathways depending on the process parameters such as reactor temperature, heating rate and pressure. The degree of secondary reaction (and hence the product yields) of the gas/vapour products depends on the time-temperature history to which they are subjected before collection. Although some research has been carried out on the individual components of biomass, most applied and larger scale work has focused on whole biomass as the cost of pre-separation is generally considered too high.

Research has shown that maximum liquid yields are obtained with high heating rates, at reaction temperatures around 500°C and with short vapour residence times to minimise secondary reactions. Fast pyrolysis processes have been developed commercially for production of food flavours (to replace traditional slow pyrolysis processes) which utilise very short vapour residence times of typically 100-500 ms. Speciality chemicals may be derived from pyrolysis liquids under carefully controlled and well specified conditions (1).

Liquids for use as fuels can be produced from dry wood which gives maximum liquid yields of around 80 wt% dry feed basis (typically 64 wt% organics and 13 wt% water) at typically 500-520°C with vapour residence times not more than 1 second. Very short residence times result in incomplete depolymerisation of the lignin due to random bond cleavage and inter-reaction of the lignin macromolecule resulting in a less homogenous liquid product, while longer residence times cause secondary cracking of the primary products, reducing yield and adversely affecting bio-oil properties.

Process characteristics and technology requirements

Although fast pyrolysis of biomass has achieved commercial status, there are still many aspects of the process which are largely empirical and require further study to improve reliability, performance, product consistency, product characteristics and scale-up.

Reactor configuration

A variety of reactor configurations have been investigated as listed in Table 1. Pyrolysis, perhaps more than any other conversion technology, has received considerable creativity and innovation in devising reactor systems that provide the essential ingredients of high heating rates, moderate temperatures and short vapour product residence times for liquids.

Table 1 : Fast Pyrolysis Reactors for Liquids

Reactor type	Organisation
Ablative plate	U. Aston
Ablative vortex	NREL
Ablative other	BBC/Castle Capital
Circulating fluid bed	CRES, ENEL/Pasquali
Entrained flow	Egemin
Fluid bed	CPERI, IWC, NREL, Union Fenosa, U. Aston, U. Hamburg, U. Leeds, U. Sassari, U. Stuttgart, U. Waterloo
Horizontal vacuum moving bed	Pyrovac/U. Laval
Rotating cone (transported bed)	U. Twente, Schelde/BTG
Transported bed with solids recirculation	Ensyn

Heat transfer

There are two important requirements for heat transfer in a pyrolysis reactor:

1. heat transfer to the reactor heat transfer medium (solid in an ablative reactor, gas and solid in fluid and transport bed reactors, gas in entrained flow reactors),
2. heat transfer from this medium to the pyrolysing biomass.

Two main ways of heating biomass particles in a fast pyrolysis system can be considered: gas-solid heat transfer as in an entrained flow reactor where heat is transferred from the hot gas to the pyrolysing biomass particle by primarily convection (for example the Egemin and GTRI processes), and solid-solid heat transfer with mostly conductive heat transfer. All processes will employ some combination of these two modes of heat transfer with radiation only providing a minor contribution. Fluid bed pyrolysis utilises the inherently good solids mixing to transfer approximately 90% of the heat to the biomass by solid-solid heat transfer with a probable small contribution from gas-solid convective heat transfer of up to 10%. It must be stressed that this conductive heat transfer in fluid beds is not ablative heat transfer. Circulating fluid bed and transport reactors rely on both gas-solid convective heat transfer from the fluidising gas and solid-solid heat transfer from the hot fluidising solid although the latter may be less significant than fluid beds due to the lower solids bulk density. Some ablative heat transfer is also likely from the high velocities of the particles.

A different heat transfer process occurs in ablative pyrolysis where contact of the biomass and the hot solid abrades the product char off the particle exposing fresh biomass for reaction under high contact pressure and high relative motion. This permits much larger particles to be successful fast pyrolysed. Attrition of the char from the pyrolysing particle can also occur in both fluid and circulating fluid beds, due to contact of the biomass with in-bed solids where solids mixing occurs. In fluid bed reactors however, attrition of the product char is relatively low and it has been observed that the char particles retain original particle shape, but are slightly reduced in size by char layer shrinkage and attrition. Attrited char that is too small to be captured in the primary cyclone(s), typically below around 50 microns, will be collected with the liquid unless a barrier filter is provided.

Char removal is an essential requirement as it is known to be catalytically active (2). It cracks organic vapours to secondary char, water and gas both during primary vapour formation and in the reactor gas environment, therefore rapid removal of char from the hot reactor environment and minimal contact with the pyrolysis vapour products is essential.

Heat supply

The high heat transfer rate necessary to heat the particles sufficiently quickly imposes a major design requirement on achieving the required high heat fluxes. Each mode of heat transfer imposes certain limitations on the reactor operation and may increase its complexity. The two dominant modes of heat transfer in fast pyrolysis technologies are conductive and convective. Each one can be maximised or a contribution can be made from both depending on the reactor configuration. For ablative pyrolysis in a vortex reactor, an ethylene cracking furnace has been proposed to provide the high heat fluxes necessar3). Other suggestions have included vapour condensation such as sodium, induction heating of the reactor wall and the use of contact electrical heaters. In a circulating fluid bed, approximately 50% of the required heat transfer is believed to be derived from the hot circulating sand which, therefore, requires an efficient sand re-heating system. In a conventional fluid bed the sand requires an external heat source. The by-product char and gas would usually be used to supply the process energy.

Feed preparation

The heat transfer rate requirements described above impose particle size limitations on the feed for some reactors. For fluid beds, maximum particle sizes of 2-3 mm are typically specified and for CFB and transport reactors the maximum size is typically set at 5-6 mm although the aspect ratio is important. Ablative reactors can utilise much larger particles such as whole tree chips. Data is not yet available to define the energy and financial penalty associated with the small particle sizes demanded of fluid bed and circulating fluid bed systems.

As the feed moisture is retained in the product together with the reaction water, drying is usually required to less than 10% wt water unless a naturally dry material such as straw is available. Higher feed moisture will give poorer quality liquid products in terms of heating value and propensity to phase separation while lower feed moisture content becomes unacceptably difficult to achieve in economic and environmental terms.

Liquids collection

This has long been a major difficulty for researchers. The pyrolysis vapours appear to exist more as an aerosol than a true vapour and thus collection is not a simple condensation problem. The vapours have similar properties to cigarette smoke and capture by almost all collection devices is very inefficient. They can be characterised as a combination of true vapours, micron sized droplets and polar molecules bonded with water vapour molecules. This contributes to the collection problem as the aerosols need to be impinged onto a surface or otherwise caused to coalesce or agglomerate to permit collection, even after cooling to below the dew point temperature. Collection by quenching in the liquid product is a popular method but which increases problems of mass balances at the R&D level.

Electrostatic precipitators are effective but can create problems from the polar nature of the product and arcing of the liquids as they flow, causing the electrostatic precipitator to short out. Larger scale processing usually employs some type of quenching or contact with cooled liquid product which is effective. Careful design is needed to avoid blockage from differential condensation of heavy ends. The rate of cooling appears to be important. Slow

cooling leads to preferential collection of the lignin derived components which is a viscous liquid which can lead to blockage of heat exchange equipment and liquid fractionation. Very rapid cooling of the product has been suggested to be effective as occurs typically in a direct contact quench. Transfer lines from the reactor through the cyclone(s) to the liquid collection system should be maintained at > 400°C to minimise liquid deposition and collection.

At present, there are no recognised design methods and most work has been empirical and specific to the characteristics of the feedstock being processed. Commercial liquids recovery processes are usually proprietary and may be specific to individual feedstocks and reactor configurations.

Char separation

Some fine char is inevitably carried over from cyclones and collects in the liquid. Subsequent separation has proved difficult. Some success has been achieved with hot gas filtration in a ceramic cloth bag house filter (4) and also candle filters for short run durations. Liquid filtration has also proved difficult as the liquid can have a gel-like consistency, apparently due to some interaction of the lignin-derived fraction with the char. Dilution with alcohol improves the filterability by reducing viscosity as well as somehow reducing the gel effect.

This aspect of char reduction and/or removal will be increasingly important as more demanding applications are introduced which require lower char tolerances in terms of particle size and total quantity. Possible solutions include changing process conditions to reduce the nature of the pyrolytic lignin, increasing the degree of depolymerisation of the lignin-derived fraction of the liquid, changing the feedstock to one with a lower lignin content, or adding chemicals to the liquid for example to improve handling properties or reduce char-lignin interactions.

It must not be forgotten that an alternative solution is to modify the application to accept a high char content bio-fuel-oil.

Ash separation

The alkali metals from biomass ash are present in the char in relatively high concentrations and cannot be readily separated except by hot gas filtration which is undergoing development as reported variously in these proceedings.

PRODUCT CHARACTERISTICS

The complex interaction of time and temperature on liquid product quality has not been explored, at least partly because the characteristics of pyrolysis oil for different applications has not been defined and there is no "standard" pyrolysis liquid. It is this definition of oil quality that is a major uncertainty and requires to be defined by potential users and may differ by application. While there are set standards and methods of measurement for conventional fuels, analogous standards and methods have not yet been defined for biomass pyrolysis liquids. Density, viscosity, surface tension and heating value are known to be typical key properties for combustion applications in boilers, furnaces and engines; but other characteristics such as char level and particle size and ash content may have a major effect.

Bio-fuel-oil has a number of special features and characteristics which require consideration in any application including production, storage, transport, upgrading and utilisation. These are summarised below showing that while some problems remain, none are insoluble (5). Recognition of problems and awareness of potential difficulties is a major contribution to dealing with any of the above difficulties.

Characteristics of Bio-oil and Methods for Modification

Suspended char can cause erosion, equipment blockage and combustion problems from slower rates of combustion leading to potential deposits and high CO emissions. The solutions include hot vapour filtration, liquid filtration, modification of the char for example by size reduction, or modification of the application.

Alkali metals can deposit solids in combustion applications particularly turbines where the damage potential is considerable. Hot vapour filtration is one solution. Alternatively processing or upgrading of oil, modifying the application or pretreating feedstock to remove ash may solve the problem.

Low pH causes corrosion of vessels and pipework. The solution is careful materials selection through use of stainless steel and some olefin polymers.

Temperature sensitivity is evidenced by liquid decomposition on hot surfaces leading to decomposition and blockage; adhesion of droplets on surfaces below 400°C. The solution is to recognise the problem by providing appropriate cooling facilities and avoiding contact with hot surfaces > 500°C.

High viscosity causes high pressure drops in pipelines leading to higher cost equipment and/or possibilities of leakage or even pipe rupture. The solution is careful low temperature heating, and/or addition of water, and/or addition of co-solvents such as methanol or ethanol.

Water content has a complex effect on viscosity, heating value, density, stability, pH, homogeneity etc. The solution is to recognise the problem and treat it accordingly, optimising with respect to the application.

In-homogeneity can cause layering or partial separation of phases giving rise to filtration problems. The solution is to modify or change process through the pyrolysis parameters; change the feedstock to one with low lignin; add additives; and control water content.

Incompatibility with polymers results in swelling or destruction of sealing rings and gaskets. Careful materials selection is again the solution.

PYROLYSIS PROCESSES

Fast pyrolysis of biomass for liquids began in North America around 1980 and has seen significant RD&D effort since then with one successful commercial organisation offering plants with a performance guarantee and several demonstration and pilot scale processes. In Europe the situation is more varied but less developed with only one substantial pilot plant. Most interest has been stimulated by the EC JOULE and AIR programmes over the last 8 years. Fast pyrolysis activities currently active and significant recent projects are summarised below. A recent review of processes that are advanced technically and/or commercially available has been published (6).

Organisations Currently and Recently Involved in Fast Pyrolysis for Liquids

Castle Capital (Canada) A 35-50 t/d continuous ablation reactor designed by BBC has been built in Nova Scotia where it is operating successfully since 1994 with combustion of the raw product gas and no liquids collection (7, 8). A two stage direct liquids quench has been successfully tested.

CPERI (Greece) A small fluid bed pyrolyser provides liquids for conversion or upgrading to chemicals including methyl aryl ethers (9)

CRES and Agricultural University of Athens (Greece) A circulating fluid bed fast pyrolysis with integral char combustion at 10 kg/h has been commissioned but is not yet producing liquids (10).

Egemin (Belgium) A 200 kg/h capacity entrained downflow system was commissioned in 1991 and operated at up to around 50 kg/h giving liquid yields around 45% wt. (11). It was closed down permanently in 1992.

ENEL (Italy) A 650 kg/h demonstration plant has been ordered from Ensyn for planned start up in Italy at the end of 1995 (12)

Ensyn (Canada) There are three operational plants: a 25 dry te/d unit at Red Arrow in Wisconsin and an 80 kg/h unit and 10 kg/h R&D unit at Ensyn in Ottawa. Others are under construction and design. Current work includes hot vapour and liquid filtration to reduce char. Oil is being supplied for engine, turbine and combustion testing and characterisation in North America and Europe.

INETI (Portugal) A 0.6 kg/h fluid bed has given 55% yield of total liquid with characteristics similar to those from other fast pyrolysis systems. Tests have also been carried out on a 300 mm square fluid bed (13).

Institute of Wood Chemistry (Germany) A 100 g/h fluid bed for processing wood wastes has been operating since 1994.

NREL (USA) NREL have been developing their 30 kg/h vortex ablative pyrolyser since 1980 and a second unit of 70 kg/h capacity was commissioned in 1994. A small fluid bed fast pyrolysis unit has also been commissioned. Zeolite cracking has been carried out on the pyrolysis vapours and a circulating fluid bed zeolite cracker with regenerator has recently been commissioned (14)

Pasquali-ENEL (Italy) A CFB unit has been designed for integration with an engine for mass supply of small scale units of up to 500 kWe.

Pyrovac (Canada) A horizontal moving bed vacuum process for biomass and wastes has been developed from the University of Laval research (15). A 15000 t/y plant has been sold in Belgium.

Resource Transforms International (Canada) Speciality chemicals are produced from bio-oil. Small scale fast pyrolysis equipment is designed and supplied.

Schelde/BTG (Netherlands) A rotating cone pyrolysis unit rated at 50 kg/h has been scaled up from early work at the University of Twente for supply to China.

Union Fenosa (Spain) A fluid bed fast pyrolysis pilot plant of 160 kg/h based on the University of Waterloo process has been operating since mid. 1993. Feeds tested include oak, pine, eucalyptus,. Liquid yields of better than 55% are currently achieved (2, 16).

University of Aston (UK) An ablative plate reactor with a capacity of 5 kg/h has been operating for two years. Liquid yields of 75-80% have been achieved (17). A small fluid bed of 2 kg/h has recently been commissioned.

University of Laval (Canada) Biomass and solid wastes are vacuum pyrolysed in a horizontal moving bed vacuum reactor which has replaced the multiple hearth vacuum unit. The process is being commercialised by Pyrovac (q.v.). An extensive bibliography is available.

University of Leeds (UK) A fluid bed reactor of about 500 g/h with close coupled and integral zeolite cracking reactor has been studied (18).

University of Naples (Italy) Models of fast pyrolysis have been derived and applied to fluid bed and ablative reactors.

University of Sassari (Italy) A fluid bed with a capacity of 10 g/h has been tested (19).

University of Stuttgart (Germany) A fluid bed with a capacity of around 3 kg/h was installed in 1994.

University of Twente (Netherlands) A rotating cone reactor has been developed in several versions of up to 50 kg/h (20), the latest including char combustion and recycle.

University of Waterloo (Canada) Two fluid bed reactors of 100 g/h and 3 kg/h have been used to extensively test a range of feedstocks and study the basic science of fast pyrolysis. There is an extensive bibliography which is readily available.

VTT (Finland) A laboratory unit of 10 kg/h has been ordered from Ensyn and other units are being constructed.

Applications

A summary of the opportunities for utilising pyrolysis liquid is shown in Figure 1. Within Europe the most promising application is seen as electricity production due to the anticipated ability to use raw bio-oil as produced in an engine or turbine without the need for extensive upgrading as well as the ability to de-couple fuel production from electricity generation with storage and/or transport of the liquid fuel which is not possible for gasification of combustion systems.

Combustion

Liquid products are easier to handle and transport in combustion applications and this is important in retrofitting existing equipment. Fast pyrolysis liquids are likely to require only relatively minor modifications of the equipment or even none in some cases. The problems that have been reported with high viscosity and suspended char causing atomisation difficulties and incomplete combustion with some fuels are being successfully addressed in the ongoing R&D described above (21, 22, 23) and pyrolysis liquids are now being routinely burned in commercial boilers (24).

Power generation with liquids

A key advantage of production of liquids is that fuel production can be de-coupled from power generation. Peak power provision is thus possible with a much smaller pyrolysis plant, or liquids can be readily transported to a central power plant using engines or turbine. There are additional benefits from potentially higher plant availability from the intermediate fuel storage. The economics of power generation suggest that a niche of up to 10 MWe is available for exploitation.

Bio-oil has been successfully fired in a diesel test engine, where it behaves very similar to diesel in terms of engine parameters and emissions (25). A diesel pilot fuel is needed, typically 5% in larger engines, and no significant problems are foreseen in power generation up to 15 MWe per engine. Gas turbine applications are also considered to be feasible although no work has been carried out in the last 10 years nor on fast pyrolysis liquids. However, a new project has recently been implemented to investigate this which is more likely to be viable for larger scale applications (26).

Chemicals

Several hundred chemical constituents have been identified to date, and increasing attention is being paid to recovery of individual compounds or families of chemicals. The potentially much higher value of speciality chemicals compared to fuels could make recovery of even small concentrations viable. An integrated approach to chemicals and fuels production offers interesting possibilities for shorter term economic implementation. Chemicals that have been reported as recovered include polyphenols for resins with formaldehyde, calcium and/or magnesium acetate for biodegradable de-icers, levoglucosan, hydroxyacetaldehyde, and a range of flavourings and essences for the food industry (1). There are substantial problems to be overcome is establishing markets for the less common chemicals and devising low cost and efficient separation and refining techniques. The only currently viable market opportunity is for speciality food flavourings with a current market size of around US$ 10 million in North America and which could expand to US $ 40-50 million in 10 years.

Economics

A key factor in the continuing development of fast pyrolysis processes to eventual commercial implementation is their economic viability. The current main interest in Europe is for electricity generation from biomass with the driving forces of environmental benefits, CO_2 mitigation, socio-economic benefits from using surplus agricultural land, and energy independence. These have led to significant fiscal incentives being offered for renewable electricity in many European countries such as prices of up to 20¢/kWh in Italy and up to 14¢/kWh in the UK according to the system, the feedstock and the operating time.

A biomass fast pyrolysis system consists of a series of operations that start at the reception of raw biomass, provide for necessary handling and storage, pretreat the material to the required size and moisture content, pyrolyse the prepared material, collect the liquid product, and finally store the product. This is shown in Figure 2. All the costs and performance data of such a system have been estimated from a wide range of published data and incorporated into a sophisticated decision support system that estimates process performance and product cost for a range of bio-electricity production systems which is reported elsewhere in these proceedings (27). It is clear that fast pyrolysis and an engine offers the most economically attractive route of the thermal conversion technologies at sizes up to around 15 MWe, and that no processes are economically viable without some financial support or a low cost feed.

Conclusions

Fast pyrolysis is becoming more accepted as an emerging technology with commercial potential for producing high yields of liquid fuels that can be used in many applications as direct substitutes for conventional fuels or as a source of chemicals. There are still problems to be resolved but it is clear that considerable progress is being made in firstly identifying these problems and then finding and defining solutions. There are some interesting challenges to be faced in modifying the fast pyrolysis technology, in upgrading the liquids and adapting applications to accept the unusual behaviour and characteristics of the liquid product. International co-operation is one of the key routes to facilitate such developments and this needs to be encouraged as bioenergy is increasingly accepted as a potentially significant resource. Further research and development of the fundamental science which provides the tools for the design engineer to achieve the performance improvements is also required for successful exploitation.

References

1 Bridgwater, A.V., Applied Catalysis A, 116, (1-2), pp 5-47, 1994

2 Radlein, D., Piskorz, J. and Scott, D.S., Proceedings 2nd EC-Canada Workshop, Toronto, May 1995, Eds. Bridgwater, T. and Hogan, E., (Aston University 1995)

3 Diebold, J.P., et al. pp 1325-1342, Advances in thermochemical biomass conversion, Ed. Bridgwater, A.V., (Blackie, 1994).

4 Diebold, J.P. et al., pp 90-108, Proc. workshop on biomass pyrolysis oil properties and combustion, Estes Park, USA, September 1994 (NREL 1995).

5 Bridgwater, A.V. pp 109-127, Proc. workshop on biomass pyrolysis oil properties and combustion, Estes Park, USA, September 1994 (NREL 1995).

6 Bridgwater, A.V. and Evans, G.D., Report to UK DTI, 254 pp (ETSU B/T1/00207/REP), 1993.

7 Black, J.W. and Brown, D.B., in Biomass Thermal Processing, 23-25 October 1990, Ottawa, Canada, p 123-125.

8 Black, J.W. and Brown, D.B., report of DSS Contract file No. 23440-9-9513/01-SZ. Alternate Energy Division: Energy, Mines and Resources Canada, Ottawa, Ontario, Canada, March 1993.

9 Samolada, E. and Vasalos, I.A., pp 859-873 in Advances in thermochemical biomass conversion, Ed. Bridgwater, A.V., (Blackie 1993).

10 Boukis, I. et al. pp 1151 - 1164 in Advances in thermochemical biomass conversion, Ed. A V Bridgwater, A.V., (Blackie 1993).

11 Maniatis, K. et al. pp 1257-1264 in Advances in thermochemical biomass conversion, Ed. Bridgwater, A.V., (Blackie 1994).

12 Trebbi, G., ENEL, Private Communication, May 1994.

13 Gulyurtlu, I., Final report of EC JOULE contract JOUB-0053, July 1993.

14 Czernik, S. et al., pp 429-436, Proceedings of the 28th Intersociety Energy Conversion Engineering Conference, (American Chemical Society, 1993)

15 Pyrovac International Inc. trade literature. Sillery, Quebec, Canada.

16 Cuevas, A., Proceedings of EC JOULE Contractors Meeting, Athens, June 1993

17 Peacocke, G.V.C. and Bridgwater, A.V., pp 147-154, Biomass and Bioenergy (1994), Vol. 7, nos. 1-6.

18. Williams, P.T. et al., Fuel, 1990, 69, p 1474-1482.

19 Conti, L., Scano, G. and Boufala, J., Proc. ACS Meeting Denver March 1993, accepted for Biomass and Bioenergy, 1995.

20 Wagenaar B.M. et al., pp 1122-1133, in Advances in Thermochemical Biomass Conversion, Ed. Bridgwater, A.V., (Blackie 1994)

21 Baxter, L. And Jenkins, B., pp 270-280, Proc. workshop on biomass pyrolysis oil properties and combustion, Estes Park, USA, September 1994 (NREL 1995).

22 Gust, S., pp 316-320, Proc. workshop on biomass pyrolysis oil properties and combustion, Estes Park, USA, September 1994 (NREL 1995).

23 Rossi, C., pp 321-328, Proc. workshop on biomass pyrolysis oil properties and combustion, Estes Park, USA, September 1994 (NREL 1995).

24 Freel, B. And Huffman, D., 309-315, Proc. workshop on biomass pyrolysis oil properties and combustion, Estes Park, USA, September 1994 (NREL 1995).

25 Solantausta, Y. et al., pp 355-361, Proc. workshop on biomass pyrolysis oil properties and combustion, Estes Park, USA, September 1994 (NREL 1995).

26 Andrews, R., et al., pp 383-392, Proc. workshop on biomass pyrolysis oil properties and combustion, Estes Park, USA, September 1994 (NREL 1995).

27 Toft, A.J. and Bridgwater, A.V. These proceedings.

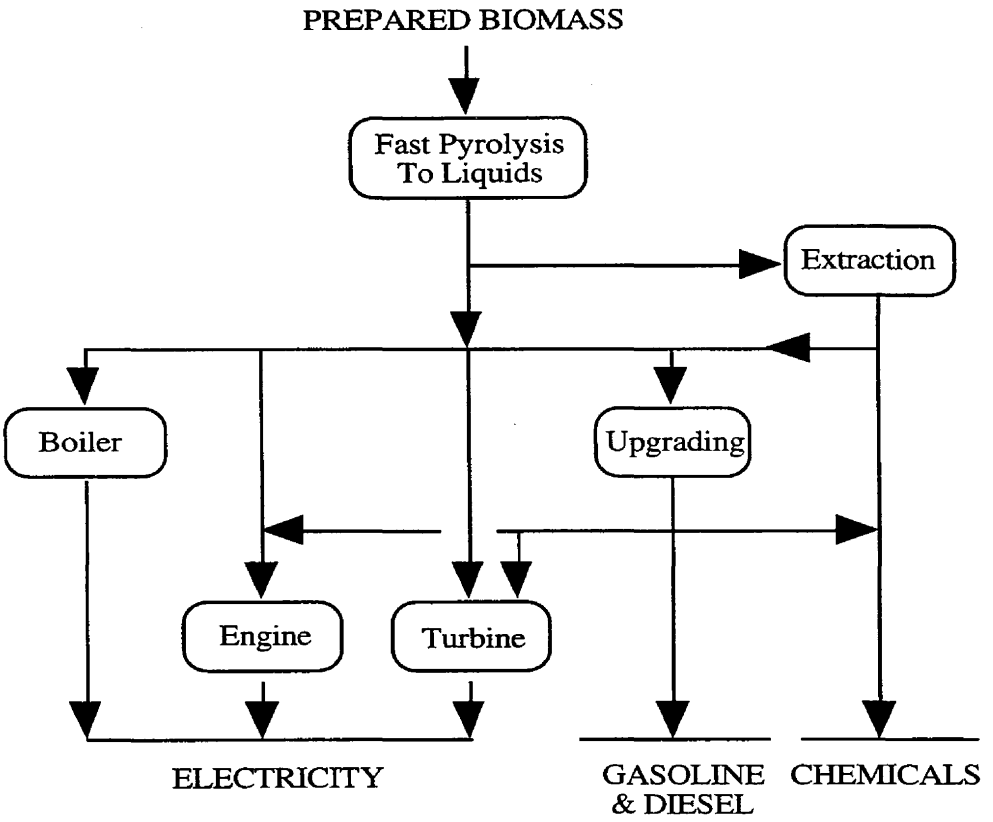

Figure 1 : Applications of Pyrolysis Liquids

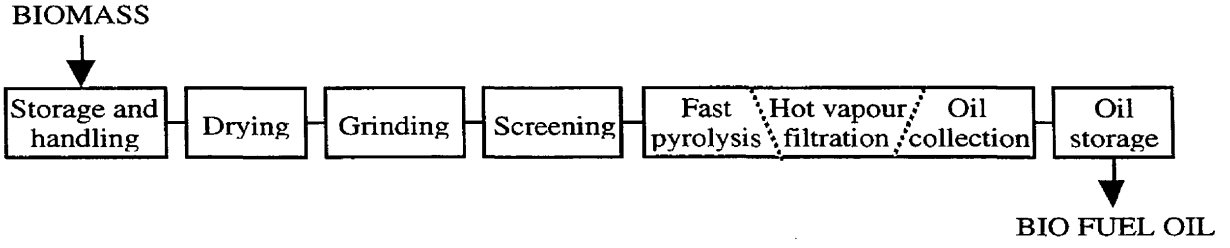

Figure 2 : Biomass fast pyrolysis system

ADVANCED LIQUID FUEL PRODUCTION FROM BIOMASS FOR POWER GENERATION

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Abstract

In the European Union, important political decisions recently adopted and concerning the evolution of the Common Agriculture Policy, the GATT trade liberalisation Agreement and new measures actually under discussion (CARBON TAX, Financial support for rural development...) will have significant impact, in a no distant future, on the bioenergy activity. Also the considerable energy import (≈ 55% of the consumption) is of increasing concerns.
The biomass potential in the E.U. is large, but the availability of commercial technologies for processing and utilising this renewable energy resource is very modest.
Thus, a strong effort for the development of new and efficient technologies (like the one implemented by ENEL / CRT) is essential, as well as the build-up of an efficient industry for the commercialisation of reliable, low-cost biomass conversion / utilisation systems. The recently founded "European Bioenergy Industry Association" will make an effort for the promotion of this specific new industrial sector. In this framework, a new research effort (in Germany / Italy) for up-grading the bio-crude-oil by high energetic electrons. This process, if demonstrated feasible, could be of great interest for the production of new liquid fuels of sufficient quality to be utilised in most types of modern power generator.

Introduction

Interest in vegetal biomass production and utilisation as a regenerable renewable energy resource is growing, because of the increasing awareness of its benefits, such as: the diversification of energy supply, the creation of new jobs especially in rural areas, and the improvement of environmental conditions (CO_2 neutral, no SO_2 emissions).

Although a considerable amount of information is available, commercial technologies lack thus preventing in practice the most effective use of biomass resources.
There is general consensus that some energy processes and products are likely to become viable in a near future. Electricity is seen as the most valuable and economically attractive biomass-derived product with considerable environmental advantage over the traditional fossil fuels that dominate electricity production in the E.U. Also, the production of oxygenated fuels (like ETBE, MTBE) as ingredients for reformulated gasoline seems economically feasible, once integrated with the power-heat production, especially if specific new energy crops like sweet-sorghum (well suited for central-south Europe) could be utilised.
The directive on the Carbon Tax recently adopted by the European Commission (May 1995) and now under discussion for approval at the European Parliament and at the Council of Ministers will be able to produce a strong promotion of renewable energy and in particular of bioenergy. This Directive propose a transition period 1996-1999 of voluntary taxation on all fuels except renewable energy resources. The amount of taxation will be related for 50% to the CO_2 emission and for 50% to the heat content of the energy product as shown in the following table:

· Gasoline (1,000 l):	44,87	ECU
· Diesel (1,000 Kg):	51,40	ECU
· Coal (1,000 Kg):	57,37	ECU
· GPL (1,000 Kg):	62,53	ECU
· Natural gas (1,000 m^3):	41,53	ECU
· Electricity (1MWh):	7,00	ECU

The other energy products will be submitted to the taxation equal to:

9.37	ECU/ton CO_2 produced	+	0.70	ECU/G J

The necessity to preserve the environment and the growing concern over the availability of traditional energy sources have stimulated, the national, and the European Union policy towards an increased interest for renewable energy sources.
In this context, beyond the energy from the sun, the wind and the water, also the concept to cultivate the land for energy production, with selected herbaceous and woody species (energy crops), is now consolidated.
This concept grew stronger in the last years, following the compulsory introduction by the E.C. of the "set-a-side" land (land retired from food production) as a consequence of the evolution of the Common agricultural policy. In the E.U. this reaches now 6.4 million hectares and is creating growing concern in the agricultural world.
Therefore, the use of agricultural lands for the production of vegetal biomass for energetic purposes can offer a real new opportunity for farms.

ENEL Bioenergy Programme

As far as the actual biomass potential in Italy is concerned, the most significant amounts are those related to:

- the "set-a-side" area: about 1 million ha. able to produce 8 M.TOE/y (5% of the total Italy energy needs);
- the marginal agricultural land (retired from the food production in the last 20 years): about 2 million ha;
- the biomass stock (≈ 70 dry ton/ha) on the 3 million ha of "bosco-ceduo" which had been abandoned in the last 20-30 years and which should be harvested to re-establish again its normal rotation (20 years).

Once quantified the biomass resource potential, it appeared at the same time important to develop suitable processes to convert biomass into gaseous and in particular liquid fuels which can be more easily handled and transported.

The penetration possibility of thermal power plants fed with biomass seems closely linked to the industrial development of conversion technologies with high efficiency, such as those based on the Integrated Gasification Combined Cycle (IGCC), or on the use of bio-crude-oil in diesel or gas-turbine generators.

In fact, biomass can be converted into more valuable fuel, called bio-crude-oil, through a flash pyrolysis process with an energy efficiency up to 75%. This bio-fuel could be utilised directly in conventional boilers of existing power plant and in furnaces, to produce electricity/heat with some advantages in comparison with solid biomass, but also with certain limits for its handling storage and transport in comparison with a conventional fuel oil.
The chemical and physical characteristics of bio-crude-oil are quite different from those of conventional liquid fuels; thus its utilisation in gas turbines or in diesel engines requires some important modifications. To avoid these problems, the bio-crude oil could suitably be upgraded through a process capable of improving its characteristics, especially in terms of viscosity, stability and net heat value. In any case, in order to arrive at the commercialisation of the flash pyrolysis technology, a wide R&D activity is needed.

ENEL has launched several programmes aimed at the development and demonstration of advanced processes and technologies to asses the feasibility of biomass conversion into electricity.

In this context, beyond an important demonstration project named "IGCC Energy Farm" of which the main characteristics are shown in the following table:

Gross Electric Power (MW) / Atm. gasifier	14.3
Net Electric Power (MW) / Two gas-turbines + steam turbine	11.9
Gas Cycle Gross Electric Power (MW)	9.4
Steam Cycle Gross Electric Power (MW)	4.9
Dry Biomass Hourly Consumption (kg)	7100
Net Thermal Efficiency (on HHV of biomass)	0.33

much attention is given also to conversion systems based on flash pyrolysis and low-cost up-grading.

As far as this specific sector is concerned, the Italian Utility (ENEL) is implementing a wide experimental programme, which comprises in particular:

- General R&D activity on characterisation, handling, combustion and emission control of bio-crude-oil in boilers and combustion chamber of gas-turbines.
- Development of large power generating system (>1 MW) based on the utilisation of a flash-pyrolysis plant (the largest in the E.U.) which will be delivered by Ensyn-Canada Inc. on September 1995. Meanwhile, in Italy the works needed for the auxiliary facilities are in progress and the biomass required for the trials to be started at the end of 1995 is being produced.
  After a sufficient period of operation (one year), it will be possible to assess the reliability and flexibility of this process and to collect all the technical-economic information useful for potential application in different areas of the country.
  This plant is considered very useful because it will make available a large amount of bio-crude-oil, which is necessary for extensive experimental research activities concerning its application on furnaces, diesel engines and gas turbines. It will be also possible to adapt the plant for upgrading of bio-crude-oil by hydrotreatment process, or other innovative upgrading systems, such as electronic and zeolites up-grading now under development in Europe. These activities will be described in more details at this Conference by other Authors.
- Development of a new biomass flash-pyrolysis/gasification technology and of an advanced small power generator (150 kWe) in collaboration with the Pasquali Co. (Italy), Energidalen (Sweden), and Stadtwerke Saarbrücken AG (Germany).
  This very sophisticated ENEL facility (CIRO) in Livorno will be able to test:
  - the new flash-pyrolysis reactor
  - three types of generators (Diesel, gas-turbine, sterling)
  - a new process for bio-crude-oil up-grading (in vapour phase).

A sketch of this experimental facility is presented in Figure 1.

European Bioenergy Industry Association (EUBIA) Activity

The 6th February 1995, in Brussels, with the patronage of the European Commission and in the headquarters of the European Parliament, the European Association of Bioenergy Industries was funded. As Chairman was elected Mr. M. Palmarocchi (Italy) of ECOFUEL / AGIP PETROLI, while Mr. T. Fiallstrom (Sweden) and Mr. T. Weber (GErmany) were elected as vice chairmen.
The objectives of the new Association are the following:

- to contribute to solving problems concerning the production, treatment, processing, marketing, and use of biomass in terms of feasibility, quality control, environmental protection, health and safety;
- to supply information and consultance on norms and guidelines of the Commission of the European Union as well as to express opinions and proposals on the initiatives of the national, international and European authorities on the subject of biomass and of scientific and technological research in the field of energy, as well as on international co-operation;
- to make authorities and public opinion aware of the positive contribution which biomass can offer in economic and technological terms as well as those in relation to the agricultural diversification and social progress;

- to assist the members of the Association in the exploitation of the resources, technologies and bioenergy products; in the definition of the company marketing and production strategies; in the promotion of international networks for the development and exploitation of resources and of technologies through joint ventures, transfers or technologies, data banks, seminars, publications and training activities.

The activity of the Association will be based on the three large areas of operation, i.e., communication, advisory assistance and consulting, and project co-ordination.

E.U.B.I.A. has already started its promotion activity for future large-scale bioenergy schemes, taking in particular consideration the now arising interest of oil Companies for oxygenated fuels (ETBE) produced from agricultural crops and required for the reformulation of gasolines.
Such interest is motivated by the fact that at present a complete, efficient exploitation of conventional crops (i.e. corn) and of promising sustainable new high yield crops (like sweet-sorghum....) makes the production of bio-ethanol feasible, if this can be combined and integrated with power-heat production.
Furthermore, the possibility to grow biomass resources on "set-a-side" land will make this production particularly attractive from the economic point of view. In Italy, a production cost for bio-ethanol of about 220 $/ton is anticipated.

As far as the technological aspects are concerned, E.U.B.I.A. is confident that beyond the fluidised bed steam raising cogeneration technology already established commercially, new processes and products which are likely to become viable in a no distant future are the following:

- Cogeneration IGCC systems;
- Cogeneration systems with engines / turbines fuelled by bio-crude-oil;
- Production of bioethanol and ethers (ETBE) combined with cogeneration;
- Hydrogenation of CO_2 and production of MTBE if integrated with the production of ETBE, power and heat.

For economic viability, large biomass schemes (thousands of ha) are more attractive, although the estimated potential market of small capacity (hundreds of kWe) cogeneration systems is very high. The main technological problem is how to get efficient (≈ 30%), reliable, low-cost (≈ 1500 ECU/kW) generators. An important research effort is under way now, in Europe, in this particular sector. Perspectives for success seems promising.

Innovative Research on "Bio-Crude-Oil Up-grading (Zentrum fur Sonnenenergie, Stuttgart)

The development of a new process for the improvement of the physical-chemical-functional characteristics of bio-crude-oil, derived from biomass by flash-pyrolysis, was initiated recently in the frame of a collaboration programme between the Zentrum fur Sonnenenergie / Institute fur physikalische Electronik (Stuttgart - Germany) and the CESVIT /University of Florence (Florence - Italy). This activity is financially supported by the Commission of the European Union (DG XII).
Last year preliminary Lab. experiments were carried out by a device schematically shown in Figure 2 following a procedure based on an "electronic-up-grading" treatment of distilled bio-crude-oil vapours.

This "electronic up-grading" or as better known from literature, the electronic stimulation of chemical reactions, has been successfully applied for flue gas cleaning, demolition of organic compounds, polymerisation, and other similar applications, in which the electron energy acts as a catalyst (Ref. 1-2-3). Therefore, it was considered interesting to test this technique for the upgrading of bio-crude-oil, as an alternative method to state-of-the-art techniques like hydrotreatment or zeolite synthesis.
The establisment of a "cold" plasma is necessary for the electronic stimulation of chemical reactions. In such a "cold" plasma the electron temperatures are very high (several eV or tens of eV, corresponding to several tens or hundreds of thousands K), whereas the gas atoms and molecules remain near room temperature. Plasmas matching these conditions can be produced either by electrical discharges or electron beams.
The high energy electrons, produced in this plasma, create very reactive radicals like e.g. $O^{\bullet}$, $H^{\bullet}$, $CH_3^{\bullet}$, $OH^{\bullet}$. All other excitation states can also be found, from vibrational and rotational excitation up to single or even multiple ionisation states.
The silent discharge device used in preliminary tests consisted of a pulsed high voltage supply and a fused silica tunnel with metal electrodes. Both discharge electrodes had a dielectric layer deposition to avoid direct contact with corrosive vapours. The high voltage supply delivered a peak to peak voltage up to 60 kV into a capacitive load. The frequency range reaches from 1 Hz to 1,5 kHz for continuos operation and up to 50 kHz in burst mode.

The fused silica plates each had a thickness of 2 mm and form a tunnel with 5 mm air gap, 150 mm height and 300 mm length. Fused silica has good dielectric properties and very homogeneous discharge can be obtained. Nevertheless, the main advantage is that the fused silica is not affected by thermal stress, that occurs inside the pyrolysis plant. Electrodes in preliminary tests were up to an area of 100x200 mm^2. For the test with temperature up to 100° C copper foil was used. For higher temperature applications materials like stainless steel, molybdenum or wolfram have to be used.
The isolation of the electrodes leads to a self-termination of the discharge by accumulation of electric charge on the surface of the dielectric. The accumulated surface charge reduces the electric field strength until the discharge terminates. Thus, the electric discharge consists only of the so-called breakdown phase of a spark. During this first breakdown phase high energy electrons with energies up to several tens of electron volts are generated. The maximum is estimated from literature between 7 and 10 eV (10), possibly up to 16 eV (11). This energy levels indicate, that the formation of radicals is preferred against the formation of ions.
Preliminary tests with some organic substances (hydrogen, methane acetaldehyde) performed in 1994 had shown that:

- From methane and acetaldehyde the formation of significant amounts of hydrogen in the electric discharge can be observed. Additionally traces of higher hydrocarbons were found. With hydrogen alone only a shift from the mass peak m=2 to m=1 can be observed.
- The discharge chamber used on the preliminary tests achieves the demand to produce radicals within volatile organic compounds. The power supply need optimisation for a better matching to the discharge impedance for the improvement of the efficiency.

The electronic upgrading reactor has also the advantage that it can easily be integrated within a pyrolysis plant. So the expense for additional heating for after-treatment methods is omitted. This saving will be partially compensated by the electrical power consumption of the unit. Also the synthesis gas (H_2, CO, CH_4), that originates from the pyrolysis process

can directly be used in the upgrading reactions. Since the chemical reactions sequences are complex and not yet understood, a prognosis about the additional hydrogen of hydrogen donor consumption cannot be anticipated. Another advantage is the fact, that only very inert dielectric materials (glass, fused silica or ceramics) are in direct contact with the corrosive oil. Therefore long term stability of the unit will be an attainable aim, in comparison with the relative fast poisoning of catalyst or zeolites cooking.

In 1995, a more sophisticated experimental facility had been designed and constructed at the Zentrum fur Sonnenenergie (Stuttgart) in collaboration with U.E.F. (Spain) and the waterloo University (Canada) always with the financial support of the DG XII E.C -Joule.
This facility is just starting now its operation to implement the first planned trials. It is hoped that some experimental data and results will be illustrated and discussed at the time of the Conference (end of August 1995).
In Figure 3 the flow-sheet of this experimental facility is given.

Operation of the pyrolysis reactor

Feeder
The biomass feedstock (for preliminary tests the use of wood sawdust with a particle size up to 1.5 mm is planned) is filled into the feeder tube. The feeding rate is influenced by the stirrer velocity and the nitrogen flow through the feeder tube. It should be adjusted in the range of 100 - 150 g/h.

Pyrolysis reactor
The whole pyrolysis reactor is build into a tubular furnace, which is regulated to a temperature of 500°C. The biomass is brought via a cooled tube into the pyrolysis zone, where the contact with the hot fluidized sand bed guarantees a very rapid heating of the feedstock. The resulting vapours are separated from char residues in a cyclone.

Upgrading unit
The hot vapours flow from the cyclone to the upgrading unit, which is situated in an oven with separate heating, which will usually be held at a temperature a little lower than in the pyrolysis reactor. The option is given to improve the C ÷ H ratio of the bio oil by adding methane before the oil vapours pass through the electronic upgrading unit, which works after the principle of the dielectric barrier discharge. Two different geometries will be tested - the construction with coaxial tubes and a stack with parallel plates. Both solutions are under construction in the workshop of the university.

Cooling
The hot vapours pass through a two stage ice water cooler, where they condensate in a heavy fuel fraction with high boiling point and a volatile light fuel fraction. Remaining gaseous components could be sampled (e.g. in a gas mouse) for further analysis.

In autumn 1995, if the experimental results from Z.F.S. - Stuttgart will be considered satisfactory, an "electronic up-grading unit of about 50 kg (B.C.O. vapours/hr will be constructed and assembled on the U.E.F. Galice flash-pyrolysis plant and/or on the CIRO Facility (ENEL). The budget for the construction and short experimentation is already provided. This facility should be adequate for the assessment of the techno-economic feasibility and potentialities of this innovative refining process for the bio-crude-oil.

Conclusion

The perspectives for economic exploitation of biomass resources in the E.U. are promising. Power generation and the integrated production of electricity and oxygenated fuels seems the most interesting short-term market products.
To accelerate the penetration of bioenergy into the energy mix, three actions are needed:

- an increased effort of R&D for modern, efficient, reliable conversion processes and technologies;
- The participation of the market forces (oil Companies, Utilities, etc.) to the development of the complex bioenergy sector and to its deployment;
- the promotion of a real bioenergy industry devoted to the commercialisation of efficient, low-cost (standardised), environmentally friendly technologies and systems.

References

1. B. Eliason, M. Hirth, U. Kogelschatz, "Ozone Formation in Dielectric Barrier Discharge in Oxygen", C.J. Timmermans (Editor): Proceedings of the 7th International Symposium on Plasma Chemistry, Endhoven, Jul. 1985, pp.339-344.
2. A. Scheurmann, W.H. Bloss: "Verfahren zur Entstickung und Entschwefelung von Verbrennungsabgasen mittels Corona-Entlandung", PEF-Bericht, Kernforschungzentrum Karlsruhe GmbH, KfK-PEF 47, Nov. 1988.
3. G.H. Ramsey, N. Plaks, C.A. Vogel, W.H. Ponder, L.E. Hamel: "The Destruction of Volatile Organic Compounds by an Innovative Corona Technology": 8th Symposium on the Transfer and Utilisation of Particulate Control Technology, San Diego 1990.
4. A.V. Bridgewater: "An Update on Biomass Pyrolysis for Liquid Fuels"; Biomass for Energy and Industry, 7th EC Conference (1992), Ponte Press, pp. 166-176.

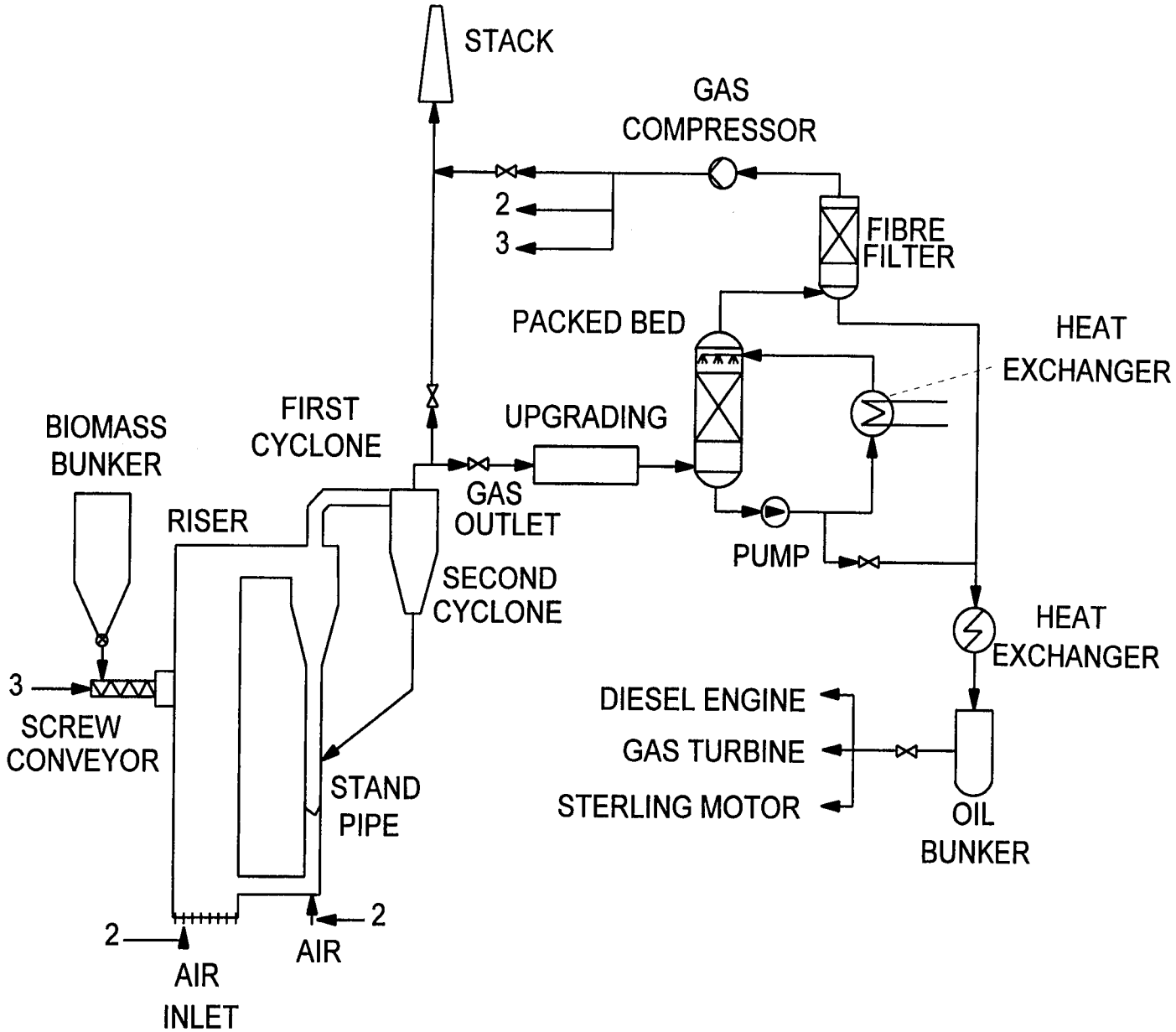
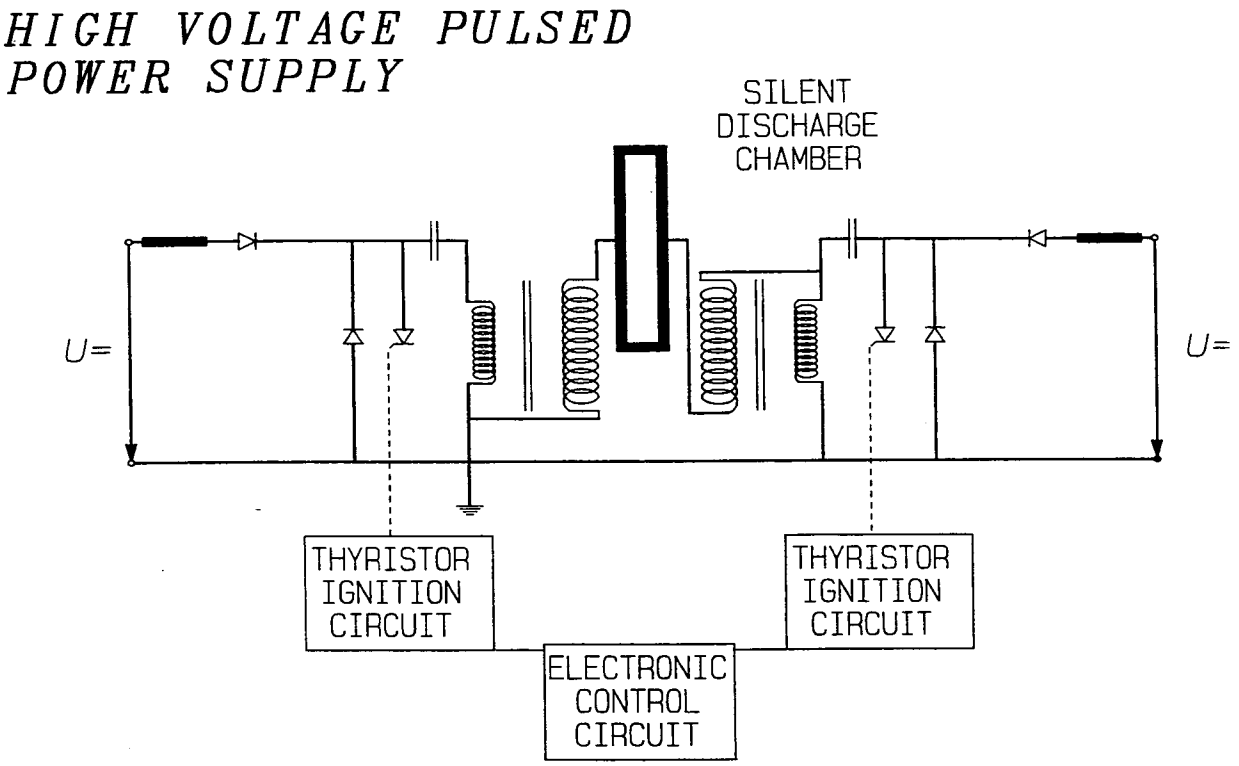


Figure 1 - CIRO Experimental facility (ENEL - CRT) in Livorno



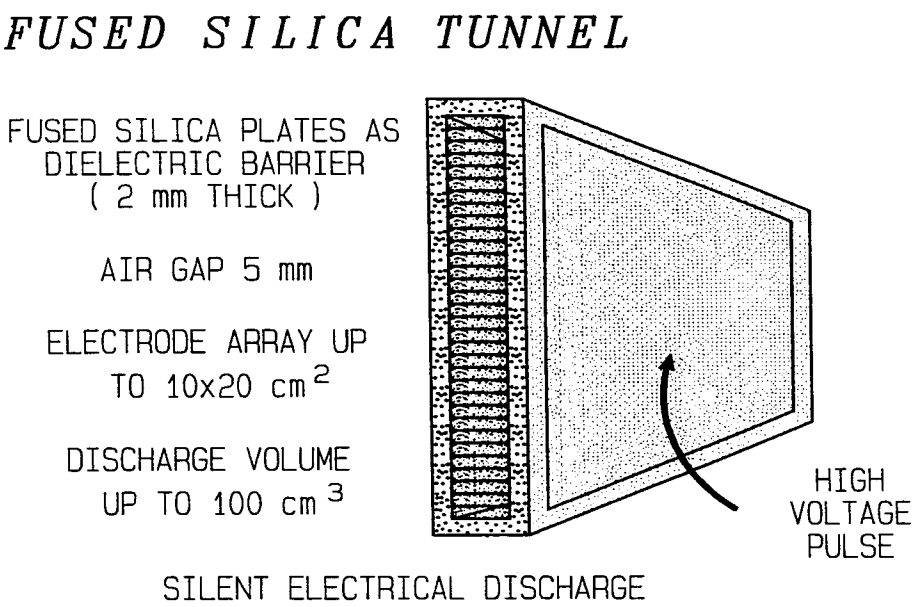


Figure 2 – DEVICE FOR "ELECTRONIC UP-GRADING OF BIO-CRUDE-OIL

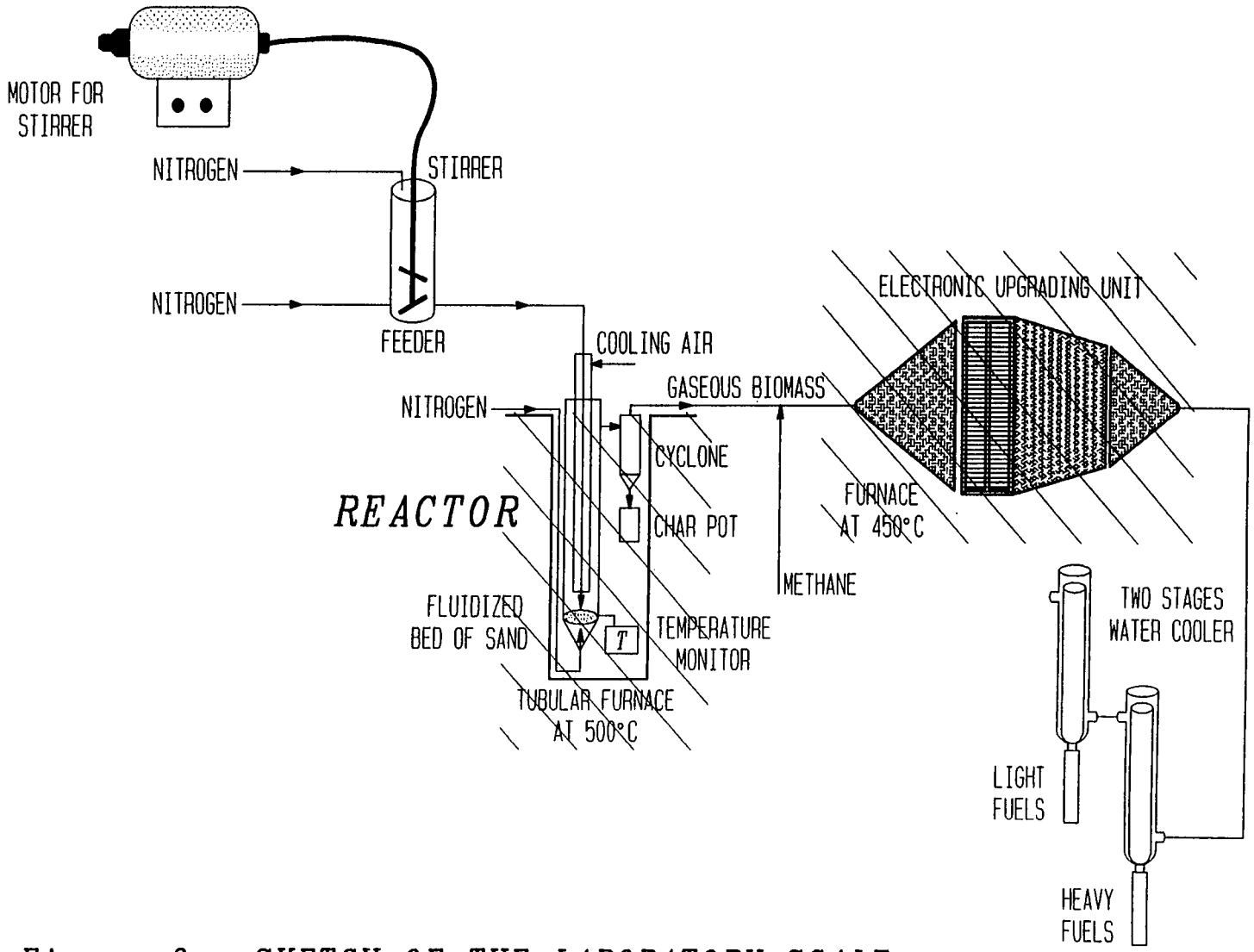


Figure 3 – SKETCH OF THE LABORATORY SCALE PYROLYSIS PLANT WITH UPGRADING UNIT

DEVELOPMENT OF END-MARKET USES FOR SLUDGE DERIVED OILS

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Abstract

Pyrolytic processes can be utilized to convert organic materials into solid and liquid fuels. The economic viability of most of these processes will be greatly affected by the end-use market for the oil, in terms of both a guaranteed outlet for the product and the potential revenue. Since these oils are not conventional products, significant effort may be required to establish firm markets.

The "Oil from Sludge" (OFS) technology developed by the Wastewater Technology Centre (WTC) has been shown to produce oil yields ranging from 10 to 30% (on a dry weight basis) from dried sewage sludge. Efforts over the last several years have focused on developing high-value, non-combustion uses for the oil, primarily in the asphalt industry. Two applications which have shown significant promise are as an asphalt antistripping agent and as an additive for recycling aged asphalt. This paper will focus on the antistripping application.

This research has been a joint effort of the WTC, the Canada Centre for Mineral and Energy Technology, the National Research Council of Canada and SNC-Lavalin. The program included preliminary characterization of the sludge derived oil (SDO), laboratory tests to evaluate its potential as an antistripping agent and to determine the effect of SDO on asphalt performance factors, field tests to evaluate engineering properties and a highway test trial on an operating highway.

The study concluded that SDO is an effective antistripping agent and provides protection against moisture induced damage comparable to that achieved with commercial additives. The addition of SDO did not adversely affect the performance of asphalt concrete but did result in increased workability and compaction, and increased resistance to damage by low temperature, rutting and fatigue.

Introduction

Environmental stewardship is based to a large extent, on the concepts of reduction, reuse and recycling. Pyrolysis is a technology which has the potential to recycle a wide variety of materials ranging from waste plastics to biomass, into some form of liquid oil. The implicit assumption is that any oil produced will have some inherent market value and therefore the process must be a positive one. This is not necessarily true. Oils produced by the pyrolysis of waste materials generally have unique properties and may not be acceptable for conventional end uses without some additional testing or modifications. If a practical outlet for the oil cannot be found, then the original waste disposal problem will not be solved but simply transformed from one material to another. Similarly, the justification for pyrolysis is often based on optimistic projections of the potential revenue from the use or sale of the oil. If either the projected revenues or the security of the markets are not realistic, then the overall economics of the technology may need to be completely re-evaluated. Assuming that the pyrolytic technology is technically sound, the establishment of markets for the end products is one of the most important components to commercial success.

Oil from Sludge Technology

The treatment and disposal of sludge from wastewater treatment facilities is becoming a major issue for large municipalities throughout the world. Costs are significant and acceptable alternatives are limited. Agricultural utilization of sludge or biosolids is being heavily promoted by both public and government organizations. However, for some cities, this approach is not practical, either because of the quality of the sludge or the lack of a market for the large quantities of material that must be disposed of. Incineration can be a technically attractive method for reducing the volume of material for ultimate disposal but currently is not perceived, by either the public or the regulators, as an environmentally attractive technology. Pyrolysis of sewage sludge has the potential to accomplish similar volume reduction and produce an end-product that can be recycled in a more efficient and flexible manner than waste heat from an incinerator.

The Wastewater Technology Centre (WTC) has developed a pyrolytic, low temperature, thermal conversion process known as the "Oil from Sludge" (OFS) technology that produces liquid and solid fuels from sewage sludge. A schematic of the process is presented in Figure 1 and a comprehensive description of the technology is available in the literature (Campbell and Martinoli, 1990). A bench-scale reactor (1kg/h capacity) and a pilot plant (40 kg/h capacity) have been used to develop the data base. The fundamental components are similar for both systems and are outlined below. Dried sludge is heated, in the absence of oxygen, to a temperature of approximately 450°C in a reactor. The organic fraction of the sludge is volatilized into the gas phase leaving a solid residue or char. In the secondary portion of the reactor, the gas is brought into contact with the char in a manner designed to maximize gas/solid contact. The char is discharged to storage and the vapours are condensed and passed through a decanter or centrifuge to separate the oil and water phases. Table 1 shows typical performance data achieved with the bench and pilot scale systems when processing raw sludge. In an integrated full-scale system, the conceptual design includes combusting the char, reaction water and non-condensible gases in a fluid bed furnace to control environmental

emissions and to provide heat for drying the sludge. The oil represents the net energy produced by the process which is then available for external use or sale.

Table 1. Performance Data for Raw Sludge

	Bench	Pilot
Feedrate (kg/h)	0.75	24
Temperature (°C)	450	450
Solids Retention Time (min)	20	20
OIL		
Yield (%)	22-46	27
Viscosity (cSt)	23-168	62
Calorific Value (MJ/kg)	33-38	31
CHAR		
Yield (%)	40-66	43
Calorific Value (MJ/kg)	7-23	16
NON-CONDENSIBLE GAS		
Yield (%)	3-12	9
Calorific Value (MJ/kg)	2-9	5
REACTION WATER		
Yield (%)	3-15	15

It should be stressed that while the primary objective of the OFS technology is to provide an environmentally acceptable sludge management alternative, the establishment of high-value markets for the end products will also enhance its economic competitiveness. The original intent was to use the oil as either an industrial fuel or as a diesel fuel. Although the option of producing an industrial fuel is technically viable, the potential revenue is relatively small. In terms of using the oil as a diesel fuel, some problems were encountered with the miscibility of the two materials and it was identified that upgrading would be required to address this issue (Boocock et al, 1988). In 1989, a decision was made to investigate alternative end-uses which did not require upgrading, based on consideration of the fundamental characteristics of the oil.

The resulting program included preliminary characterization, laboratory and field investigations and ultimately a highway pavement test strip. The experimental work was conducted at either the Energy Research Laboratory of the Department of Natural Resources Canada (CANMET) or the National Research Council's Institute for Research in Construction (NRC). The program was funded jointly by the WTC, SNC-Lavalin, CANMET and NRC.

Preliminary Characterization

The preliminary characterization was conducted by CANMET and included elemental, compound type and functional group analyses. The elemental analysis and physical properties are presented in Table 2. The oil was also separated into various fractions based on boiling point and the individual fractions analyzed. The compound type analysis for two of the fractions is shown in Table 3. The conclusions of the study were that the average chemical structure was that of a large complex molecule, with a hydrocarbon skeleton and functional groups containing nitrogen (pyrroles, amides) and oxygen (esters). Such structures indicate protein origins, tend to be very polar and especially because of the abundance of nitrogen groups, suggested utilization in asphalt.

Table 2. Elemental Analysis and Physical Properties

Physical Properties		Elemental Analyses (%)	
Density, 15°C, kg/m^3	1002	C	72.4
Heat of combustion, MJ/kg	35.3	H	9.9
Viscosity, 40°C, cSt	330	N	6.4
Pour point, °C	0.0	O	10.8
Flash point, °C	65	S	1.1

It was determined that the large nitrogen content could be exploited for adhesion improvement in road asphalt either as an antistripping agent or as a rejuvenating agent for recycling aged asphalt. Although both approaches showed significant potential in preliminary trials, subsequent development work focused on the antistripping application as the most desirable end use.

Table 3. Compound Type Analysis

Compound Type, %	+150°C	+250°C
Asphaltenes	34.7	38.7
Naphthene Aromatics	3.9	4.1
Polar Aromatics	31.1	31.0
Saturates	10.1	10.3
Material not desorbed with methanol and trichloroethylene	20.7	15.9

Laboratory Investigations

Asphalt road pavement consists of a mix of aggregates and 5 to 8% of asphalt cement.

Asphalt cement does not adhere well to certain aggregates and the separation of these two materials is a major cause of pavement failure. In order to utilize aggregates of this nature, transportation agencies specify the use of approved antistripping agents to improve adhesion. The high polar component of the sludge derived oil (SDO) suggested that SDO would be an effective alternative to commercially available antistripping agents.

An extensive research program to evaluate the potential of SDO as an antistripping agent was conducted by CANMET. A summary of the results of this study has been reported in the literature (Clelland et al, 1993). The program included evaluation of the compatibility of SDO with conventional asphalt cements, the resistance to stripping of SDO amended asphalt and the impact of SDO on the performance properties of asphalt cement.

SDO was determined to be compatible with asphalt cement based on the high ductility of SDO and commercial asphalt blends. Incompatibility in an asphalt blend causes a drastic decrease in ductility that is easily detected.

The resistance to stripping was measured using static immersion tests in which a 95% retained coating is normally required to meet specifications. Test variables included the type of asphalt (hard or soft), the source of the SDO, the addition rate of SDO and comparison to commercial antistripping agents. Typical results are shown in Figure 2 where the retained coating increases from less than 60% without SDO to approximately 95% for both the soft (150/200) and the relatively hard (85/100) penetration asphalt at an SDO concentration of 3%. The performance of SDO was comparable to commercial antistripping agents but slightly higher dosages were required.

The impact of SDO on other properties of asphalt cement was evaluated by measuring performance parameters such as penetration, viscosity, ductility, etc. Thin film oven tests and Marshall testing were also conducted on the various samples of SDO amended asphalt. In general, the addition of 3% SDO did not result in any significant deterioration in asphalt performance and all applicable specifications could be achieved. The addition of 5% SDO did result in increased loss of volatiles in the thin film oven test and softened the resulting asphalt. The SDO Marshall stability (strength test) was found to be comparable to that of the commercial additive.

Subsequent to this phase of the study, a number of process changes were tested with the WTC pilot plant. The SDO samples from these trial runs were supplied to CANMET to determine if the processing modifications had a measurable impact on the antistripping properties of the oils. A similar program to that described above was conducted on these samples. Figure 3 shows the antistripping performance of four of these samples when tested with two different asphalt cements. With the exception of one sample, acceptable performance was achieved with the addition of 3% SDO. At 3% SDO concentration, modification of the asphalt cement's properties (penetration, viscosity and weight loss after thin film oven test) was marginal.

In 1992 the National Research Council (NRC) of Canada's Institute for Research in Construction became involved in the program. It was identified that, in order for SDO to be accepted for use in the asphalt pavement industry, highway authorities would require

additional information related to the effect of SDO on a variety of performance characteristics. The research program conducted by NRC was designed to develop an effective SDO application technique, to optimize the application rate, to compare performance to commercial additives and to determine the impact of SDO on low temperature damage, permanent deformation and fatigue cracking of asphalt pavement. The investigation was conducted in two phases; a laboratory phase followed by confirmation under actual field conditions.

There are two fundamental methods of adding an antistripping additive to asphalt pavement; it can either be mixed with the asphalt cement before batching with the aggregate or it can be added directly to the aggregate before adding the asphalt cement. The impact of the SDO application method was evaluated by conducting indirect tensile strength tests on specimens that had been moisture conditioned (soaked) at 60°C for 2 days and monitoring for evidence of stripping. The results are presented in Table 4.

Table 4. Influence of SDO Application Technique

Moisture Conditioning	Ave. Strength (kPa)	Change in Ave Strength
Regular Mix		
Control (dry)	557	
Two day soaking	514	8% decrease
SDO Added to Asphalt		
Control (dry)	444	
Two day soaking	461	4% increase
SDO Added to Aggregate		
Control (dry)	502	
Two day soaking	519	3% increase

Following the two day soaking period, the regular mix showed signs of stripping. Stripping in the mix with SDO added to the asphalt was minimal while no evidence of stripping was observed when the SDO was added to the aggregate. This was consistent with the tensile strength results. The regular mix lost 8% of its strength following moisture conditioning while both SDO mixes showed a slight increase in strength. In addition to the stripping observations, the mix with the SDO added to the aggregate showed higher strength in both the dry and moisture conditioned samples than when the SDO was mixed with the asphalt cement. Additional tests confirmed that superior results could be achieved by adding the SDO to the aggregate.

The effectiveness of SDO was compared to a commercial antistripping agent on the basis of short-term (2 day) and long-term (7 day) exposure to moisture conditioning (soaking) as well as observation of any visual stripping. The results are presented in Table 5.

The regular mix specimens showed evidence of significant stripping after the long-term moisture exposure tests. The commercial additive reduced the amount of stripping while with the SDO treated mix, no evidence of stripping was observed. These observations were again consistent with the tensile strength results. The regular mix showed significant loss in strength following moisture conditioning. The commercial additive treatment showed a lower loss in strength but there was still significant loss in strength after long-term moisture exposure. No impact of moisture

Table 5. Comparison to Commercial Additives

Moisture Conditioning	Ave Tensile Strength (kPa)	Change in Ave Strength
Regular Mix		
Control (dry)	974	
Short term (2 days)	845	13% decrease
Long term (7 days)	748	23% decrease
Mix with Commercial Additive		
Control (dry)	926	
Short term (2 days)	888	4% decrease
Long term (7 days)	758	18% decrease
Mix with SDO		
Control (dry)	848	
Short term (2 day)	864	2% increase
Long term (7 day)	867	2% increase

conditioning, either short or long term, was measured with the SDO treated samples. Based on these results, SDO was more effective than the commercial product in reducing the moisture susceptibility of the mix.

The final component of the laboratory investigation evaluated the impact of SDO on the performance of asphalt pavement with respect to low temperature, permanent deformation (rutting) and fatigue. Tensile tests conducted on samples conditioned at temperatures ranging from -5°C to -35°C concluded that SDO did not influence low temperature performance of typical asphalt concrete mixes. The potential for rutting was measured using a uniaxial compression test. Softening of the mix as a result of adding SDO was anticipated to cause increased rutting of the treated mix, however, the test results indicated that the SDO treated mix sustained less permanent deformation than the regular mix. It was suggested that softening of the mix may have contributed to better compaction of the SDO mix under laboratory conditions. No reduction in fatigue life was observed with the SDO treated mix.

Field Investigations

Laboratory tests are a useful tool to evaluate the impact of changing variables under controlled conditions. However, the absolute value of measurements obtained on asphalt concrete samples produced in the laboratory may not be representative of the performance of pavements in the field. Factors which are difficult to evaluate in the lab include the method of field placement, curing under ambient conditions, exposure to weather and uncontrolled loading conditions. In an attempt to address these issues, two sections of experimental road were constructed on NRC property in Ottawa. The 25 metre sections were laid side-by-side and consisted of a regular mix and an SDO modified mix. Cores were taken at specific time intervals and tested in the laboratory.

The results from the field testing essentially confirmed the earlier findings in the laboratory. Moisture damage analysis conducted on conventional and SDO-modified cores proved the effectiveness of SDO to provide long-term resistance to stripping. The addition of SDO to the mix led to improved resistance to permanent deformation, a higher resistance to low temperature induced stresses and improved resistance to fatigue. The improved resistance to permanent deformation was again somewhat surprising based on the expectation that the SDO would soften the mix. The SDO appeared to provide a lubricant effect which enhanced aggregate movement and reorientation during compaction producing a favourable structure which proved to be denser and more stable than that of the regular mix.

Highway Test Strip

The final-step in receiving approval from transportation authorities for the use of new materials in the manufacture of asphalt pavement, is generally the construction of a test strip of highway which will be subjected to ordinary traffic conditions. The Ministry of Transportation of Quebec (MTQ) was approached with a request to construct a highway field test using SDO amended asphalt. Laboratory trials, conducted by the MTQ, to assess the performance of SDO with the proposed aggregate were positive and approval was given for the field test.

The field site was constructed in September 1994, in L'Annonciation, Quebec, on Highway 117. This road had a history of stripping problems and was noted for continuous heavy traffic, including logging trucks. During the trial, approximately 370 tonnes of asphalt cement were utilized to construct almost one half a kilometre of highway surface. Samples of the mix were collected randomly by a third party under contract to MTQ, for QA/QC purposes.

There were no visual differences between the completed section of SDO amended pavement and the conventional pavement. Two observations were noted during the placement of the SDO section. The asphalt concrete containing SDO showed a much improved workability for the roller operator (compaction) and other paving crew personnel (handling with rakes). The roller driver observed that the road with SDO asphalt did not "crack" while the conventional pavement did. As well, there were significant amounts of white smoke released by the paving machine during laying of the SDO asphalt. This smoke was attributed to the presence of water and low boiling

organics in the SDO used. Redistilling the SDO under more controlled conditions essentially eliminated the presence of smoke in a subsequent small trial.

Since the site was an operating highway, traffic was allowed on the pavement immediately following completion of compaction. Within minutes of placement, fully loaded logging trucks were observed on it. A visit to the site 6 weeks after completion indicated no observable differences between the SDO pavement and the conventional portion. The performance of the test strip will be evaluated during the summer of 1995.

Conclusions

The comprehensive development program outlined in this paper has been successful in documenting the potential of using SDO as an antistripping agent in the production of asphalt cement.

SDO provides a level of protection against moisture damage that is equivalent to or greater than commercial products currently approved by transportation authorities.

The addition of SDO provides supplementary benefits in terms of increased compaction and workability, and increased resistance to damage by low temperatures, rutting and fatigue.

The anticipated modifications from conventional construction methods such as adding the SDO to the aggregate rather than the asphalt, do not appear to present any significant practical problems.

Future Work

Negotiations are under way with the Ministry of Transportation of Ontario (MTO) to establish a similar highway test trial in Ontario using a different aggregate. A program to develop appropriate techniques for the utilization of SDO for recycling aged asphalt cement will be pursued.

Acknowledgements

The authors wish to acknowledge the support of the contractors on the various components of the program and the financial support provided by the Federal Panel on Energy Research and Development.

References

Campbell, H.W. and D.A. Martinoli (1990). A Status Report on Environment Canada's Oil From Sludge Technology, presented at WPCF Specialty Conference "Status of Sludge Management in the 1990's", New Orleans.

Clelland, I., J. Houde, H. Sawatzky and B.A. Farnand (1993). A Non-Fuel Market for Sludge Derived Oil, presented at the 15th Canadian Waste Management Conference, Saint John, New Brunswick.

Boocock, D.G.B., F.A. Agblevor, F. Chirigoni, T. Crimi, A. Khelawan and H.W. Campbell (1988). The Mechanisms of Sewage Sludge Liquefaction During Thermolysis, presented at the International Conference on "Research in Thermochemical Biomass Conversion", Phoenix, Arizona.

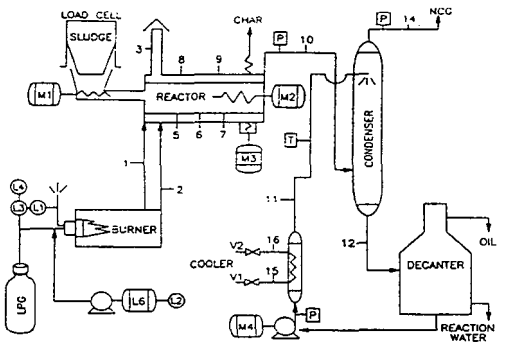

Figure 1. Schematic of pilot-scale converstion system.

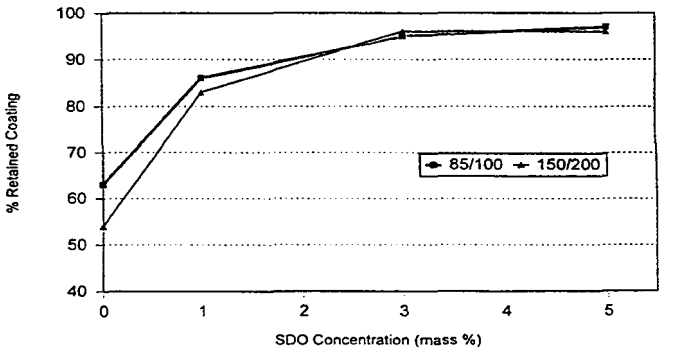

Figure 2. Antistripping by static immersion.

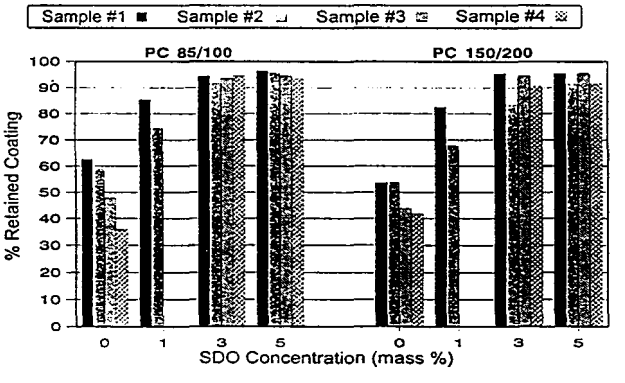

Figure 3. SDO antistripping properties

RECYCLING OF TREATED WOOD POLES

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Abstract

There are approximately 150 million utilities poles in service in North America. Of the 3 million poles removed from service each year, many poles still contain a sound and structurally intact core and only the outer layer has deteriorated. Since most of the old poles are treated with either pentachlorophenol or creosote there are limited disposal options available to pole users. The practice of giving old poles away to farmers or other interested parties is falling into disfavour since this practice does not absolve the utility of the environmental liability associated with the treated wood.

TWT has commercialised a thermolysis (Pyrolysis) based process capable of removing oil based preservatives from treated wood. The patented process involves: the shaving of the weathered pole exterior; the rapid distillation of oil based preservatives in an oxygen depleted environment; condensation of the vapours; and separation of liquids. TWT has constructed a 30,000 pole per year facility east of Calgary and has provided recycled poles for the construction of two power lines now in use by TransAlta Utilities Corporation, Canada's largest investor owned electric utility.

TWT has tested two thermolysis (Pyrolysis) technologies and has determined that contact thermolysis using a heated auger design performed better and with less plugging than a fast fluid bed reactor. The fluid bed reactor is prone to coke formation and contamination of the oil by fine char particles.

Residual PCP concentration in the shavings was reduced from 9500 ppm to 10 ppm. Leachate testing on the char yielded a PCP concentration of 1.43 ppm in the Leachate, well below the EPA standard maximum of 100 ppm.

Introduction

The recycle and reuse philosophy continues to gain acceptance in the industrialised world. New industries are finding profitable niches using wastes streams from other industries. TWT Wood Products was formed to take advantage of a pending disposal problem in the treated wood industry. Treated wood has been used in construction for many years. Coal tar derivatives commonly referred to as creosote found widespread applications in the manufacturing of railway ties and bridge timbers and was the preservative of choice for most utility poles put into service prior to 1960. Since 1960 pentachlorophenol has replaced most of the creosote utility poles. Pressure from environmental groups and more stringent government regulations limited the use of creosote and PCP to industrial applications only (i.e. ties and poles). Water based heavy metal preservatives have totally replaced the organic preservatives in consumer wood products. The familiar green wood found at most lumber years is pressure treated with water based copper chromium arsenate (CCA). The only oil based treating solution available in the domestic market is zinc or copper napthanate and is recommended to treat saw cuts and other non treated exposed surfaces.

All preservatives have one thing in common, that is how to dispose of treated wood once it has been removed from service. Landfilling is the obvious choice in many jurisdictions but it is becoming more expensive and less acceptable politically. Wood is a low density waste and does not compact as readily as regular municipal waste and some landfills are limiting the disposal of wood in landfills. Furthermore, the landfill operator normally only stores the waste and does not take title to the waste. If for some reason treated wood was to be reclassified as a hazardous material, then the pole owner, in this case the utility, could be responsible for its removal from the landfill and subsequent disposal. The incineration of PCP and CCA treated wood is not recommended or permitted in many jurisdictions because of the potential for formation of dioxins, furans, and free arsenic.

As utilities move towards deregulation and search for means to reduce capital and inventory costs, recycling of salvaged poles becomes more attractive. TWT has demonstrated that utility poles can be recycled and provided back to the utility for less than the cost of a new pole and thereby reduce the cost of line installations. For example on a line constructed in the fall of 1994 TransAlta Utilities Corporation saved approximately $30,000 on the cost of 41 poles. In a competitive market, these savings are passed onto the consumer resulting in equivalent service at a reduced cost.

TWT Wood Products Inc. was formed in 1993 specifically to develop disposal methods for treated wood. The initial partners in the venture were Worthing Industries Inc., a firm specialising in environmental technology and TransAlta Utilities Corporation, Canada's largest investor owned utility. Worthing has recently signed a letter of intent to purchase TransAlta's shares of TWT. Part of the sale/purchase agreement is a contract for TWT to supply TransAlta with recycled poles.

Age and Life Span of Utility Poles

The useful life of a treated wood pole can exceed 40 years, however relatively few poles are retired because they have reached their age limit. Bell Canada reported that poles are replaced early because they are too small to carry the required equipment (Millette, 1994). The average age of poles in service at Bell Canada was 23 years and in recent years the average has dropped to about 12 years (Millette, 1994). TWT has not conducted a statistical analysis of poles delivered to its plant, but it is safe to say that may poles where the brand is still visible were manufactured in the late 1970 to early 1980. Poles recycled in 1976 by Bell Pole Company for TransAlta Utilities were removed from service in the fall of 1994. These poles have been refurbished and returned to service for a third time. Refurbishing reduces the size and class of a pole and hence it is returned to service in lighter capacity than its first or second service period. Refurbishing ensures that the pole will reach its projected life span of fifty years. Furthermore the retreatment of the pole should kill any incipient rot that may have gone undetected in the inspection process and a recycled pole should last as long as a new pole. By extending the life of a utility pole beyond its initial projected service life fewer trees will be cut for poles and the forest will have sufficient time to grow new trees for poles.

Utility Pole Management

The management of poles arriving at TWT's yard is shown in Figure 1. Prior to inspection all poles are scanned for nails, staples, bolts and hardware. A standard metal locator is used to detect metal that could damage the peeler or saws. There is a complete spectrum of pole quality arriving at the plant. Some poles can be returned to service after inspection, while others are too rotten or damaged to warrant additional work. About 35% of the salvaged poles are suitable for reuse as utility poles. Of the remaining 65% about 35% is being cut into lumber for exterior uses. The remaining 30% is peeled and sales are developing in the agricultural and off shore markets.

Poles that can be recycled are peeled to remove the weathered surface. Generally less than 1 cm is removed from the pole exterior and no attempt is made to remove all of the treated layer. Thick sapwood species like pine have preservative penetrations in excess of 2.5 cm, while thin sapwood species like western red cedar have penetrations in the range of 1 cm. Only enough wood is removed from the pole to expose sound fibre and no attempt is made to remove all of the treated portion.

Shavings from the pole peeler are conveyed to the thermolysis plant were the treating solutions are distilled and condensed. The pole is then retreated and returned to service. Wood too small for utility poles is used in construction of pole barns, sheds, fence posts, and landscaping. The cleaned shavings are sold to a concrete additive firm for use in the manufacture of speciality concrete. Pildysh & Associates (a local Calgary, Alberta firm)

have developed a patented process whereby the additive can increase the percentage of flyash used in the manufacture of cement. Fly ash is a by-product of thermal power generation and its incorporation into cement reduces the cost of the cement and solves a fly ash disposal problem.

TWT has succeeded in finding markets for all the by-products of pole recycling. A contract has been signed with a pole treating company to purchase the recovered preservatives for reuse in the manufacture of treated wood. Wood has its highest value as a pole and offsets the small margins available for the other products. With the exception of the wood for poles, any revenue generated by the char and the recovered oil contributes positively to the bottom line and offsets what would otherwise be a disposal cost. TWT has completed a test program to saw non utility grade wood into dimensioned lumber. The quality of the wood exceeded expectations and there is a strong market for dimensioned lumber in the agricultural markets.

Thermolysis Process

Thermolysis is used as a synonym of Pyrolysis. For a number of reasons the term pyrolysis has a somewhat tainted reputation in western Canada. For marketing reasons it was decided to use a new term with a similar meaning.

Fast Thermolysis

The initial called for the conversion of TWT's mobile fast thermolysis plant into a mobile preservative recovery facility. The thermolysis process has been described in detail elsewhere (Fransham, 1992). The process uses a fluidized bed design with heated recycle gas as the fluidizing gas. The plant was designed to operate with a bed temperature of 550 degrees C. PCP vaporises at 310 degrees C and the operating temperature was reduced to 330 degrees C. Initial testing on western red cedar shavings were successful and the PCP concentration in the char was reduced to 2 ppm from 10,000 ppm. The shavings were slightly charred and chemical analyses indicated the presence of some pyrolysis products. Carry over of char from the cyclone into the captured oil resulted in the sludge formation and pump blockages. The addition of filter elements eliminated all stoppages due to sludge for western red cedar. There were however blockages in the recycled gas lines due to coke formation. This aspect is discussed in detail in a following section.

In October 1994 TWT received a truckload of southern yellow pine poles from Tennessee. The poles were peeled and a test run was conducted. The test run was far from satisfactory. A viscous resinous sludge was formed that upon cooling became a vitreous solid. Virtually all product recovery lines became totally blocked after one hour of running. It was clearly evident that present design would not stay running on resinous southern yellow pine. Since southern yellow pine is the dominant species used for poles

in the southern US. it was imperative that a method be located to treat salvaged yellow pine poles.

Contact Thermolysis

Bench scale testing during a preliminary feasibility study showed that a clean oil could be evaporated from shavings using heat and a nitrogen purge gas. While the amount of sample tested was small (less than 50 grams) there was no evidence of sludge formation or coking. Based on these results, again with western red cedar, it was decided that a contact thermolysis design using a slow rotating auger could solve some of the sludging and coking problems. Heated augers have been used in the agricultural industry for many years to prepare feed and auger pyrolysis of sewage sludge has been described by Campbell (1991). Since the auger system can operate without recycle gas, it was felt that the sludge problem could be eliminated if the gas velocity could be reduced. A recycle gas pump was added to the system to test the effects of gas velocity on performance. The recycled gas was heated in the oven to 350 degrees prior to entering into the auger section.

A 2 kg/hr bench scale unit was designed and built during the winter of 1994-95. A flow sheet for the bench scale apparatus is shown in Figure 2. In simplistic terms a stainless steel auger is heated to 350 degrees C in a direct fired furnace. A blower removes the vapours from the auger section to a spray tower where first stage condensation occurs. The temperature in the spray tower is maintained at 120 degrees C to ensure that all water remains in the vapour state. A second heat exchanger cools and condenses the aqueous phase. Excess gas is flared through the furnace and the standard volume of gas is moved through the system by a blower. The entire process is simpler than the fluidized bed design used previously and given the relatively low volume of gas recycled through the system, there is less char carry over into the oil phase.

Results and Discussion

Operations

TWT's fast fluid bed thermolysis unit was designed to operate at 550 degrees centigrade with a recycled gas flow of approximately 350 cubic metres per hour. The gas velocity gives a reactor residence time of under one second. Prior to entering the reactor the recycled gas is heated indirectly in a furnace to a temperature of 770 degrees centigrade. For operation as a preservative distillation unit the furnace parameters remain the same but the quantity of feed is increased to reduce the reactor temperature to the pentachlorophenol distillation temperature of 350 degrees centigrade.

Given the above mentioned operating parameters, it was possible to reduce the concentration of PCP in the wood shavings from 10,000 ppm to under 3 ppm. However,

continuous operation was not possible because of severe coking in the quench tower. The quench tower consists of a 25 cm diameter by 50 cm high cylinder packed with Pall Rings. Within eight hours of operation the top surface of the pall rings became encrusted with a vitreous like, black, porous carbon material. Recycled gas flow was reduced and hot reactor gas was forced into the main feed hopper and resulted in combustion of the wood shavings in the hopper.

Furthermore, carry over of fine char into the oil resulted in the formation of a sludge at the bottom of the product tanks. Since this sludge is rich in PCP, it required disposal at a hazardous waste processing facility at a cost of over $400. per barrel.

The bench scale unit performed satisfactorily only when recycled gas was not used to purge the auger section. When recycled gas was used, there was a rapid plugging of the tube between the auger and the spray tower. The conclusion drawn here is that the coke formation is directly related to the flow of recycled gas in the auger section. Further tests if planned to confirm the relationship between coking and gas velocity.

Results

The results shown in Figure 3 are for southern yellow pine. The October tests were run on the larger fluid bed reactor and samples were obtained before the total blockage of all product collection pipes. The December and January tests were run on the bench scale contact thermolysis unit. There are two interesting trends in the data. The first is the apparent loss of penta in the stored samples. Samples were stored in 20 litre plastic pails with tight fitting lids. Between October and January the initial concentration of PCP decreased from 9970 ppm to 1100 ppm. The pre-thermolysis wood was previously hammer milled to a size fraction approximately 1 mm in thickness and 10 mm in length. The PCP is: either evaporating during storage; photodegrading or bio-degrading.

The second trend is the reduction in PCP concentration in the char. The PCP concentration in the post thermolysis char was systematically reduced from 1100 ppm to 10.6 ppm through changes in residence time and temperature. A toxicity characteristic leaching procedure (TCLP) test was performed on the shavings and yielded a value of 1.43 ppm, well below the EPA requirement of 100 ppm.

Conclusion

TWT technologies has demonstrated the technical feasibility of removing oil based wood preservatives from salvaged utility poles. A demonstration facility has been constructed near Calgary, Alberta, Canada and has been recycling salvaged utility poles. Two power lines have been constructed using recycled poles and the utility and field crews are satisfied with their performance.

Fast pyrolysis with high recycle gas velocities appears to cause coking and sludge formation problems. The formation of theses unwanted materials has been solved by switching the technology to a heated auger contact thermolysis process.

References

Campbell, H.W., Converting Sludge to Fuel - A Status Report, Biomass Thermal Processing, Proceedings of the first Canada/European Community R&D Contractors Meeting, Ottawa, 1990, pp78 - 85..

Fransham, Peter, Fast Pyrolysis Demonstration Plant, Biomass Thermal Processing, Proceedings of the first Canada/European Community R&D Contractors Meeting, Ottawa, 1990, pp74 - 77.

Millette, Louise, Les Problematiques Associees au Bois Treaite Chez Bell Canada, Proceedings of a conferences sponsored by The Canadian Institue of Treated Wood, Ottawa, Ontario, June 20-21, 1994.

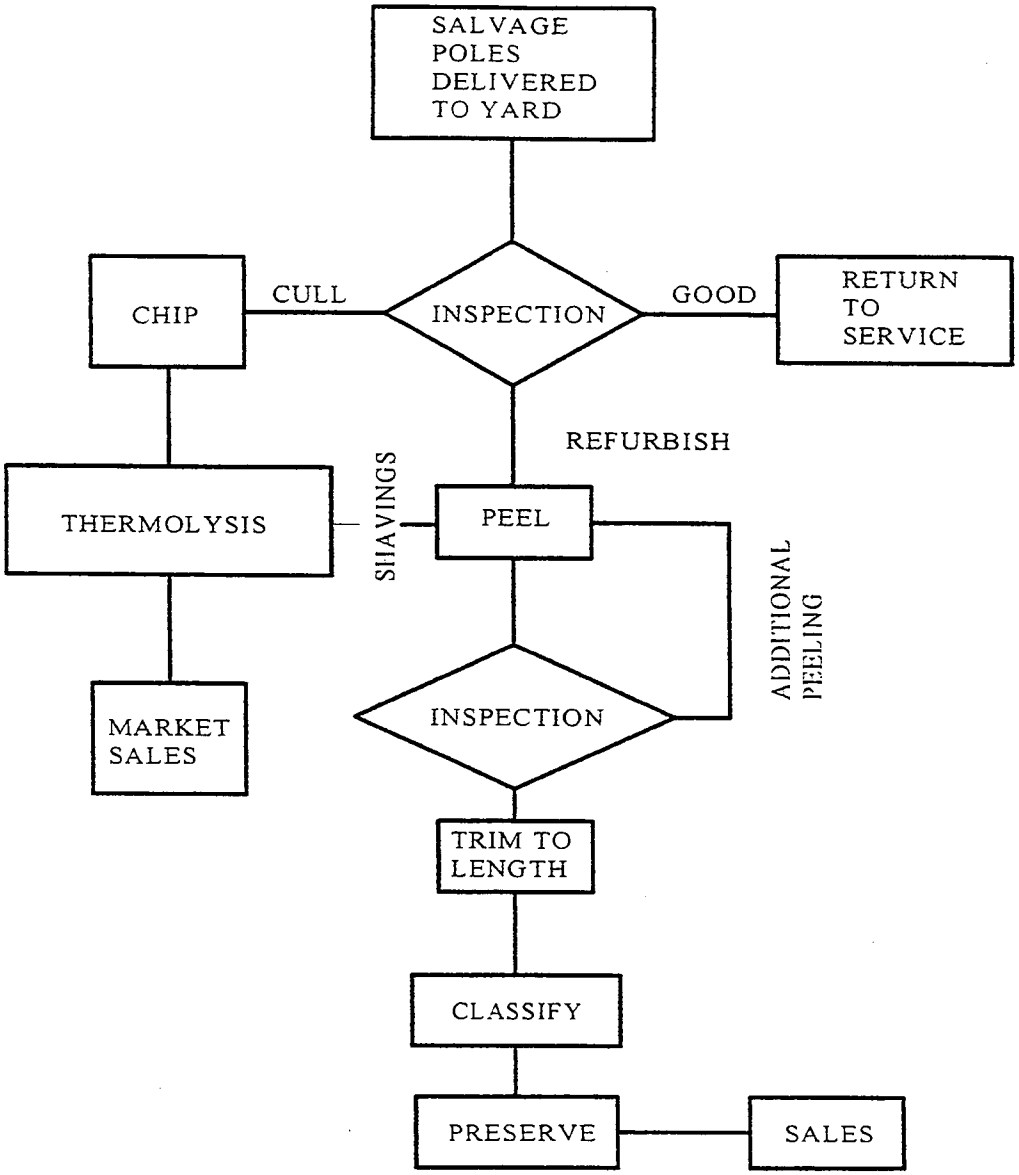
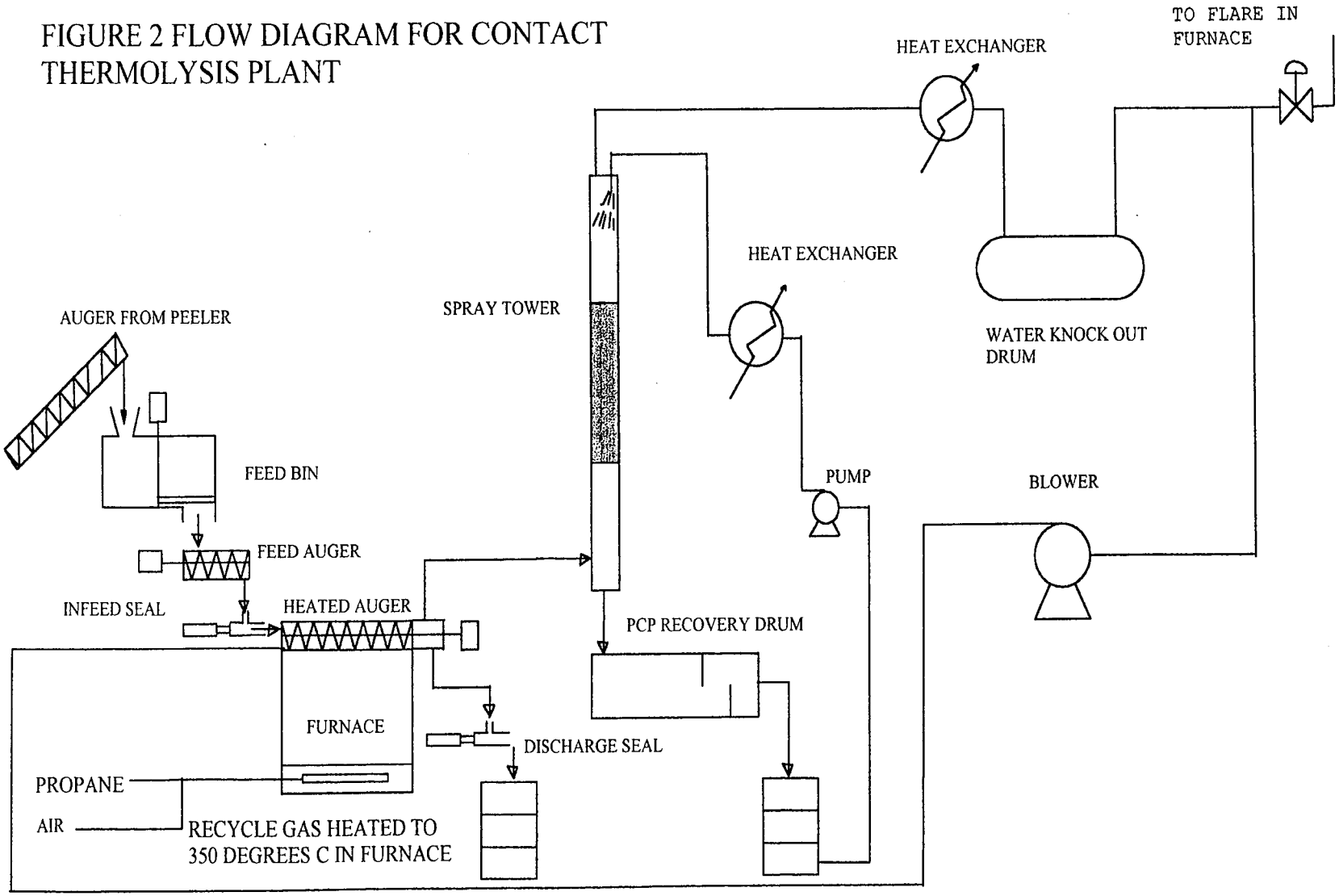
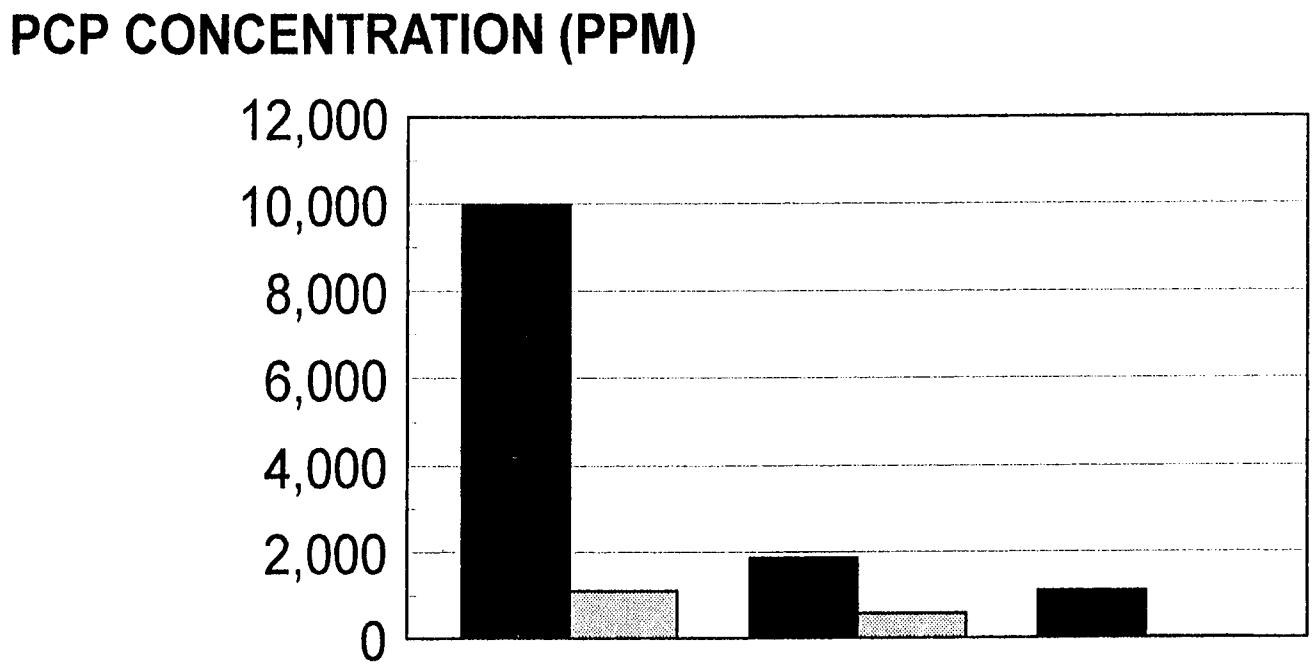


FIGURE 1. RECYCLED POLE MANAGEMENT FLOW DIAGRAM

FIGURE 2 FLOW DIAGRAM FOR CONTACT THERMOLYSIS PLANT





TEST DATE	OCT	DEC	JAN
BEFORE	9,970.0	1,860.0	1,100.0
AFTER	1,100.0	566.0	10.6

Fig. 3. PCP Concentration Before and After Thermolysis

CHARACTERISTICS OF A FAST PYROLYSIS BIO-FUEL AND ITS MISCIBILITY WITH OXYGENATED AND CONVENTIONAL FUELS

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Abstract

A bio-fuel produced by ENSYN Technologies Inc. using the RTP method was thoroughly characterized for its pH, specific gravity, viscosity, water content, ash content, alkali content, flash point, vapor pressure, elemental composition, heating value, stability behavior, filterability as well as its distillation and separation characteristics. In addition, its miscibility characteristics with some oxygenated compounds and conventional fuels were investigated. The objective was to determine the essential bio-fuel properties needed for applications such as storage and combustion in turbines. The bio-fuel consisted of 49.8 wt% C, 7.5 wt% H, and 42.7 wt% O. Its flash point was 76°C and heating value was 17.5 MJ/Kg. About 58.0 wt% of Bio-fuel was low boiling fraction (<200°C), 6.0 wt% high boiling fraction (200-450°C) and 36.0 wt% non-volatiles (>450 °C). The viscosity and heating value were significantly affected by its water content. The stability of the bio-fuel (studied by monitoring its pH, density, viscosity and distillation characteristics over a 1 year period) changed with time. The bio-fuel was miscible with methanol, ethanol and acetone (oxygenated compounds (OC)). Addition of small amounts of OC decreased its viscosity and density and increased its heating value. The miscibility characteristics of Bio-fuel and Bio-fuel+OC (termed feeds) with Diesel and Bunker C were investigated. Based on 100g of feed, the optimum amount of Diesel required to obtain stable miscibility over a test period of 24h were: 16g in Bio-fuel, 21g in Bio-fuel+Methanol, 25g in Bio-fuel+Ethanol and 19g in Bio-fuel+Acetone. The bio-fuel was miscible with Bunker C in all proportions. Other miscibility studies involving mixtures of WIF (water-insoluble fraction of Bio-fuel)+OC will be discussed. These studies showed that there was a potential for utilizing Bio-fuel directly or indirectly with conventional fuels.

Introduction

The bio-oil produced by ENSYN uses the Rapid Thermal Processing (RTP) method[1,2] which is one of the fast pyrolysis technologies. In order to use the bio-oil for any application, it is necessary to characterize it thoroughly[3]. Characterization normally requires measurement of the bio-oil properties such as density, viscosity, flash point, heating values, surface tension, volatility and its distillation characteristics. Monitoring of these properties over time is also important for identifying the bio-oil stability characteristics. In addition, bio-oils may contain particulate and mineral matter which would require their measurement and/or removal before being used.

Thus, the objective of this study was to determine the physical properties of some fast pyrolysis bio-oils, study their filtration, distillation, separation characteristics as well as stability behavior. Since bio-fuels are being considered as alternative sources of fuel, it was of interest to investigate its miscibility characteristics with both oxygenated (such as ethanol, methanol, acetone) and conventional fuels such as diesel and bunker C.

Experimental

Bio-oil Preparation

Three different types of bio-oils (designated as Bio-oil A, B and C) were investigated for their physical properties. Bio-oil A was produced from commercial hardwood sawdust with the ENSYN RTP-3 Pilot Plant which was operated at approximately 525°C and residence time of 450-500 ms. Bio-oil B was produced from birch wood flour with the ENSYN Research Unit (using reactor configuration RTP-3A) which was operated at approximately 515°C and residence time of 500 ms. The bio-oil vapors were hot filtered prior to condensation. Bio-oil C was a commercial bio-oil sample produced from hardwood sawdust (Maple/Oak) with the ENSYN 25 TPD Plant. The plant was operated at approximately 500°C and residence time of 700 ms. The bio-oil was wet scrubbed.

Methods for Measurement of Bio-oil Properties

The CHN content of the oils was determined with Perkin Elmer 2000 CHN Analyzer. The oxygen content of the bio-oil was obtained by difference. The total ash content of the bio-oil was determined following the procedure outlined in ASTM D 482-80 for petroleum products[4]. The alkali content was determined by thermal ashing of the bio-oil followed by ICP-AES (i.e. Inductively Coupled Plasma-Atomic Emission Spectroscopy) method.

The water content was determined by Karl Fischer (KF) method. The procedure outlined in ASTM E 203-75 was followed[4]. With normal KF reagents, the presence of aldehydes, ketones and carboxylic acid[5] in the bio-oil react with the KF titrant to produce water, thus, the amount of water is usually over-estimated. Instead, Hydranal-composite reagents, AQUASTAR Comp 5K and Solvent K (ALDRICH, USA) were used for the titration. These reagents limit the water formed during titration. The pH of the bio-oil was determined with a Fischer Scientific Accumet Model 10 pH/mV meter equipped with controls and connections necessary to compensate automatically for effects of solution temperature and to standardize the meter with buffers. The flash point of the bio-oil was determined following the procedure described in the ASTM D 93-80 method[4]. The density measurements were made with a 10 mL pycnometer and viscosity measurements were performed with a cone/plate Brookfield Digital Viscometer (Model DV-II).

The surface tension (ST) of the oil was measured with a Fisher Surface Tensiomat Model 21. The meter uses the Ring Method (platinum-iridium ring) to determine the surface tension. The instrument was calibrated with ethanol (ST = 22.75 mN/m), acetone (ST = 23.70 mN/m), and methanol (ST = 22.61 mN/m). Effect of water content on the properties of Bio-oil A was also studied. By using a desiccator (drierite, i.e., anhydrous

calcium sulfate) the water content of Bio-oil A was varied and the heating value, viscosity, density and pH measured. Also, the stability behavior of Bio-oil A was examined by monitoring the changes in its properties over a 1 year period.

Bio-oils need to be dewatered in order to increase their heating values. Our observations indicate that by adding extra water to bio-oil, it separated into a water soluble fraction (WSF) and an organic fraction (Water Insoluble Fraction, (WIF) which contained very low water content). Thus, about 2 g of water was added to 10 g bio-oil and the contents were shaken vigorously and left for 24 hr. After 24 hr, WSF was separated from the WIF. The physical properties of the WIF and WSF products were determined. The effect of temperature (between 23-80°C) on the yield of WIF was also investigated.

Filtration characteristics of the bio-oils were also studied. Pyrolytic bio-oils contain tar and particulates in the form of char. Thus, attempts were made to identify the most effective means of removing these particulates to determine the amount of tar using fritted glass funnels, screens and centrifugation. Bio-oil A only was used for these studies. The distillation characteristics (studied (at atmospheric pressure) of the bio-oil also was The objective was to investigate the extent of volatility of the bio-oil under normal conditions of temperature and pressure as well as to determine the composition (by GC and GC-MS) of the volatile fractions. The distillation procedure described in Standard Method IP 24 for crude petroleum[7] was followed

Methods for Measurement of Bio-oil Miscibility Characteristics

Since bio-oils are potential fuel alternatives, it would be worthwhile to utilize it with traditional fuels such as diesel and bunker C. Hence, miscibility of bio-oil (and WIF) with oxyfuels (namely, methanol, ethanol and acetone) with Diesel and Bunker C was examined. Later, the miscibility of mixtures of Bio-oil and oxyfuels with diesel and bunker C were investigated.

Procedure

About 10 g of feed (bio-oil, WIF, bio-oil+Oxyfuel or WIF+Oxyfuel) was placed in a 50 mL bottle. A pre-determined quantity of diesel was added. The proportion of feed to Diesel was varied from 9:1 to 1:9 weight ratio. The mixture was stirred for 30 min at a speed of 1500 rpm. The miscibility of the mixtures during stirring and the time taken for the mixture to remain miscible were monitored. These observations were carried out at regular time intervals for about 4 h. After 24 h, the mixture was observed for miscibility/separation. Usually, some amount of diesel was found to separate from the mixture forming a layer of diesel above the mixture. The quantity of this diesel was determined by collecting it with a micro-pipette and weighing. The amount of diesel that was miscible with the feed material was determined by difference between the quantity of diesel added and the diesel separated from the mixture after 24 hr. This quantity of diesel was designated as permanently "soluble" diesel. Changes in the miscibility associated with temperature was studied by conducting the experiments at room temperature (23°C) and at 45°C. The Bio-oil-Oxyfuel and WIF+Oxyfuel mixtures used were prepared in the weight ratios; 9:1, 4:1 and 1:1. The properties of some of the feed material+diesel mixtures were also determined.

A similar procedure was followed with the Feed+Bunker C miscibility studies. In these runs, it was observed that only acetone was miscible with Bunker C. Also, preliminary results showed that the miscibility of Bio-oil+Methanol and Bio-oil+Ethanol with Bunker was exceptionally poor. Hence, these tests were discontinued. Thus, only the Bio-oil and Bio-oil+Acetone with Bunker C test was investigated in detail.

Results and Discussion

Bio-oil Properties

The results show (Table 1) that the bio-oils were highly oxygenated in nature. No nitrogen was detected which is very favorable from environmental point of view. The ash and alkali content of Bio-oil B were substantially lower than those of Bio-oil A. Especially, the calcium and potassium contents of Bio-oil B were much lower. However, the sodium content of Bio-oil B was still comparable to that of Bio-oil A. Also, the ash content of Bio-oil C is comparable with Bio-oil B.

Table 1 Properties of Bio-oils and Combinations of Light and Heavy Bio-oil.

	Bio-oil A	Bio-oil B	Bio-oil C
CHN Analysis, wt%			
C	49.80	43.00	49.70
H	7.50	7.20	7.60
N	0.00	0.00	0.00
O (By difference)	42.7	49.8	42.60
Alkali Content, ppm			
Na	500	8.6	
K	250	<0.5	
Ca	50	40	
Density, g/mL			
20°C	1.210	1.217	1.243
40 °C	1.199	1.202	1.225
Viscosity, cSt			
20 °C	81	30	1600
40 °C	15	6	151
Water Content, wt%	21.2	25.0	18.0
pH	2.80	2.45	2.66
Surface Tension, mN/m	29.3	29.1	
Ash Content, ppm	4800	600	1000
Heating Value, MJ/Kg	17.5	16.3	18.8

The three bio-oil samples contained between 18 and 25 wt% water. Compared to petroleum fuels, the amount of water in the bio-oil was substantially high and therefore, the heating values of the bio-oils will be low. The bio-oils were highly acidic in nature. Bio-oil B (2.45) is more acidic than Bio-oils A and C. The flash point is the lowest temperature at which vapors above the fuel ignite when exposed to a flame. Limits of the flash point must be determined for safe handling. Normally flash points above 50°C are considered safe[7]. Thus, it was necessary to measure the flash point of the oils. The flash point of Bio-oil B was lower than that of Bio-oil A (53°C compared to 76°C). Compared to diesel[7] (Flash point between 45 and 70°C) the flash point of both oils fall within acceptable limits. The surface tension of Bio-oils A and B were similar (29.3 and 29.1 mN/m, respectively). Compared to summer grade diesel (ST = 22.2 mN/m), the surface tension of the bio-oils were higher. The densities were higher than those for diesel (0.8-0.9 g/cc) but comparable with Bunker C oil (1.18 g/cc). With temperature, the densities changed only slightly. Among the three oils, the viscosity of Bio-oil B was the lowest and Bio-oil C was highest.

Effect of Water Content on the Properties of Bio-oil A

The results (Table 2) show that the viscosity increased as the amount of water in the bio-oil decreased. Between 12-21 wt% water, the viscosity increased gradually. However, when the water content decreased to 10 wt% and below, there was a drastic increase in

the viscosity. The pH of the bio-oil increased to about 2.90 when water was removed. Thereafter, it barely changed with decrease in water content. As expected, the density of the bio-oil increased with decrease in water content. Between 1.9-2.6 wt% of bio-oil was removed from the bio-oil in the form of volatiles. These were probably adsorbed by the drierite. The heating value of the bio-oil increased with a decrease in its water content.

Table 2 Effect of Changes in the Water content of Bio-oil A on some of its Physical Properties

Basis: 100g bio-oil

Water Content, wt%	pH	Density, gm/mL	Volatiles Removed, wt%	Viscosity, cP		Heating Value, MJ/Kg
				20 °C	40 °C	
21.2	2.81	1.22	----	410	113	17.5
16.3	2.90	1.23	1.9	486	102	18.0
14.6	2.87	1.23	2.1	504	109	18.6
12.2	2.89	1.24	2.4	837	175	19.1
10.4	2.89	1.25	2.4	1,390	306	19.5
5.2	2.89	1.33	2.6	2,200	601	20.3

Bio-oil Filterability/Separation

Of the various techniques used, centrifugation was found to the best method for the removal of particulates from the bio-oil. It provided one of the best methods of particulate removal in relatively less time. Also, after the particles have been removed, the viscosities of the clarified bio-oil were comparable with those of the parent bio-oil. In addition, it retained a higher amount of tar in the product. This was preferable because it allowed more organic material in the clarified bio-oil which is favorable from heating value point of view. Losses were also minimal. The results also showed that filtration/separation at 50°C was better than at room temperature. An optimum of 3.60 wt% char was removed. This char fraction contained 0.13 wt% ash. Also, 9.9 wt% of the oil was removed in the form of tar. At 50°C, up to 0.18 wt% ash, 3.65 wt% char and 7.72 wt% tar were separated from the oil.

Bio-oil Distillation Characteristics

The amount of volatiles obtained at each cut temperature was determined[8]. Based on 100 g bio-oil, the first distillate drop was obtained at approximately 49°C. At 100°C about 8.49 wt% of bio-oil was volatile. It was interesting to note that most of the water contained in the bio-oil evaporated between 108 and 115°C. This observation is indicative of the phenomenon of boiling point elevation of a volatile solvent (or liquid) which results when one or more non-volatile solute are dissolved in the volatile solvent (or liquid). The pH of the volatile fractions was 2.56 at 73°C and increased to 2.80 at 100°C indicating that the volatile fraction was highly acidic in nature. The volatile fraction was composed of water and various organic compounds. Of the organic compounds, organic acids and esters were the main components[8]. Propanoic acid, 3-hydroxy butanoic acid, and dibutyl ester of ethanoic acid were the main components. The presence of high amounts of organic acids and esters of organic acids may be the reason for high acidity of the volatile fractions as well as the bio-oil itself.

Stability Characteristics of Bio-oil

The major changes occurred in the viscosity and the distillation characteristics of the bio-oil. The pH and density of the bio-oil remained almost unchanged with time. The results also showed that the bio-oil appeared to be unstable initially but its stability appeared to improve over time[8].

Separation of Bio-oil by Addition of Water
The yield of WIF varied significantly with temperature and with bio-oil type. Bio-oil C which was wet-scrubbed gave the highest yield of WIF (76-82 wt% of Bio-oil) followed by Bio-oil A (38.5-58 wt%) and B (24.3-41.2 wt%). The WIF fractions barely flowed and their viscosities were exceptionally high compared to that of the original bio-oil. However, they were readily soluble in acetone, methanol, ethanol and isopropyl alcohol. It was sparingly soluble in hexane, octane, xylene, toluene, tetralin, ethers, anisole and petroleum ether. The WSF fractions[8] consisted of acids and esters, alcohols, ketones, aldehydes, ethers and phenols.

Miscibility Characteristics of Bio-oil

Bio-oil+Oxyfuels Miscibility and Properties
The bio-oils were readily miscible with methanol, ethanol and acetone in all proportions. No separation was observed over time. The important physical properties are given in Table 3 for mixtures of Bio-oil A and its WIF with these oxyfuels. As expected, addition of oxyfuel increased the pH and substantially lowered the viscosities of both bio-oil and WIF.

Table 3. Some properties of Bio-oil A+Oxyfuel mixtures (Measured at 20°C).

Proportion	pH	Density, g/cc	Viscosity, cP	Heating Value, MJ/Kg
Bio-oil A	2.80	1.210	93	17.5
WIF		1.200	28000	22.1
Methanol				23.0
Ethanol				29.0
Acetone				29.5
Bio-oil+Methanol				
9:1	3.23	1.16	73.7	18.0
4:1	3.44	1.11	40.1	18.4
1:1	3.96	0.98	12.3	N/A
Bio-oil+Ethanol				
9:1	3.20	1.16	49.3	17.9
4:1	3.40	1.11	24.5	18.5
1:1	4.00	0.97	1.9	N/A
Bio-oil+Acetone				
9:1	3.24	1.16	46.1	N/A
4:1	3.76	1.11	16.9	17.9
1:1	3.90	0.97	1.2	N/A
WIF+Methanol				
9:1	3.40	1.16	49.1	20.5
4:1	3.62	1.12	26.1	20.1
1:1	4.17	1.00	8.0	N/A
WIF+Ethanol				
9:1	3.26	1.16	49.0	20.5
4:1	3.45	1.12	24.2	20.6
1:1	4.13	1.00	6.5	N/A
WIF+Acetone				
9:1	3.45	1.16	51.3	21.5
4:1	3.65	1.12	26.5	23.5
1:1	3.96	1.00	3.8	N/A

However, the pH of the WIF+Oxyfuel were higher than those of the Bio-oil+Oxyfuel. The viscosities were much the same. The addition of oxyfuel also increased the heating value of the bio-oil.

Bio-oil Miscibility with Diesel

In order to identify how the bio-oil could be utilized within the traditional petroleum based fuels infrastructure, the miscibility of the bio-oil with diesel was investigated. Table 4 shows the miscibility characteristics of Bio-oil A with Diesel. Various observations are as follows:

1. The bio-oil was miscible with diesel only at low proportions of diesel. As the amount of diesel was increased above the ratio 7:3 (Bio-oil:Diesel), the miscibility decreased substantially. The miscibility of Bio-oil+Diesel (9:1 weight ratio) mixture was stable for up to about 4 h. After 4 h, a layer of diesel was formed indicating separation or breakdown of miscibility.
2. The time taken for bio-oil to remain miscible with diesel decreased with increase in the proportion of diesel.
3. Some amount of diesel remained permanently "soluble' in the bio-oil. A maximum of about 16g Diesel per 100g Bio-oil was obtained.

These observations indicate that a mixture of 8 parts bio-oil to 2 parts diesel is the optimum proportion for mixing bio-oil with diesel.

Table 4. Miscibility of Bio-oil (B) with Diesel (D).

B:D Wt. Ratio	Miscibility at 23°C	[1]Amt	Miscibility at 45°C
9:1	* Miscible for about 4 h * Small diesel layer visible after 4 h * Small diesel layer after 24 h	10.0	Same as at room temperature
8:2	* Miscible for 2-3 h * Small diesel layer after 3 h * Small diesel layer after 24 h	16.0	Same as at room temperature
7:3	* Miscible for about 1 h * Separation developed after 1 h Large layer of diesel	16.0	* Miscible for about 30 min * Separation developed after 30 min
6:4	* Not completely miscible * Pockets of bio-oil and diesel observed during stirring * Separation developed immediately after stirring.	---	Same as at room temperature
5:5	Same as 6:4	---	Same as 6:4
4:6	No miscibility observed	---	Same as 4:6
3:7	Same as 4:6	---	Same as 4:6
2:8	Same as 4:6	---	Same as 4:6
1:9	Same as 4:6	---	Same as 4:6

[1]Amt: Maximum amount (g) of diesel per 100 g bio-oil needed for stable miscibility.

Bio-oil+Oxyfuel Miscibility with Diesel

In order to improve the miscibility, Bio-oil A was first dissolved in methanol (ethanol and acetone were used as well) in the weight ratios 9:1, 4:1 and 1:1. This mixture was termed A. Various proportions of this mixture were mixed with Diesel (Table 5) and the miscibility studied. Summary of the results is as follows:

1. Mixture A was miscible with diesel only at low proportions of diesel.
2. The time period for Mixture A to remain miscible with diesel decreased with increase in the proportion of diesel.
3. The miscibility decreased with increase in temperature.

4. The miscibility decreased with increase in the amount of methanol (oxyfuel) added. Thus, the mixture containing Bio-oil:Methanol of 9:1 ratio provided the best miscibility.
5. A maximum of about 21.5g Diesel per 100g Bio-oil A was found to be permanently "soluble" in Mixture A. Thus, the miscibility increased with addition of oxyfuel compared to when methanol was not added (Table 4). Thus, compared to Bio-oil (only)+Diesel, the addition of oxyfuel increased the miscibility time.
These observations indicate that the mixture containing Bio-oil and Methanol in the weight ratio 9:1 gave the best miscibility with Diesel. A ratio of 7:3 (Mixture A:Diesel) provided the optimum miscibility.

Table 5. Miscibility of Bio-oil:Methanol (9:1, Mixture A) with Diesel (D).

A:D Wt Ratio	Miscibility at Room Temperature, 23°C	Amt	Miscibility at 45°C
9:1	* Miscible up to about 3 hr * Miscible but with small diesel layer after 3 hr * Small diesel layer after 24 hr	8.5	* Miscible up to about 1 hr * Miscible but with small diesel layer after 1 hr * Small diesel layer after 24 hr
8:2	* Miscible for about 1 h * Small diesel layer visible after 1 h * Small diesel layer after 24 hr	18.9	* Miscible for about 30 min * Small diesel layer visible after 30 * Small diesel layer after 24 hr
7:3	* Miscible for about 10 min * Small diesel layer visible after 10 min * Small diesel layer after 24 hr	21.5	* Miscible when stirred * Small layer visible almost immediately after stirring * Large diesel layer after 24 hr
6:4	* Miscible when stirred * Small layer visible after 5 min * Large diesel layer after 24 hr	----	* Miscible when stirred * Separation starts immediately after stirring
5:5	* Not completely miscible during stirring * Separation visible immediately stirring	----	Same as at room temperature
4:6	Same as 5:5	----	No miscibility. Specks of bio-oil in diesel
3:7	* Not miscible. Specks of bio-oil in diesel	----	Same as 4:6
2:8	Same as 3:7	----	Same as 4:6
1:9	Same as 3:7	----	Same as 4:6

Various miscibilities were performed with ethanol and acetone in addition to methanol. A summary of the optimum conditions required for the best miscibility are given in Table 6. For example, Row 1 indicates that for Bio-oil (as such) and Diesel miscibility studies, 8 parts of Bio-oil and 2 parts Diesel were required to obtain the optimum miscibility. The mixture thus obtained contained 16g diesel per 100g Bio-oil which was permanently "soluble" after 24h. Row 3 indicates that in the miscibility studies involving mixtures of Bio-oil and methanol with Diesel, 9 parts Bio and 1 part methanol was the best feed for mixing with Diesel. About 7 parts of Bio-oil+Methanol mixture and 3 parts Diesel were required to obtain the optimum miscibility. This optimum mixture contained 21.5g Diesel per 100g Bio-oil which was permanently "soluble". It appears that the best results are obtained with a mixture of Bio-oil+Ethanol (9:1) and the second best with a mixture of Bio-oil+Methanol (9:1).

Table 6. Summary of the Optimum Miscible Fractions.

Row Number	Feed	Optimum Wt. Ratio of Feed to Diesel	Optimum Amount of Diesel per 100 g Bio-oil
1	Bio-oil A	8:2	16.0
2	Centrifuged Bio-oil	8:2	10.4
3	Bio-oil:Methanol (9:1)	7:3	21.0
4	Bio-oil:Ethanol (9:1)	7:3	25.0
5	Bio-oil:Acetone (9:1)	8:2	19.0
6	WIF:Methanol (9:1)	9:1	6.5
7	WIF:Ethanol (9:1)	9:1	6.4
8	WIF:Acetone (9:1)	8:2	10.8

Miscibility Studies of Bio-oil with Bunker C
At room temperature, Bio-oil A was miscible with Bunker C at all proportions. The miscibility was stable for over 24 h and extended into days. The miscibility characteristics with Bo-oil B is given in Table 7 as an example.

Table 7 Miscibility of Bio-oil B (FB) with Bunker C (C)

FB:C Weight Ratio	Observation	Observation
	Room Temperature, 23°C	45°C
9:1	Miscible up to about 24 h	Miscible up to about 2 h
7:3	Miscible up to about 6 h	Miscible up to about 2 h
5:5	Miscible up to about 6 h	Miscible up to about 3 h
3:7	Miscible up to about 6 h	Miscible up to about 6 h
1:9	Miscible up to about 24 h	Miscible up to about 6 h

Miscibility of Bio-oil B+Acetone and Bunker C
Generally, this feed was miscible with Bunker C in all proportions. The time for stable miscibilities was in the order of hours. However, as the amount of oxyfuel (i.e., acetone) was increased the miscibility times decreased also. The results showed that the miscibility of the Bio-oil and Bio-oil+Acetone mixtures with Bunker C were appreciably high irrespective of the proportions. Thus, acetone can be added to the Bio-oil+Bunker C mixtures in order to reduce the viscosity and make it more fluid while maintaining long miscibility times in the order of hours. Compared to Diesel, Bio-oil was more miscible with Bunker C than with diesel.

Miscibility of WIF and WIF+Acetone with Bunker C
At room temperature, WIF was miscible with Bunker C in all proportions. The miscibility was stable for over 24 h and extended into days. However, the viscosity of these mixtures appeared to be exceptionally high. Also, WIF+Acetone and Bunker C were miscible in all proportions. Again, the miscibilities were stable for over hours.

Properties
The properties of some of the mixtures with diesel and bunker C are given in Table 8. The most important observation is the increased heating values with addition of Diesel and Bunker and the reduced viscosity with the addition of the oxy-fuels.

Table 8. Some properties of Bio-oil A+Oxyfuel mixtures (Measured at 25°C).

Proportion	pH	Density , g/cc	Viscosity , cP	Heating Value, MJ/Kg
Diesel				40.8
Bunker C				33.8
Bio-oil+Diesel (9:1)	2.94	1.11	277	18.9
Bio-oil A + Bunker C (5:5)	N/A	N/A	N/A	25.1
(Bio-oil A:Methanol (9:1))+Diesel (8:2)	3.21	1.11	148	21.6
(Bio-oil:Ethanol (9:1)) + Diesel (8:2)	3.21	1.08	82.8	22.0
(Bio-oil:Acetone (9:1)) + Diesel (8:2)	3.26	1.10	88.7	23.0
(Bio-oil:Acetone (9:1)) + Bunker C (5:5)	N/A	N/A	N/A	25.9
(WIF:Acetone (9:1)) + Bunker C	N/A	N/A	N/A	27.0

Conclusions

1. The bio-oils were thoroughly characterized to obtain their physical properties. Some of these properties changed with time. Also, the bio--oil properties changed with its water content.
2. Centrifugation appeared to be the best method for particulate removal from bio-oil. Particulate removal at 50°C was found to be better than at room temperature.
3. The potential exists for utilizing bio-oil directly with diesel and bunker C or in combination with oxy-fuels such as methanol, ethanol and acetone.

References

1. B.A. Freel, R.G. Graham, D.R. Huffman and A.J. Vogiatzis, "Rapid Thermal Processing of Biomass (RTP): Development, Demonstration, and Commercialization", In: D.L. Klass (Ed.), *Proceedings of conference on Energy and Wastes XVI*, Florida, Institute of Gas Technology, Chicago, 811-826 (1992).
2. R.G. Graham, B.A. Freel and R.P. Overend, "Thermal and Catalytic Fast Pyrolysis of Lignin by Rapid Thermal Processing (RTP). In: E. Hogan (Ed.). *Proceedings of the 7th Canadian Bioenergy R&D Seminar*, Ottawa, Canada, 668-673 (1989).
3. J. D. Adjaye and N.N. Bakhshi, "Properties and Characteristics of ENSYN Bio-oil", *Proceedings: Biomass Pyrolysis Oil Properties and Combustion Workshop*, Estes Park, Colorado, USA, September 26-28, (1994).
4. *Annual Book of ASTM Standards*: Petroleum, Products, Lubricants, and Fossil Fuels, ASTM, Easton, MD, USA (1985).
5. E. Scholz, *HYDRANAL Water Reagent* according to Eugen Scholz for Karl Fisher Titration, (1982).
6. *Diesel Fuel Qualities and Typical Inspections*, PETRO-CANADA Report, (1991).
7. *Standard Methods for analysis and Testing of Petroleum and Related Products*, Volumes 1&2, John Wiley & Sons, Chichester, Gt. Britain (1988).
8. J.D. Adjaye and N.N. Bakhshi, *Characterization and Stabilization Study of the ENSYN Fast Pyrolysis Bio-oil*, DSS Contract No. 23440-3-9472/01-SZ, CANMET, Canada (1995).

POTENTIAL PRODUCTION OF HYDROCARBONS FROM THE CONVERSION OF A WOOD-DERIVED OIL OVER SOME ALUMINOPHOSPHATE CATALYSTS

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Abstract

A wood-derived oil (WDO) (obtained from ENSYN Technologies Inc.) was converted catalytically over three aluminophosphate catalysts, namely, SAPO-5, SAPO-11 and MgAPO-36. The oil was produced by the Rapid Thermal Processing (RTP) method and its elemental composition was 49.8 wt% C, 7.5 wt% H, and 42.7 wt% O. The catalysts were selected based on their molecular sieving property, acidity and pore size. The test runs were performed in a fixed bed micro-reactor which was operated at 3.6 WHSV and a temperature range of 330-410°C. The objective was to investigate the potential for the production of both liquid and gaseous hydrocarbon products from the conversion of WDO using aluminophosphate catalysts and to determine their performance in comparison with HZSM-5 and silica-alumina catalysts. The products included an organic liquid product (OLP), aqueous fraction, coke, char and gas. The OLP and gas were the desired products. Between 12-22 wt% of WDO was obtained as OLP. SAPO-5 gave the highest yield of 22 wt% OLP, followed by 19.9 wt% by SAPO-11 and 16.3 wt% by MgAPO-36. The OLP contained an optimum of 61.5, 56.8 and 57.0 wt% (for SAPO-5, SAPO-11 and MgAPO-36, respectively) liquid hydrocarbons. The major products were benzene, n-hexane, heptane and isooctane. All three catalysts were selective for both aromatic and aliphatic hydrocarbons in comparable proportions. On the other hand, in comparison, HZSM-5 was highly selective for aromatic hydrocarbons whereas silica-alumina was selective for mostly aliphatic hydrocarbons. The gas yield was between 8-17 wt% of WDO. Its composition consisted mostly of C_1-C_4 hydrocarbons and CO_2. Among the hydrocarbon gases, ethylene, propylene, propane, n-butane and some C_4 olefins were the major products. The catalyst pore size and acidity influenced the yield and product distribution. Also, a detailed comparison with the results obtained with HZSM-5 and silica-alumina catalysts is presented.

Introduction

Currently, bio-oils are obtained from two main sources, namely, the fast pyrolysis of wood and from vegetable sources such as canola, soybean, linseed, palm, flax plants etc. The process to convert these oils to liquid and gaseous products which contain high hydrocarbon contents have been the focus of a number of research activities[1-4]. These oils have the potential for the production of liquid fuels such as high octane gasoline, or liquid products with high cetane numbers. In addition, the gas fraction is rich in various hydrocarbons such as ethylene, propylene and n-butane[2].

In the literature, the conversion of bio-oils to hydrocarbons has been performed with typical hydrotreating catalysts such as Co-Mo/Al_2O_3[1,3], zeolite catalysts such as HZSM-5[2,5] and activated alumina[4]. Our recent work[6] on the upgrading of a wood-derived oil (WDO) over various catalysts, namely, H-Y, H-mordenite, silicalite, and silica-alumina has shown that by changing the catalyst type or its functionality (such as its acidity and/or pore size) the product distribution as well as the composition of the desired liquid and gaseous products could be changed. For instance, it was observed that HZSM-5 catalyst provided a high selectivity for aromatic hydrocarbons whereas silica-alumina catalyst provided a high selectivity for aliphatic hydrocarbons.

Recently, a large family of novel aluminophosphate molecular sieve catalysts has been reported in the literature[7]. These catalysts not only exhibit properties of zeolites but also show unusual physicochemical properties ascribed to their unique chemical composition. The application of these molecular sieve catalysts in processes such as cracking of isooctane, crude oil upgrading, isomerization of xylene and hexane as well as deoxygenation[7-12] have shown their potential to be useful and scientifically challenging as their aluminosilicate zeolite counterparts.

Thus, in this work, the conversion of a wood-derived bio-oil was studied over SAPO-5, SAPO-11, and MgAPO-36 catalysts. The results obtained were compared with the conversion of the same bio-oil over HZSM-5 and silica-alumina catalysts.

Experimental

Feed material

The wood-derived bio-oil (obtained from maple wood) was obtained from ENSYN Technologies Inc., Gloucester, Ontario, Canada, where it was produced by the rapid thermal pyrolysis process[13]. The yield of the bio-oil was 74 wt% and it contained 21 wt% water. It consisted of 49.8 wt% carbon, 7.5 wt% hydrogen, and no nitrogen (CHN elemental analysis). The balance of 42.7 wt% was oxygen.

Catalyst Selection, Preparation and Characterization

The three catalyst were selected in order to take advantage of the differences in pore size and acidity. The objective was to study the effect of these catalyst properties on the product yield and selectivities. In terms of pore size, SAPO-5 and MgAPO-36 contain large pores (0.8 and 0.75 nm, respectively) and SAPO-11 contains medium pores (0.56

Table 1. Overall material balances (wt% of WDO fed) and Composition of Organic Liquid Product from the Conversion of WDO some Aluminophosphate Catalysts.

Catalyst	SAPO-5			SAPO-11			MgAPO-36		
Temperature, ^{o}C	330	370	410	330	370	410	330	370	410
Product									
Coke	10.0	13.3	16.2	4.1	7.5	13.0	13.4	17.3	21.5
Char	25.0	16.7	12.8	23.6	18.0	15.0	28.3	21.4	15.6
Gas	8.0	10.3	14.0	7.6	12.2	16.7	5.5	10.1	15.2
Organic Liquid Product (OLP)	20.8	22.2	19.5	18.1	19.9	17.5	14.9	16.3	12.5
Tar	12.5	9.5	7.0	18.2	11.9	5.2	14.5	10.1	5.1
Aqueous Fraction	22.2	24.2	26.1	24.1	26.3	29.5	21.5	23.1	26.9
Unaccounted Fraction	1.5	3.8	4.4	4.3	4.2	3.1	1.9	1.7	3.2
Composition (wt% of OLP) of Organic Liquid Product									
Aliphatic Hydrocarbons	20.4	23.5	26.1	18.9	24.4	21.3	34.5	26.7	21.6
Aromatic Hydrocarbons									
Benzene	28.3	27.5	34.7	30.5	29.1	27.0	21.2	23.4	27.8
Toluene	0.3	----	----	----	----	----	---	---	---
Xylenes	2.7	1.6	0.7	----	1.7	2.1	0.5	0.7	0.9
C_9+	6.3	2.9	----	1.7	1.6	1.3	0.8	0.8	0.9
∑Aromatic Hydrocarbons	37.7	32.0	35.4	32.2	32.4	30.4	22.5	24.9	29.6
Oxygenated Compounds									
Acids & Esters	----	----	1.2	2.3	----	----	0.5	---	---
Alcohols	8.9	7.1	10.7	15.0	12.8	15.0	12.3	10.5	9.5
Furans	4.1	5.3	5.1	3.7	4.2	3.5	5.2	5.0	4.4
Ketones	2.2	7.3	6.2	8.0	8.7	9.9	9.9	8.7	7.3
Phenols	2.7	3.5	1.0	1.9	1.9	3.0	2.0	2.2	2.2
∑Oxygenated Compounds	17.9	23.2	24.2	30.9	27.6	31.4	29.9	26.4	23.4
Unidentified Compounds	24.0	21.3	14.3	18.0	15.6	16.9	13.1	22.0	25.4

nm). In addition, SAPO-5 and SAPO-11 have relatively higher acidity compared to other aluminophosphate-based molecular sieves. On the contrary, pure aluminophosphate (ALPO's) catalysts are primarily non-acidic in nature. Hence their direct use as cracking catalysts is limited. However, incorporation of metals into ALPO's is known to increase their acidity as well as enhance their resistance to coke formation[14]. The acidity in decreasing order is known to be as follows: Mg>Co>Zn>Si>Mn>Be>Fe[7,15]. Thus, MgAPO-36 was selected for the present work.

SAPO-5 and SAPO-11 catalysts were synthesized according to the method described by Lok et al.[16] and MgAPO-36 catalyst was synthesized according to the procedure outlined by Wilson et al.[17]. The catalysts were characterized by the following techniques: x-ray powder diffraction (XRD), temperature programmed adsorption and desorption (TPD) with ammonia and measurement of their BET surface area and pore sizes. Elemental compositions as well as the solid state MAS NMR spectra were also determined. Details on the catalyst preparation and characterization can be found elsewhere[18].

Equipment Set-up, Procedure and Product Analysis

Catalytic runs were carried out in a fixed bed micro-reactor made of 316 SS tubing, 380 mm long and 12.5 mm ID. It was operated at atmospheric pressure, over a temperature range 330-550°C and at 3.6 WHSV. Details of the reactor setup, run procedure and analysis are given elsewhere[19,20].

Results and Discussion

Overall Product Distribution

The definitions of the terms yield and selectivity as used in this work are given in Appendix 1. In all the runs, the overall mass balances were better than 96%. In order to check for reproducibility, a number of runs were repeated. The experimental error was found to be less than ±4%. The overall material balances for the conversion runs and the OLP compositions are given in Tables 1.

Among the three catalysts, SAPO-5 gave the highest yield of OLP followed by SAPO-11 and MgAPO-36 in that order. As the BET surface area and catalyst acidity decreased[18], the OLP yields also decreased indicating that these properties had a significant influence on the yield of the OLP. For all the catalysts, conversion of WDO to OLP increased with temperature reaching maximum values at 370°C. These values were 22.2, 19.9, and 16.3 wt% for SAPO-5, SAPO-11, and MgAPO-36, respectively. Thereafter, the yields decreased with increase in temperature. The decrease in the yield of OLP at high temperatures was due to the conversion of WDO to gaseous products and coke. A similar observation was made during the upgrading of the same oil with HZSM-5 catalyst[20].

Composition of Organic Liquid Product (OLP)

The OLP consisted of aliphatic hydrocarbons, aromatic hydrocarbons and oxygenated compounds. The oxygenated compounds mostly consisted of acids and esters, alcohols, furans, ketones and phenols.

The concentration of aromatic hydrocarbons varied with catalyst type and ranged between 22.5-37.7 wt% of OLP. SAPO-5 gave the highest yield of aromatic hydrocarbons with a maximum value of 37.7 wt% at 330°C and MgAPO-36 gave the lowest yield with a maximum value of 29.6 wt% at 410°C. It is interesting to note that the effect of temperature on the three catalysts was significantly different. With SAPO-5, a minimum of 32.0 wt% aromatic hydrocarbons was obtained at 370°C, whereas with SAPO-11 a slight decrease at high temperature (410°C) was observed. With MgAPO-36, the yield of aromatic hydrocarbons increased progressively with temperature. These observations indicate that a complex combination of catalyst acidity, catalyst pore size and temperature influence the formation of aromatic hydrocarbons.

It was interesting to observe that, benzene was the single most abundant aromatic hydrocarbon produced, (in most cases, over 90 %) in the aromatic hydrocarbon fraction. Toluene and xylenes were obtained in relatively small amounts. This observation is in complete contrast to the results obtained from the conversion of the same oil over HZSM-5 catalyst[20]. With HZSM-5, the selectivity for toluene and xylenes was high. The high yields of benzene with the aluminophosphate catalysts are probably due to a low rate of alkylation reaction which is the consequence of their lower acidity compared to the HZSM-5 catalyst[21,22]. The acid site density for HZSM-5 was high in comparison with all three aluminophosphate catalyst[18] and may have resulted in higher rates of alkylation reactions leading to higher selectivities for C_7 and C_8 than C_6 aromatic hydrocarbons with HZSM-5 catalyst. Milne et al.[23] also states that the amount of benzene relative to that of xylene is an indication of the degree of methylation (or alkylation). The lower the ratio of benzene to xylene, the higher the extent of alkylation reactions.

The yield of aliphatic hydrocarbons in the OLP ranged between 20.4-34.5 wt% for the three catalysts. It was made up mostly of C_6-C_8 aliphatic hydrocarbons. Among the three catalysts, MgAPO-36 gave the highest aliphatic yield of 34.5 wt% at 330°C. Among the aliphatics, the major compounds were n-hexane, heptane and 2,2,4-trimethyl pentane (isooctane - a fuel standard with an octane number of 100). Temperature had a significant effect on the production of aliphatic hydrocarbons. For instance, there was an increase in the concentration of aliphatic hydrocarbons for SAPO-5 and a decrease for MgAPO-36 catalyst. On the other hand, with SAPO-11 catalyst aliphatic hydrocarbon yield increased with temperature up to 410°C and then decreased. These results are in contrast to those obtained with HZSM-5 catalyst in which low yields of aliphatic hydrocarbons were observed. Again, these higher yields of aliphatic hydrocarbons with aluminophosphate catalysts can be attributed to the lower acid strength possessed by these catalysts compared to HZSM-5 catalyst[18].

In most cases, the results show that the aromatic hydrocarbon content of OLP increased with an increase in the acid density of catalyst. Consequently, SAPO-5 with its higher acid density gave high yields of aromatic hydrocarbons compared to MgAPO-36 which was low in acidity and strength. These observations are in agreement with the those reported in the literature[24].

These observations indicate that the reaction temperatures needed for optimum yields of aromatic hydrocarbons were: 330°C for SAPO-5, 370°C for SAPO-11 and 410°C for MgAPO-36 catalyst. The relative performance based on the optimum yields for aromatics hydrocarbons was of the order: SAPO-5>SAPO-11> MgAPO-36. Similarly, the optimum aliphatic hydrocarbon yields were obtained at the following reaction temperatures: 410°C for SAPO-5, 370°C for SAPO-11 and 330°C for MgAPO-36 catalyst and the catalysts performance followed the order: MgAPO-36>SAPO-5>SAPO-11.

The amount of oxygenated compounds was significant in the OLP fractions indicating that further deoxygenation may be required in order to optimize the yield of both gaseous and liquid hydrocarbons. The maximum concentration of oxygenates for SAPO-5, SAPO-11 and MgAPO-36 were 24.2, 31.4 and 29.9 wt%, respectively. Methanol and acetone were the main components among these oxygenated compounds. In comparison, the yields of oxygenated compounds with HZSM-5 catalyst were low. This result re-emphasizes the role of catalyst acidity in the conversion of WDO. Since the rate of deoxygenation is a function of acid strength, it appears that the low extent of deoxygenation with aluminophosphate catalyst is a direct consequence of low acidity. For instance, in our earlier work[25] on the conversion of canola oil with a variety of catalysts, it was observed that catalysts with relatively low acidity such as aluminum-pillared clay and silica-alumina produced high amounts of oxygenated compounds in their OLP fractions compared with catalysts such as HZSM-5 and H-Y.

Gas Yield and Composition

As expected, the amount of gas product increased monotonically with temperature (Table 1). The major hydrocarbons present in the gas fraction were ethylene, propylene, butane and C_4 olefins. Of particular interest was the olefinic content of the gas phase. Plots (Figure 1) of olefin/paraffin ratio show a number of interesting observations. With SAPO-5 and SAPO-11, the hydrocarbon gas fraction was highly olefinic in nature. On the other hand, with MgAPO-36, the olefinic fraction was low especially at 330 and 370°C. These observations imply that where high fractions of olefins (mostly ethylene and propylene) in the gas product are desired SAPO-5 or SAPO-11 should be used. Ethylene and propylene are well known as the primary building blocks for the production of various plastics.

Proposed Reaction Pathway

Based on the above results an attempt was made to suggest a reaction pathway (Figure 2) that describes the conversion of WDO over aluminophosphate catalysts.

The formation of the desired aromatic and aliphatic hydrocarbons in the liquid product as well as gaseous hydrocarbons from WDO involves a complex reaction mechanism. The primary steps are the polymerization to form char (step 1), cracking and partial deoxygenation to form an intermediate heavy volatile components and water (step 2). The char formation is the consequence of only thermal effects rather than catalytic effect. Further cracking and deoxygenation (step 3) of the heavy volatile components results in the formation of various olefins and paraffins as well as CO, CO_2 and water. Some of the olefins and paraffins thus produced compose the observed aliphatic hydrocarbon fraction. In addition, some of the intermediate olefins aromatize to produce benzene (step 4). The production of aromatic hydrocarbons from olefins has been well documented in the

literature[24,26] and may consist of reactions such as oligomerization, cyclization and hydride transfer. Coke is formed through polymerization reactions of heavy volatile components (step 5).

The formation of aromatic and aliphatic hydrocarbons as well as the olefinic content of the gas products appear to be significantly affected by catalyst acidity and pore size. For instance, the more acidic catalysts (SAPO-5 and SAPO-11) produced more aromatic than aliphatic hydrocarbons. The olefinic content of the gas phase also appears to be affected by a combination of catalyst acidity and pore size. High olefin formation seem to be favored by high acidity and smaller pore size. For instance, SAPO-11 produces more olefins in the gas product than SAPO-5 and MgAPO-36 as a consequence of its medium pore structure and comparatively higher acidity than MgAPO-36. Also, the extent of coke formation is controlled by the pore size of the catalyst. As mentioned earlier, the larger the pore size the greater the coke formation.

Comparison of upgrading performance with HZSM-5 and Silica-alumina catalysts

In the literature, HZSM-5 has been used[1-3,5,6] to upgrade WDO. The OLP produced with HZSM-5 mostly consisted of aromatic hydrocarbons. Recently[6], we also carried out upgrading studies using silica-alumina as the catalyst. In this case, it was interesting to observe that the OLP consisted mostly of aliphatic type hydrocarbons. It was therefore of interest to compare the performance of the catalysts used in this study with the results obtained with HZSM-5 and silica-alumina catalysts.

The three aluminophosphate catalysts used in this study produced lower amounts of OLP compared to both HZSM-5 and silica-alumina catalysts. The low OLP yields are due to high tar, char and coke formation with the three aluminophosphate catalysts. As can be seen from Table 2, the aluminophosphate catalysts produced more than three-fold the amount of tar compared to HZSM-5 catalyst. Also, the combined coke and char yields were substantially higher with the aluminophosphate catalysts than with HZSM-5 catalysts.

Table 2. Comparison between aluminophosphate, silica-alumina and HZSM-5 catalysts in terms of their optimum yields for various products from the conversion of WDO.

	Catalysts				
Product	SAPO-5	SAPO-11	MgAPO-36	Silica-alumina	HZSM-5
OLP	22.2	19.9	16.3	25.2	33.6
Coke + Char	29.0-35.0	25.5-27.6	37.1-41.7	30.8-41.0	20.5-30.2
Tar	7.0-12.5	5.2-18.2	5.1-14.5	0-10.4	0-4.1
[1]Total Hydrocarbons	61.5	56.8	57.0	54.7	86.7
[1]Aromatic Hydrocarbons	37.7	32.4	29.6	6.5	85.9
[1]Aliphatic Hydrocarbons	26.1	24.4	34.5	48.2	18.6

[1]wt% of OLP

The OLP fractions obtained with aluminophosphate catalysts were concentrated in hydrocarbons than silica-alumina catalyst. However, these values were lower than that of HZSM-5 catalyst. Also, whereas the aluminophosphate catalysts were highly selective for benzene (about 90 % of aromatic hydrocarbon fraction), HZSM-5 was mostly selective for toluene and xylene. As mentioned earlier, compared to HZSM-5, the low hydrocarbon yields with aluminophosphate catalysts are primarily due to the low catalyst acidity[22]. It is interesting to note, however, that whereas the hydrocarbon content of OLP with HZSM-5 was predominantly aromatic in nature, those obtained with the aluminophosphate catalysts consisted of significant amounts of both aromatic and aliphatic hydrocarbons. On the other hand, silica-alumina catalyst produced significantly high fractions of aliphatic hydrocarbons. Thus, it appears that HZSM-5 could be used as catalyst where a highly aromatic hydrocarbon liquid product is desired and silica-alumina where a highly aliphatic hydrocarbon content of OLP is desired. On the other hand, where a mixture of both aromatic and aliphatic hydrocarbons in the OLP is desired, the aluminophosphate catalysts appear to be the desired catalysts.

Conclusions

1. WDO was converted over aluminophosphate catalysts to organic liquid products (12.5-22.2 wt% of WDO) containing 22.5-37.7 wt% aromatic hydrocarbons (such as benzene, toluene and xylene) and 18.9-34.5 wt% aliphatic hydrocarbons (such as n-hexane, heptane and isooctane). The selectivity for benzene was exceptionally (about 90% of aromatic hydrocarbon fraction) with these aluminophosphate catalysts compared to HZSM-5, H-Y and H-mordenite which have shown relatively high selectivity for toluene, xylene and other alkylated benzenes. Overall, the optimum yield of hydrocarbons (57-61.5 wt% of OLP) was comparable with that of silica-alumina (54.7 wt% of OLP) but lower than HZSM-5 catalyst (86.7 wt% of OLP).

2. The extent of gas production with WDO was between 5.5-16.7 wt%. SAPO-5 was highly selective for ethylene and propylene, SAPO-11 for propylene and MgAPO-36 for i-butane. The results show that aluminophosphate catalysts are highly selective olefins than to HZSM-5.

References

(1) Baker, E.G.; Elliott, D.C., in *Research in Thermochemical Biomass Conversion*, Elsevier Appl. Sci., London, 1988, pp. 883-895.

(2) Sharma, R.K .; Bakhshi, N.N., *Energy and Fuels*, **1993**, 306-314.

(3) Craig, W.; Coxworth, E., in *Proceedings of the Sixth Canadian Bioenergy R&D Seminar*, Ganger, C., Ed., Richmond, Canada, 1987, pp. 407-411.

(4) Boocock, D.G.B., Konar, S.K., Mackay, A., Chang, P.T.C. and Liu, J., *Fuel*, **1992**, 71, 1291-1297.

(5) Chantal, P.; Kaliaguine, S.; Grandmaison, J.L.; Mahay, A., *Appl. Catal.*, **1984**, 10, 317-332.

(6) Adjaye, J.D.; Bakhshi, N.N., in *29th Intersociety Energy Conversion Eng. Conf.*, Monterey, CA, Part 4, 1994, pp.1578-1583.

(7) Flanigen, E.M.; Lok, B.M.; Patton, R.L.; Wilson, S.T., in *Proceedings of the 7th*

International Zeolite Conference, Kondash and Elsevier, Tokyo, 1986, pp. 103-112.
(8) Rabo, J.A.; Pellet, R.J.; Coughlin, P.K.; Shamshoum, E.S., *Studies in Surface Sci. and Catal.*, Elsevier, Amsterdam, 1989, 46, pp. 1-18.
(9) Martens, J.A.; Grobet, P.J.; Jacobs, P.A., *J. Catal.*, **1990**, 126, 299-305.
(10) Inui, T.; Matsuda, H; Okaniwa, H.; Miyamota, A., *Appl. Catal.*, **1990**, 58, 155-162.
(11) Akolaker, D.B., *J. Catal.*, **1994**, 149,1-10.
(12) Pellet, R.S., Coughlin, P.K., Shamshoum, E.S. and Rabo, J.A., in Molecular Sieve Science, ACS Sym. Ser., 1988, pp. 512-531.
(13) Graham, R.G; Freel, B.A; Overend, R.P., In *Proceedings of the 7th Canadian Bioenergy R&D Seminar*, Ottawa, 1989, pp.669-673.
(14) Scherzer, J., *Catal. Rev.-Sci. Eng.*, **1989**, 31 (3), 215-354.
(15) Szostak, R., *Molecular Sieves: Principles of Synthesis and Identification*, Van Nostrand Reinhold, New York, 1989.
(16) Lok, B.M.; Messina, A.C; Patton, R.L.; Gajik, R.T.; Lannan, T.R.; Flanigen, E.M., US Patent 4,440,871, **1984**.
(17) Wilson, S.T.; Flanigen, E.M., US Patent 4,567,029, **1989**.
(18) Katikaneni, S.P.R.; Adjaye, J.D.; Bakhshi, N.N., Energy and Fuels, **1995** (submitted).
(19) Adjaye, J.D.; Bakhshi, N.N., *Biomass and Bioenergy* , **1994**, 7, 201-211.
(20) Adjaye, J.D.; Bakhshi, N.N., *Fuel Processing Technol.*, **1995**, (in press).
(21) Bhatia, S., *Zeolite Catalysis: Principles and Applications*, CRC Press Inc., Baco Raton, USA, 1990.
(22) Carson, R.; Coke, E.M.; Dwyer, J.; Hinchliffe, A.; O'Malley, P.J.O., in *Zeolite As Catalysts, Sorbents and Detergents Builders: Applications and Innovations, Studies in Surface Science and Catalysis*, Karge, H.G. and Weitkamp, J., Eds., Elservier, Amsterdam, 1989, 46, pp. 45-48.
(23) Milne, T.A.; Evans, R.J.; Filley, J., in *Research in Thermochemical Biomass Conversion*, A.V. Bridgwater and J.L. Kuester (Eds), Elsevier Appl. Sci., London, 1988, pp. 910-926.
(24) Pines, H., The *Chemistry of Catalytic Hydrocarbon Conversions*, Academic Press, London, 1991.
(25) Katikaneni, S.P.R.; Adjaye, J.D; Bakhahsi, N.N., *Can. J. Chem. Eng.*, **1995** (in press).
(26) Chen, N.Y.; Garwood, W.E.; Dwyer, F.G., *Shape Selective Catalysis in Industrial Applications*, Marcel Dekker, Inc., New York, 1989.

Appendix 1

The terms "Yield" and "selectivity" as used in this paper are defined as follows:

Yield (wt%) = (P (g)/Bio-oil Fed (g)) x 100 (1)
Selectivity, S = (P (wt%))/(100-P (wt%)-UA (wt%)) (2)

where P represents the products, i.e., char, coke, gas, organic liquid product and aqueous fraction. UA represents the Unaccounted Fraction. R is residue.

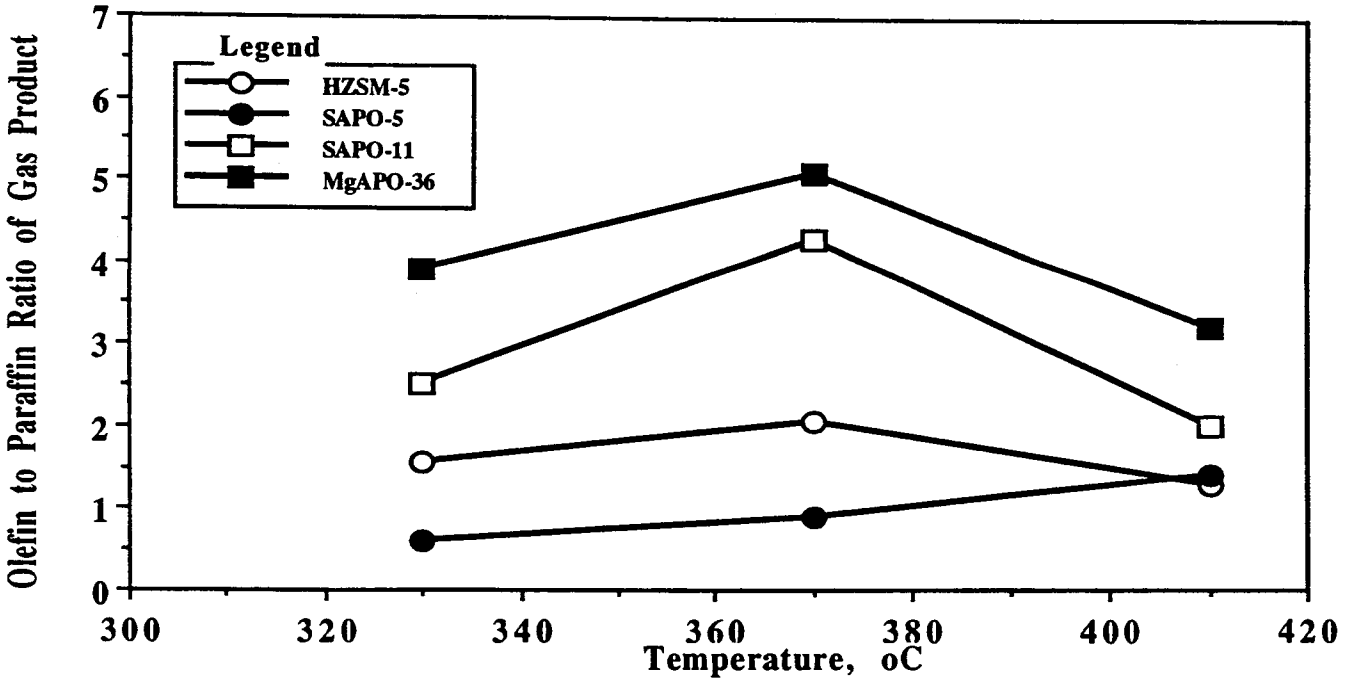

Figure 1. Comparison of the olefin to paraffin ratio of the gas products.

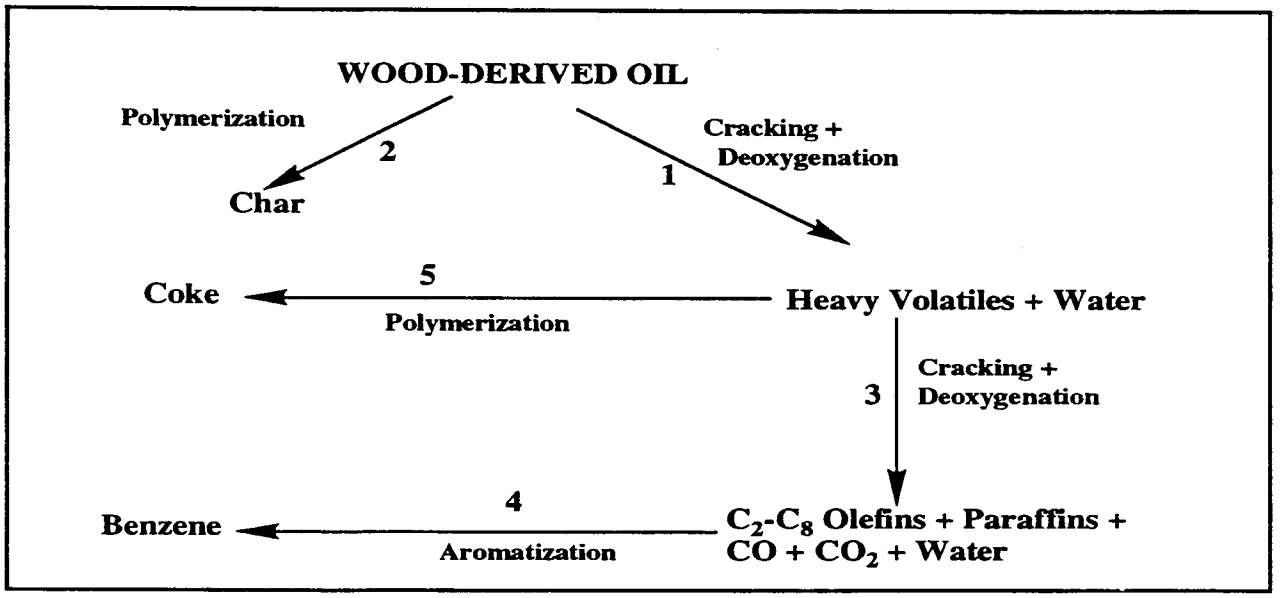

Figure 2. Proposed reaction pathway for the conversion of wood-derived bio-oil.

PLANT VARIABILITY AND BIO-OIL PROPERTIES

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Abstract

Thermochemically converting biomass feedstocks to fuels is one of the major thrusts of renewable energy research at the National Renewable Energy Laboratory. Among several thermochemical routes is the fast pyrolysis process which produces liquid fuels from woody and herbaceous biomass feedstocks. Because of the large variability in the composition of biomass feedstocks due to plant variety and environmental factors, it is important to assess how these variabilities affect the properties of thermochemical liquid fuels (bio-oils) produced from these resources.

Similar varieties of switchgrass (*Panicum virgatum L.*) that were grown at three different locations and three hybrid poplar clones that were grown at one location were used in these studies. The feedstocks were pyrolyzed in a fluidized bed reactor at 500 °C. The gas products were analyzed on-line and the liquid products were analyzed for elemental composition and higher heating values.

Apart from small differences in the yield of char/ash, the yields of pyrolysis oils and gases were similar for switchgrass feedstocks grown at all three locations. The char/ash yields ranged from 21.1 to 22.9%; total liquids (organic liquids + water) yields ranged from 59%-60.5%; and the gas yields ranged from 11%-12% (wt). The higher heating values (HHVs) of the oils were similar (24.3-24.6 MJ/kg).

For the hybrid poplar feedstocks, total liquids (65%-69%), char/ash (10%-11%), and gas yields (15.6%-17%) were similar for all three poplar clones; however, the elemental composition and the HHVs of the pyrolysis oils had statistically significant differences. The NC5260 pyrolysis oils had lower HHV (22.0±0.5 MJ/kg) compared to the DN clones (23.2±0.3 MJ/kg). The yields of total liquids and organics for the three clones were higher than those for the switchgrass feedstocks. The gas yields for the hybrid poplar clones were higher than those for the switchgrass, but had compositions similar to those of the switchgrass feedstocks. The char/ash yields of the switchgrass were twofold those of the hybrid poplar clones.

Introduction

Because of the large variability in the composition of biomass feedstocks caused by plant variety and environmental factors, it is important to assess how these variabilities affect the properties of thermochemical liquid fuels (bio-oils) produced from these resources.

Most published studies in literature [1,2,3] have not addressed these issues, therefore, we found it expedient to undertake the current studies. This work assesses the influence of plant location and plant variety on the thermochemical conversion process and on the properties of biomass pyrolysis oils.

Experimental

Biomass Feedstocks

For this study, hybrid poplar feedstocks were selected from the following clones: DN17 (*deltoides x nigra*), DN182 (*deltoides x nigra*), and NC5260 (*tristis x balsamifera*). The selection was aided by summative analysis of the poplar clones which showed significant differences in the composition of the feedstocks [4]. The poplar clones were harvested from sites in Ashland, Wisconsin, by the United States Department of Agriculture Forest Service (USDA-FS), North Central Experiment Station, Rhinelander, Wisconsin.

Switchgrass (*Panicum virgatum L.*) samples were harvested from plots in Mead, Nebraska, West Lafayette, Indiana, and Ames, Iowa. The samples from each plot were too small for triplicate runs to be conducted in the fluidized bed reactor, therefore, samples from several plots were combined to give enough sample for triplicate runs. This approach was justified because the summative analysis studies revealed no significant difference in the composition of switchgrass from different plots at the same location [5].

Switchgrass and hybrid poplar samples were prepared for pyrolysis by knife milling in a Wiley mill (model 4) until all the samples passed through a 2-mm screen. The milled materials were then sieved to -20/+80 mesh size and dried at room temperature to a moisture content of 4%-6% before pyrolyzing in the fluidized bed reactor. The Sauter mean diameter of the feedstocks was 345-400 μm.

Fluidized Bed Pyrolysis of Feedstocks

To assess the influence of plant location and plant variety on thermochemical conversion products, the feedstocks (switchgrass and hybrid poplar) were pyrolyzed in a fluidized bed reactor.

The reactor consisted of a 2-in. (50 mm) schedule 40 Inconel steel pipe, 20 in. (500 mm) long (including a 5.5 in. (140-mm) preheater zone below the gas distribution plate) and equipped with a 100-μm porous metal gas distributor. The fluidizing medium was silica sand, and the bed was fluidized with nitrogen. The reactor was externally heated with a three-zone electric furnace. The reactor tube contained a bubbling fluid bed with back-mixing of the feed and sand. The static sand bed height was 3.5 in. (90 mm), expanding to 4.7 in. (120 mm) when fully fluidized. The silica sand particles had a Sauter mean diameter of 350 μm.

The biomass was loaded into a feed hopper (batch-wise) and conveyed by a twin-screw feeder into an entrainment compartment where high-velocity nitrogen gas entrained the feed and carried it through a jacketed air-cooled feeder tube into the fluidized bed.

The pyrolysis temperature was maintained at 500 °C and the apparent pyrolysis vapor residence time was about 0.4 s. The apparent vapor residence time in the reactor was estimated by the Waterloo Fast Pyrolysis Process methodology [6]. In this approach, the apparent residence time of gases and vapors is defined as the free reactor volume (the empty reactor volume minus the volume of hot sand) divided by the entering gas flow rate expressed at reactor conditions. Runs lasted from 1.5-3.5 h, and the feed rate was 80-100 g/h. The feed rate, gas flow rate, and reactor temperature were kept constant during each run. Feed gas flow rate was kept at 9 L/min (STP), and the fluidizing gas flow rate was kept at 16 L/min (STP). The feed hopper was slightly pressured with gas flowing at less than 1 L/min (STP).

Pyrolysis gases and vapors exiting the reactor passed through a heated cyclone to separate char/ash and any entrained sand. The cyclone and char-pot temperatures were maintained at 400 °C to avoid condensation of the pyrolysis vapors. The pyrolysis gases and vapors were then passed through a condensation train consisting of a chilled water condenser, an ice/salt mixture condenser, electrostatic precipitator, and a coalescence filter (all connected in series). The electrostatic precipitator was maintained at 18-20 kV throughout each run. The temperatures, gas flow rates, pressure drop across reactor, and electrostatic precipitator voltage were controlled and/or monitored by an MKS™ data acquisition unit.

The gaseous products were analyzed using an on-line HP 5890 Series II gas chromatograph (GC). The gaseous products were sampled and analyzed every twenty-five minutes during the run. In addition, gas samples were collected in syringes between GC runs and these were analyzed after the run. Total gas volume was measured by a dry test meter. To ensure good mass closure, the entire setup (excluding the dry test meter) was weighed before and after each run.

Pyrolysis oils were recovered (after weighing the pyrolysis unit) by rinsing the condensers with acetone. The oil-acetone mixture was filtered through a 40-60 μm fritted glass filter, and the moisture content of the filtrate was determined by Karl Fischer analysis. The weight of the acetone-insoluble fraction of the filtrate was added to the weight of the char/ash recovered from the char-pot and the fluidized bed reactor.

These were recorded as total char/ash produced from each run. The acetone was evaporated under vacuum (40 °C and 61.3 kPa), and the recovered oils were analyzed for elemental composition and HHV. The char/ash samples were not analyzed further.

Elemental analysis and HHVs of the pyrolysis oils were determined in triplicate at Huffman Laboratories in Golden, Colorado.

Results

Switchgrass Feedstocks Pyrolysis Products

Assessing the influence of plant location on the pyrolysis products of the switchgrass feedstocks was based on the following criteria: total liquids (organic liquids + pyrolysis water), gas, and char/ash yields, elemental composition, and HHV of the pyrolysis oils.

The yields of total pyrolysis liquids (organic liquids + water) from feedstocks grown at all three locations (Mead, Ames, and West Lafayette) were very similar and ranged from 59%-60% (see Table 1). However, there were significant differences between organic liquid yields from the three sites. The West Lafayette sample had a slightly lower organic liquids yield (49.9±2.0%) than the other two sites, which had average organic liquid yields of 53.2%. The pyrolysis oils were dark brown, viscous, single-phase acidic liquids with a pH of 2.5-3.0. The char/ash content of the oils before filtration through 40-60 μm filter was 1%-2%.

The condensation train segregated the oils into a light fraction with high moisture content and a heavy fraction with low moisture content. The light fraction condensed in the chilled water condenser. The heavy fraction was mostly aerosols that formed during the pyrolysis process and did not condense in the chilled water condenser. These were captured in the electrostatic precipitator. The heavy oil fraction contained very little water and was extremely viscous and sticky. The sticky oils accumulated on the electrostatic precipitator electrodes and often led to voltage leakage and arcing. The heavy oil fraction conducted electrical current probably because it contained char/ash which had about 2% potassium. The oils stuck to the walls of the glass containers, and once they dried did not dissolve readily in acetone or methanol. The glass equipment was usually cleaned with alcoholic potassium hydroxide, the only solvent that could dissolve these dry oils.

The char/ash was defined as the acetone-insoluble material recovered from the cyclone separator, fluidized bed reactor, and 40-60 μm filter. About 90% of the char/ash was recovered from the cyclone separator, 1%-2% from the filtration of the oil, and the rest from the reactor. The char is mostly carbonaceous material, with small amounts of oxygen and hydrogen. Most of the ash in the original feedstock is associated with this carbonaceous material; hence, the material had a high ash content (unreported data).

Char/ash yields from the different sites showed statistically significant differences at 95% confidence level. The Mead site feedstock had the highest char/ash yield (22.9±0.6%) and the Ames site feedstock had the lowest (21.2±0.2%).

Table 1. Material Balance and Gas Analysis of West Lafayette, Mead, and Ames Switchgrass Pyrolysis Products*.

	West Lafayette, IN	Mead, NE	Ames, IA
Mass Balance (%)			
Gas	11.5±0.8	11.8±0.3	11.0±2.0
Water	9.3±2.2	6.1±0.9	7.3±0.3
Organics	49.9±2.0	53.2±0.6	53.2±0.3
Char/ash	21.8±0.4	22.9±0.6	21.2±0.2
Total	92.6±0.6	94.0±1.5	92.6±2.5
Gas Analysis (%)			
CO_2	8.5±0.4	8.6±0.2	8.0±1.9
CO	2.1±0.2	2.5±0.3	2.4±0.4
CH_4	0.2±0.1	0.2±0.1	0.3
C_2H_2	0.2±0.05	0.4	0.1
C_2H_6	0.1±0.05	0.1	0.2
C_3H_8	0.2±0.05	0.1	0.1
C_4H_6	0.3±0.15	0.3±0.1	0.3±0.1
Total	11.5±0.8	11.8±0.3	11.0±2.0

*The analysis is based the on oven-dry weight biomass. The oil yields were determined gravimetrically and were not washed with acetone before the determination. Errors are standard deviations from three determinations from three pyrolysis runs.

Gas yields from all three sites were similar, and differences were not statistically significant (Table 1). Most of the gas was carbon dioxide and carbon monoxide, with small amounts of hydrocarbons. The hydrogen and water vapor contents of the gases were not analyzed. Multiple analyses of the gas fraction during each run, which lasted 2-3 h, revealed no significant differences in the composition of the gases over the

duration of the run, indicating that very little or no cracking of pyrolysis vapors took place on the fresh char retained in the reactor. Where there was cracking on the fresh char, the carbon monoxide and carbon dioxide contents of the gases increased significantly [7].

The elemental compositions and HHVs of the pyrolysis oils did not appear to be dependent on feedstock origin. There was a small statistically insignificant difference in the HHV of the oil from the West Lafayette feedstock compared to the other oils (see Table 2).

Table 2. Elemental Analysis and HHVs of Switchgrass Pyrolysis Oils*.

Composition (%)	**West Lafayette, IN**	**Mead, NE**	**Ames, IA**
Carbon	55.8±2.3	57.6±1.1	57.6±1.5
Hydrogen	7.4±0.6	6.8±0.2	6.9±0.1
Oxygen#	36.1±1.6	35.3±1.8	33.9±0.6
Nitrogen	1.24±0.04	1.40±0.14	1.39±0.24
Sulfur	0.07±0.01	0.16±0.08	0.13±0.06
Chlorine	<0.1	<0.1	0.10
Ash	<0.01	<0.01	0.16±0.07
HHV(MJ/kg)	24.3±0.8	24.6±0.8	24.6±0.8

oxygen by difference.
*Error bars are standard deviations of three determinations from three pyrolysis runs. The oils were recovered by rinsing the apparatus with acetone and then vacuum rotary evaporating the acetone (all data are on moisture-free basis).

Hybrid Poplar Feedstock Pyrolysis Products

Assessing the influence of clonal variation on the pyrolysis products of the hybrid poplar feedstocks was based on the following criteria: total liquids (organic liquids + water), gas, char/ash yields, elemental composition, and HHVs of the pyrolysis oils.

The yields of pyrolysis oils for all three poplar clones were very similar and ranged from 65%-69% (see Table 3). The oils were dark brown, viscous, single-phase acidic liquids with a pH of 2.5-3.0. These oils were less sticky than the switchgrass pyrolysis oils. Their moisture contents were similar to those of the switchgrass, but the char/ash content before filtration was about 0.5%. Unlike the switchgrass

feedstocks, there was no significant difference between the organic liquid yields from the different clones.

The condensation train behavior of the poplar pyrolysis oils were similar to those of the switchgrass pyrolysis oils. However, the poplar pyrolysis oils were less viscous and less sticky than the corresponding switchgrass pyrolysis oils, and did not accumulate on the electrostatic precipitator electrodes; thus, no voltage leakage or arcing occurred during the pyrolysis runs. The oils were much easier to handle than the corresponding switchgrass oils. They dissolved readily in acetone and did not stick tenaciously to the glassware.

Table 3. Material Balance and Gas Analysis of Hybrid Poplar Pyrolysis Products*.

	DN17	**DN182**	**NC5260**
Mass Balance (%)			
Gas	16.6	15.6	17.2
Water	6.2	6.2	7.0
Organics	61.1	59.3	62.3
Char/ash#	10.1	11.0	10.7
Total	94.0	92.1	97.2
Gas Añalysis (%)			
CO_2	10.8	10.1	9.8
CO	4.5	4.8	6.5
CH_4	0.6	0.3	0.3
C_2H_2	0.2	0.1	0.1
C_3H_8	0.1	0.1	0.1
C_4H_6	0.4	0.3	0.4
Total	16.6	15.6	17.2

Char/ash is the mixture of carbonaceous material and sequestered inorganic material recovered from the char pot, fluidized bed reactor, and acetone insoluble material recovered after filtration.
*The analysis is based on oven-dry biomass. The oil yields were determined gravimetrically and were not washed with acetone before the determination.

Char/ash yields ranged from 10%-11% (Table 3). About 95% of the char was recovered from the cyclone separator, 0.5% from the filtration of the oil, and the rest from the reactor. The char/ash from the reactor and the cyclone were shiny black lightweight materials, whereas the sample recovered from the filtration was fine and dull black. The char is mostly carbonaceous material, with small amounts of oxygen and hydrogen [8].

Gas yields ranged from 15.6%-17.2% (Table 3) and were higher than those for the switchgrass feedstock. The compositions of the gases were similar to those of the switchgrass feedstocks.

Elemental composition of the pyrolysis oils showed statistically significant differences between clones (Table 4). The pyrolysis oil from NC5260 clone feedstock had a slightly lower (but statistically significant at 95% confidence level) HHV compared to the pyrolysis oils from the DN17 and DN182 clones. The DN17 and DN182 feedstock pyrolysis oils had similar HHVs. The differences in the HHVs are reflected in the carbon content of these pyrolysis oils. The NC5260 feedstock pyrolysis oil had a lower carbon content than the other hybrid poplar clone feedstock pyrolysis oils.

Table 4. Elemental Analysis and HHVs of Hybrid Poplar Pyrolysis Oils.

Composition (%)	**DN17**	**DN182**	**NC5260**
Carbon	55.8±0.8	55.4±0.4	53.6±1.1
Hydrogen	6.7±0.2	6.4±0.3	6.2±0.6
Oxygen#	37.9±0.1	38.9±0.7	41.1±1.3
Nitrogen	0.20±0.04	0.20±0.05	0.17±0.02
Sulfur	0.04±0.01	0.02±0.00	0.03±0.00
Chlorine	<0.1	<0.1	<0.1
Ash	<0.01	0.01	0.01
Higher heating value (MJ/kg)	23.2±0.3	23.0±0.2	22.0±0.5

oxygen by difference.
* Error bars are standard deviations of three analyses. The oils were recovered by rinsing the apparatus with acetone and then vacuum rotary evaporation of the acetone.

Discussion

Influence of Plant Location on the Pyrolysis Products of Switchgrass

The yield of pyrolysis products from switchgrass varieties grown at Ames, Mead, and West Lafayette sites were similar except for the char/ash yields, which showed significant differences. The Mead site switchgrass gave the highest yield of char/ash compared to the switchgrass from the other sites, and the Ames switchgrass gave the lowest char/ash yield. The differences in the yields were significant at the 95% confidence level.

The differences in the yields of char/ash were attributed to the protein and lignin contents of the feedstocks rather than the ash contents. Although the ash in biomass feedstocks promotes char formation [9], the ash contents of the feedstocks from the three sites were similar [5]. It is therefore unlikely that the ash caused the differences in the char/ash yields. The lignin and nitrogen compounds (proteins) also promote char formation [10], and are a probable cause of the observed differences in char/ash yields. The data show that the protein content of the Mead switchgrass (7%) was higher than that of the Ames and West Lafayette feedstocks (5%). Because proteins tend to denature and also react with carbohydrate decomposition products at high temperatures [11], this is a likely source of the higher char/ash yield for this switchgrass

The small but statistically insignificant differences in the char/ash yields of the Ames and West Lafayette feedstocks were probably caused by the differences in their lignin contents, because the ash and protein contents of these feedstocks were similar.

Although the char/ash yields of the feedstocks differed significantly, the pyrolysis oil yields and HHVs of the oils were similar for all switchgrass feedstocks (Tables 1 and 2). This was probably because the nitrogen compounds (protein) formed mostly char/ash during the pyrolysis process and did not form a significant component of the oils. Most of the oils originated from the lignocellulosic component of the feedstocks; and hence, the HHVs of the oils were similar.

The difference in the yield of char/ash from the different switchgrass feedstocks suggests that the time and frequency of fertilization may play some role in the quality of the feedstock. A heavily fertilized field, may result in higher protein or nitrogen compound content in the feedstock, resulting in high char/ash yields and subsequently lower the liquid and gaseous product yields. These data also suggest that perhaps low protein switchgrass varieties may be better feedstocks for thermochemical conversion process.

The time of harvest of the switchgrass may also be an important factor with respect to the protein content of the feedstock. The crude protein content of grasses is lowest during the winter and highest during spring [12]. Thus, if the switchgrass is harvested in the fall when the plant is matured, the protein content will be low and the fiber

content will be high and therefore this will make a better feedstock for thermochemical conversion.

Influence of Clonal Variation on Hybrid Poplar Pyrolysis Products

The hybrid poplar clones showed no significant differences in the yields of various products from pyrolytic conversion; however, statistically significant differences were observed in the carbon contents (and consequently the HHVs) of the pyrolysis oils. The pyrolysis oil from the NC5260 poplar clones had a significantly lower HHV compared to the DN poplar clones, which can be attributed to the differences observed in the summative composition of the feedstocks [4]. The NC5260 poplar clones were significantly lower in lignin (21%) and higher in cellulose content (46%) compared to the DN poplar clones (23% and 43% lignin and cellulose respectively). This difference in composition implies lower carbon content and higher oxygen content. Since higher carbon and lower oxygen contents translate into high energy content, it follows that the energy content of the pyrolysis products of the NC5260 clones will be lower than that of the DN clones.

The extractives component of woody species tend to have higher energy content than the lignocellulosic component, but no statistically significant differences were detected between the extractives component of the poplar clones [4]. Thus, the differences in the HHVs of the pyrolysis oils were attributed solely to the differences in the lignin/cellulose content of the original feedstocks.

Conclusions

For all practical applications, it appears that plant location did not significantly affect the properties of pyrolysis oils generated from the switchgrass used in this study. However, for the hybrid poplar studied here, clonal variation did have a significant effect on the higher heating values (HHV) of the pyrolysis oils. Feedstocks with high cellulose/low lignin content (such as NC5260) had lower HHVs, but the overall oil yield was similar for all poplar clones.

Pyrolysis oil and gas yields were not significantly affected by plant location, but the small differences in the protein and lignin contents of the switchgrass occurring because of the different plant locations affected the char/ash yields. The protein and lignin appear to promote char formation reactions and increased char yields. Because most protein in the switchgrass appeared to be converted into char/ash, it had very little influence on the properties of the oils.

Plant cultural practices may be an important factor for the production of herbaceous thermochemical feedstocks. Low protein, high fiber switchgrass varieties may be the most suitable switchgrass for thermochemical conversion processes.

References

1. Moser, L.E. "Quality of Forage as Affected by Post-Harvest Storage and Processing." In *Crop Quality, Storage, and Utilization.* Hoveland, C.S. Ed.; ASA-CSSA, Madison, WI. 1980 p. 227.

2. Jirjis, R.; and Theander, O. "The Effect of Seasonal Storage on Chemical Composition of Forest Residue Chips." *Scan. J. For. Res.* 1990, 5, 345-448.

3. White, M.S.; Curtis, M.L.; Sarles, R.L.; and Green, D.W. "Effects of Outside Storage on the Energy Potential of Hardwood Particulate Fuels: Part 1. Higher and Net Heating Values." *For. Prod. J.* 1983, 33 (11/12), 61-65.

4. Davis, M.F.; Johnson, D.K.; Deutch, S.; Agblevor, F.; Fennell, J.; and Ashley, P. "Variability in the Composition of Short Rotation Woody Feedstocks." In this proceeding.

5. Johnson, D.K. et. al. In this proceeding.

6. Palm, M.; Piskorz, J.; Peacock, C.; Scott, D.S.; and Bridgewater, A.V. "Fast Pyrolysis of Sweet Sorghum Bagasse in a Fluidized Bed." In Proceedings of, *First Biomass Conference of the Americas: Energy, Environment, Agriculture, and Industry.* National Renewable Energy Laboratory, Golden, CO, 1993, p. 947.

7. Boronson, M.L.; Howard, J.B.; Longwell, J.P.; and Peters, W.A. "Heterogeneous Cracking of Wood Pyrolysis Tars over Fresh Wood Char Surfaces." *Energy and Fuels,* 1989, 3, 735-740.

8. Agblevor, F.A.; Besler, S.; and Wiselogel, A.E. "Fluidized Bed Pyrolysis of Stored Biomass." *Energy and Fuels*, 9(4), July/August, 1995, in press.

9. DeGroot, W.F.; and Shafizadeh, F. "Influence of Exchangeable Cations on the Carbonization of Biomass." *J. Anal. Appl. Pyro.* 1984; 6(3) 217-232.

10. Agblevor, F.A.; Rejai, B.; Evans, R.J.; and Johnson, K.D. "Pyrolytic Analysis and Catalytic Upgrading of Lignocellulosic Materials by Molecular Beam Mass Spectrometry." In *Energy from Biomass and Wastes XVI*; Klass, D.L., Ed.; Institute of Gas Technology (IGT), Chicago, IL, 1993, pp. 767-795.

11. Theander, O.; and Nelson, D.A., "Aqueous High Temperature Transformation of Carbohydrates Relative to Utilization of Biomass," *Adv. Carbohydrate Chem. Biochem.* 1989, 46, 273-326.

12. Waller, G.R.; Morrison, R.D.; and Nelson, A.B. "Chemical Composition of Native Grasses in Central Oklahoma From 1947-1962." *Oklahoma State University, Agricultural Experiment Station, Bulletin B-697*, January 1972.

BIO-FUEL OIL COMBUSTION IN A 0.5 MW FURNACE

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Abstract

Within the framework of a research partially financed by EU, ENEL-CRT has carried out combustion tests on two different kinds of bio-fuel oil derived from the fast pyrolysis of vegetable biomass.
The tests have been performed utilizing a multi-purpose test rig, that includes a vertical 0.5 MWt furnace equipped with an industrial swirl-type design burner installed at the top of the combustion chamber.
The scope was to compare the behavior of bio-fuel oil with a No.6 fuel oil, in view of investigating on the possible utilization in power systems of this new fuel, in replacement of conventional mineral fuel oils.
To that purpose some minor modifications of the existing experimental facility were necessary, in order to adapt the rig to the specific research.
The paper presents the encouraging results of the experiments, during which the stable combustion that it was possible to achieve, allowed the monitoring of operating conditions and of flame quality, with particular attention to the thermal furnace load, final O_2, flow rates, pressures and temperatures.
Flue gas sampling and analysis of NO_x, CO, SO_2 and CO_2 were also performed, together with solid particulate sampling.

Introduction

Biomass fuels are attracting growing world-wide interest because of their environmental benefits. Liquid fuels derived from biomass pyrolysis have a potentially wide range of applications in industrial process heating, steam rising or power generation.
The research, carried out by ENEL in this field, is essentially aimed at evaluating the potentialities of using these bio-oils as a fuel to replace heavy oils in power plants, especially of small and medium size.

Aim of the test

The objective of this investigation, carried out with the partial financing support of EU, was to characterize the combustion behavior of two biomass derived pyrolysis oils supplied by ENSYN (Canada), and Union Fenosa (Spain), respectively.
The biomass fuels were compared with a No. 6 fuel oil.
The experimental activity was performed at the ENEL CRT Experimental Area of Livorno (Italy).
The tests included flue gas analysis as regards the traditional pollutants, the sampling of solid particles and their chemical and physical characterization.
Particular attention was devoted to handling, pumping and atomization problems.
This study has not assessed the problems posed by the corrosive characteristics of bio-oils, due to their acidity. In fact a longer test period would be necessary for a comprehensive investigation on this subject.

Experimental apparatus

The 0.5 MWt furnace used for the tests is an experimental facility built up by ENEL to perform experiments on different types of fuel: indeed, this furnace may be fired with fuel oil, gas oil, L.P.G., pulverized coal and coal-water slurries.
The plant consists of a 0.8m x 0.8m x 3.2m vertical furnace (see Fig. 1) fed by one single burner at the top. Water-cooled probes can be introduced into the furnace, in order to control heat extraction and flue gas outlet temperature.
The furnace is normally run under slight depression, using a suction fan.
The burner, with radial blade layout, may burn fuel oil and pulverized coal. It is fed through two independent lines: the primary air line, used for conveying coal, and the secondary air line. The secondary air swirl number is controlled by varying the inclination angle of blades.
Oil atomization is assisted by compressed air.
All the main operating parameters are collected with a data acquisition and display system installed in the control room.

Fuel characterization

The results of chemical-physical analysis of the bio-fuels are given in Table 1.

The reference fuel used was a heavy oil commonly fired in ENEL thermoelectric power plants with an average sulphur content of 0.95% and nitrogen content of 0.55%.
The two bio-oils have similar chemical-physical characteristics, but are markedly different as regards water content (19% for ENSYN vs 23% for Union Fenosa) and viscosity (ENSYN ehxibits a higher viscosity than Union Fenosa oil).
The nitrogen content of both fuels is very low (approximately 0.05%).
Sulphur is also present in small concentrations, however in lower concentrations compared to heavy oil.
A high content of water and oxygenated compounds is typical of bio-oils; the oxygen content, calculated by difference, is therefore very high in both fuels (approximately 50%). This value decreases to about 27% or O_2 available for combustion, taking into account the contribution of water present in the fuels.
The heat value of both bio-oils is approximately 40% of heavy oil heat value. It was therefore necessary to feed more then two times the amount of bio-oil to obtain the same thermal input into the furnace.
The carbon residue for the two bio-oils is approximately double compared to that found in heavy oils, indicating their trend to produce more unburnt material.

Plant modification

The use of bio-fuels required the solution of some problems, especially in consequence of their high acidity and viscosity.
A stainless steel tank, equipped with a stirrer to prevent stratification phenomena, was therefore provided for bio-oils storage. Bio-oil was not pre-heated, to prevent the separation of water.
The fuel was fed to the burner through an existing feeder line of stainless steel, designed for testing coal-water slurries (CWS) and a moyno pump was utilized. The bio-oils flow rate was controlled by varying the pump's speed with a frequency converter. The line was equipped with an insulated heating system, in order to maintain proper viscosity levels of the fuel at the burner's inlet nozzle. Figure 2 shows the viscosity curve of the fuels as a function of temperature.
Fluid mechanics of the burner was characterised prior to starting the tests; the results showed that the pressure-flow characteristics, i.e. the flow rate at the outlet, met the requirements to run the furnace with bio-oils.
The atomization of the fuels was made with air, on the basis of knowledge acquired on fuels with viscosity similar to that of bio-oils. A 5-hole Y-mixing atomizer was manufactured to be used both with fuel oil and bio-oils.
The fuel's pressure at the inlet nozzle was fixed at 10 bar, whereas the pressure for atomization air was slightly higher.
The presence of fine solid particles suspended in the bio-oils was not considered as a disturbing factor considering the type of atomizer that had been chosen. No filters were therefore installed in the feeding system of bio-oils.

Measurement methods

Measurements of gaseous and solid (soot) species concentrations were performed only at the exit of the furnace.
In-flame temperature was measured by a shielded thermocouple of type S.

Experimental procedure

The main target of this test campaign was to evaluate the possibility of running the plant with bio-oils, in conditions of stationary combustion, without aid auxiliary fuels, and providing a good combustion quality.
During the first period of the campaign, the plant's best operation conditions for fuel oil were established, considering flame quality and gas emissions. Table 1 shows the characteristics of fuel oil.
The following variables were considered: position of the oil inlet nozzle, position of the primary pipe inside the burner's throat, blade angle, primary air flow rate and injection angle of fuel spray.
The best layout resulting from the tests was also characterized for solid particulate at three oxygen levels in the flue gas (3%, 2%, 1%) and for three different loads: 100%, 75%, 50% of nominal load.
Bio-oils were tested with this layout, sampling solid particulate under the same operation conditions used for oil, with a thermal load of 100%, 75% and 60%. The test planned at 50% of the load was not performed, since the feeding pump in this case could not guarantee a stable flow rate as required.
At the beginning of the tests with bio-oils, difficulties occurred as the atomizer holes clogged up; this problem was solved increasing the diameter of outlet and atomizing air holes.
The CWS feed line has no heating; the system thermal coating could keep the line warm, but could not guarantee sufficient heating and an accurate temperature control. The bio-oil temperature was therefore maintained within the range of 40÷55°C.
The following main parameters were checked during the tests and used for analyzing the behavior of bio-fuels combustion process:

- gas emissions (O_2, CO, CO_2, SO_2, NO_x);
- combustion air flow rate, pressure and temperature;
- oil and bio-oil flow rate, pressure and temperature;
- flue gas temperature inside the combustion chamber.

Fuel oil tests

Fuel oil tests, carried out before characterizing the bio-fuels, allowed to find out a set of operating conditions, characterized by a stable flame and reduced polluting emissions, to be used for testing the various fuels.
This configuration was the following:

- standard position of the burner inlet nozzle;
- standard position of the primary air pipe;
- primary air flow rate 16% of the total flow rate;
- secondary air flow rate 84% of the total flow rate;
- blade angle of swirl 35° (=° = closed);
- Y-mix atomizer T5-1.5-80°, CT 3.5-4-1.2.

During the tests some problems occurred regarding the behavior of the flame, which was however stable in the various layouts tested, even with reduced loads. The graphs in Fig. 3 and 4 show the results obtained.

Union Fenosa bio-oil

As stated above, the main problems experienced during the test campaign on bio-oils, regarded atomization, in particular the obstruction of the atomizer head outlet holes. This problem appeared during the tests with Union Fenosa bio-oil and became more marked as this bio-oil could not be heated up to a temperature higher than 40°C,.
The outlet hole diameter was increased from 1.5 to 2 mm, in order to solve this problem; in addition, the diameter of the counter-head hole for fuel was increased from 3.5 to 4 mm and that of the atomization air holes from 1.2 to 2 mm, thus obtaining a higher air flow rate and preventing the hole's obstruction.
In consequence of these modifications, the holes did not clog up and no adverse effect on the flame stability was observed.
Fig. 5 and 6 show the most important results obtained during the tests.
Combustion did not show any particular problems. The switching from gas, used in the furnace pre-heating stage, to bio-oil operation was made gradually, and ignition did not show any problems. However, the construction features of the combustion chamber, completely insulated with refractory, resulted to be a very favourable environment for a regular development of the combustion process.
Visual control of the flame showed a combustion of essentially good quality. The flame was never detached from the burner; indeed, no damages to the boiler were found after the tests. Marked improvements in atomization were obtained, even when bio-oil was atomized at a temperature lower than design temperature. At the end of the tests on Union Fenosa bio-oil, during which about 1500 kg bio-oil were burnt, the atomizer outlet holes showed an oval shape and a larger section compared with the geometric conditions at the beginning of tests. It should however be stressed that the atomizer tip was made of steel to be hardened, but that had not been actually hardened. A through evaluation of these phenomena should require proper further tests.

Ensyn bio-oil

During the operation with Ensyn bio-oil, the bio-oil line was strengthened, thus increasing temperature from 40°C to 50/55°C and obtaining a lower viscosity. Atomization was carried out with the modified atomizer used for the previous tests.
Test results are given in Fig. 7 and 8.
Combustion tests were performed without any particular difficulties during the switching from gas to bio-oil and during bio-oil combustion under all test conditions.
An increase of the atomizer hole diameters, similar to that experienced with Union Fenosa oil, was observed at the end of the tests, during which about 1500 kg of bio-oil were burnt.

System cleanup

During operation no feed line cleaning was usually performed. At the end of each test the fuel gun was cleaned with ethanol. Pipeline cleaning with ethanol was performed only at the end of each campaign with bio-oil, by flushing with a 60% ethanol solution.

Data analysis

Figures 9 and 10 show the NO_x emission and solid particulate curves as a function of oxygen content in the combustion gas. The graphs refer to 100% thermal load. NO_x values are normalized at 3% oxygen in the flue gas, whereas the values for solid particulate are all normalized at the oxygen test value. CO concentrations during the tests were always very low, so that it was not possible to find an evident correlation with other parameters.
When observing the NO_x curves, it appears that bio-oils, with a reduction of approximately 300 ppm, offer an advantage in comparison with fuel oil. This difference of emissions at the same plant operating conditions can be explained considering the different organic nitrogen content that is much lower in bio-oils (see Table 1), and the lower temperature of bio-oil combustion.
Figure 11 shows the temperature profiles inside the combustion chamber at 100% thermal load. The different temperature profiles for the two bio-oils show a gap of about 100°C near to the burner, thus explaining the markedly different NO_x emissions from bio-oils with a similar organic nitrogen content.
The difference of temperature is due to the bio-oils different water content: Ensyn bio-oil has a lower water content compared to Union Fenosa bio-oil (about 19% vs 23%). Flame temperatures are therefore higher, when thermal input is the same.
Also the different atomization conditions play a role. Ensyn bio-oil was heated up to a higher temperature and therefore was characterized by a lower viscosity in comparision with Union Fenosa bio-oil. In consequence of that an improved atomization, a better mixing between air and fuel and higher NO_x emissions were obtained. The above results may at least partially explain the differences of NO_x emissions at the same temperature (see Fig. 12).
The values for solid particulate reflect the ash content of the three fuels (see Table 1). In particular, Union Fenosa bio-oil showed higher particulate emissions compared with Ensyn fuel oil.

Conclusions

An experimental investigation was carrried out on the combustion characteristics of two biomass pyrolysis fuels prepared by ENSYN (Canada) and Union Fenosa (Spain) respectively. The experimental studies were performed at the ENEL CRT Experimental Area of Livorno.
The bio-fuels flame was compared with a No.6 oil flame (ENEL).
The peculiar chemical-physical characteristics of the two bio-oils required some care especially as regards storage and feeding system.
As regards Ensyn bio-oil, a preheating up to a temperature ranging between 50°C and 60°C solved the problem of polymerization occuring at ambient temperature in the feeder line and in the atomizer.

Union Fenosa bio-oil did not cause problems after heating it up to 40°C.
Gas emissions showed a difference of 120 ppm of NO_x between the two bio-oils during the tests carried out by ENEL, probably due to the fuel's different water content and, consequently, to the different temperature in the flame zone.
ENEL tests proved that NO_x emissions were significantly reduced because of the low organic nitrogen content of bio-oils compared to oil No. 6. Solid particulate concentrations were higher for bio-oils compared to oil No. 6, according to the different ash content.
A complete combustion of both bio-fuels was obtained in the burner used for the tests.
In conclusion, the experimental capaign has proved that a high-quality stable combustion of liquid fuels obtained from biomass flash pyrolysis is possible.

References

P. Barbucci, G. Benelli, S. Ligasacchi, C. Rossi: "Bio-oil and bio-oil ethanol mixtures combustion tests"
Presented at the Poster session of the 8th European Conference on Biomass for Energy, Enviroment, Agriculture and Industry. Vienna, 3-5 october 1994.

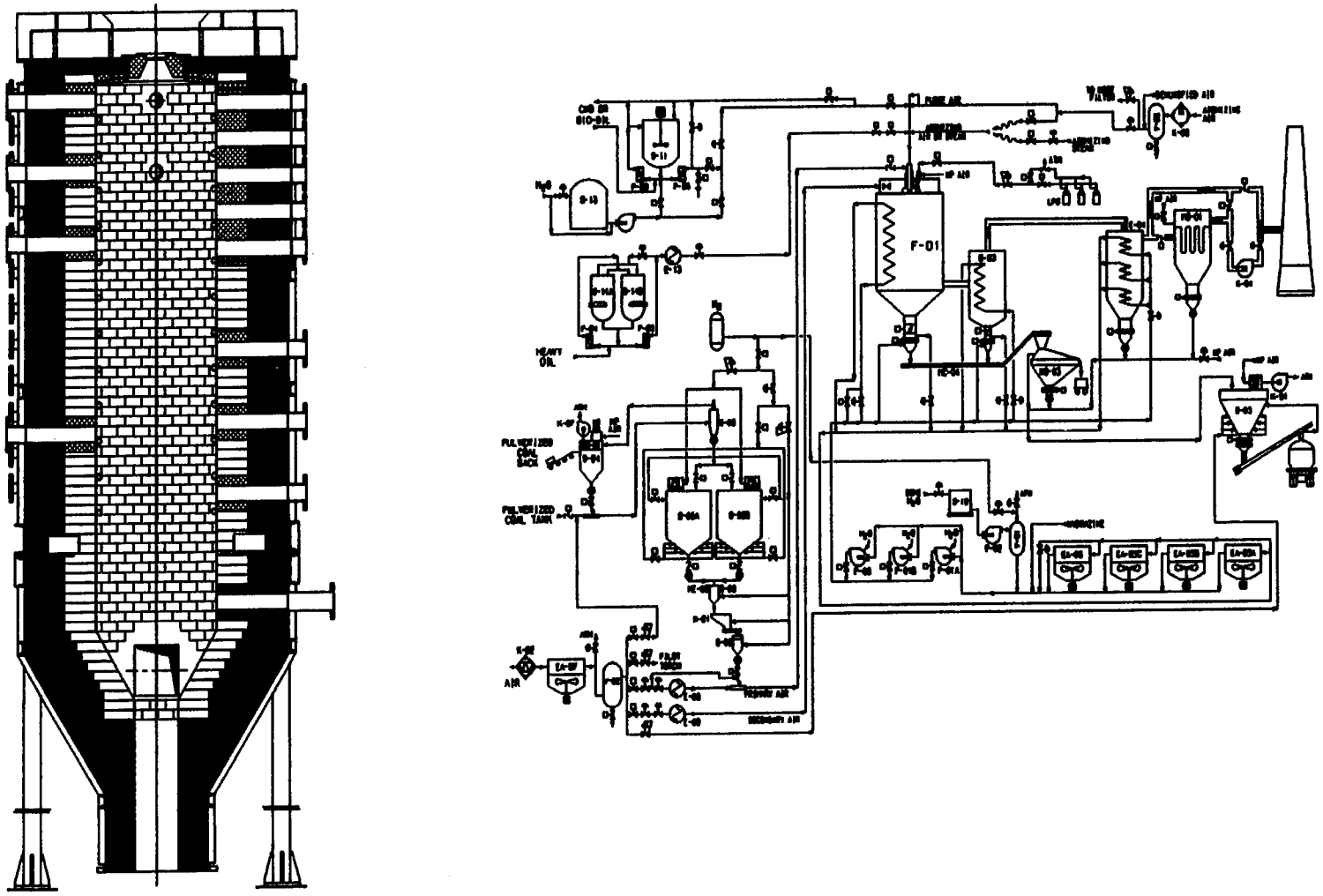


Fig. 1. Experimental 0.5 MWt furnace and flow-sheet

0.5 MWt FURNACE - LIVORNO

BIO-OIL COMBUSTION TESTS

November 1994 - February 1995 Tab.1

		Evaluation of Fuels		
		Ensyn oil	Fenosa oil	No.6 oil
Viscosity 23 °C	E°		89.82	
Viscosity 35 °C	E°	77,4		
Viscosity 50 °C	E°	23,6	14.85	46.36
Viscosity 80 °C	E°	4,61	2.99	
Viscosity 100 °C	E°			4.35
Viscosity 120 °C	E°			2.66
Density 15 °C	g/cm3	1,25	1,276	0.98
Moisture	%	19.0	23.0	
Ultimate analysis (as received)				
Ash	%	0,05	0.12	0.03
Carbon	%	45,89	44.72	85.54
Hydrogen	%	7,22	4.6	10.34
Nytrogen	%	0,055	0.05	0.55
Sulphur	%	0,029	0.08	0.95
Oxigen	%	46,76	50,43	
HHV	MJ/Kg	18,1	17,64	43,42
LHV	MJ/Kg	16,5	16,2	41,19
Carbon residue	%	21,28	23.7	12.04
Ash analysis				
Na2O	%	12,32	14.68	
NiO	%	n.d.	0.7	
MgO	%	3,21\	2.56	
CaO	%	34,14	8.21	
K2O	%	22,61	5.49	
F2O3	%	1,07	24.2	
Al2O3	%	1,25	4.56	
SiO2	%	19,25	38	

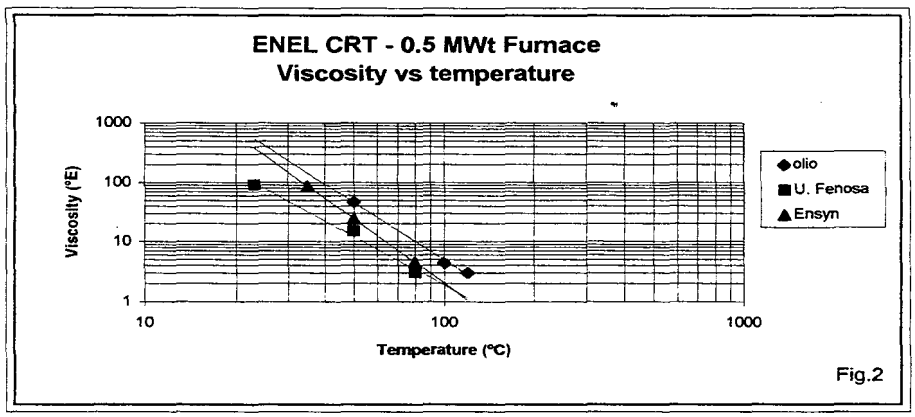
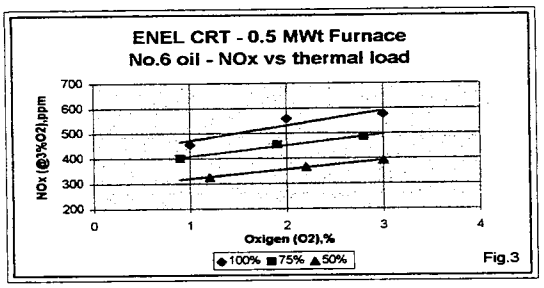
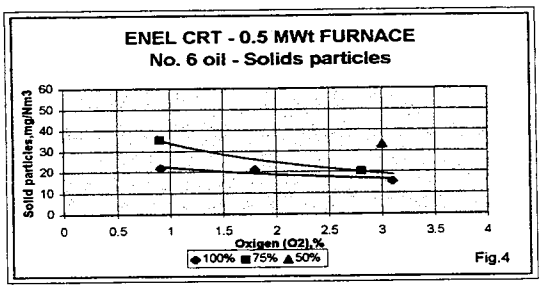
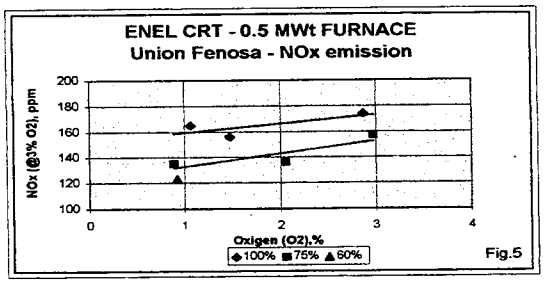
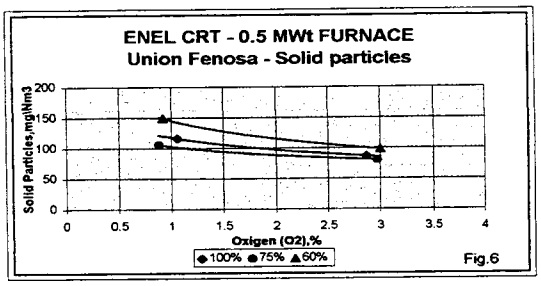


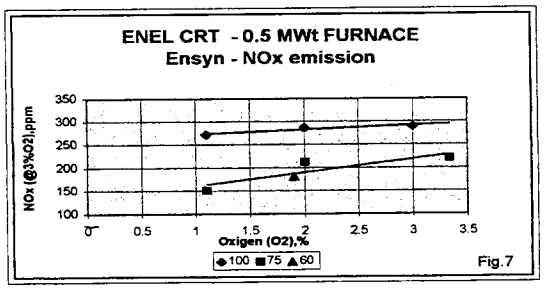
Fig. 2. Viscosity vs. temperature











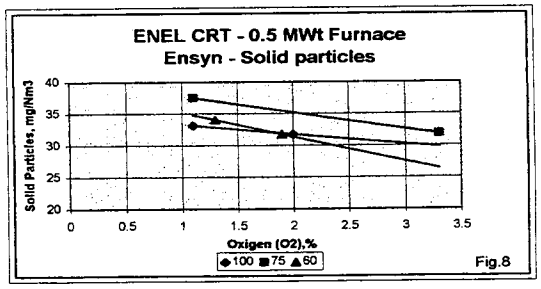


Fig. 3. **No. 6 oil - NOx vs. thermal load**

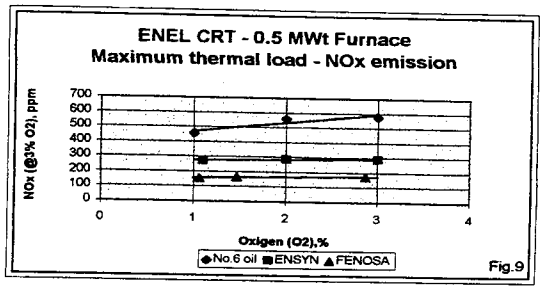
Fig. 4. **No. 6 oil - Solids particles**

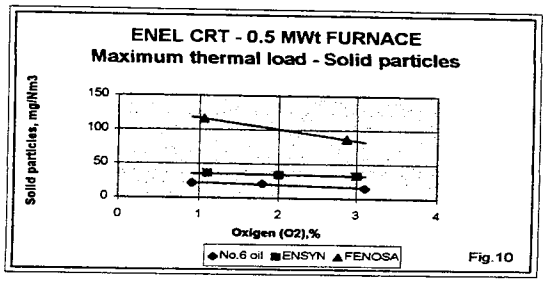
Fig. 5. **Union Fenosa - NOx emissions**

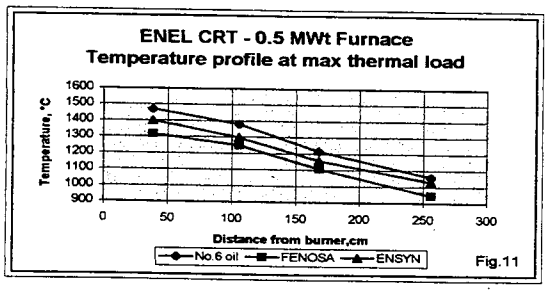
Fig. 6. **Union Fenosa - Solid particles**

Fig. 7. **Ensyn - NOx emissions**

Fig. 8. **Ensyn - Solid particles**







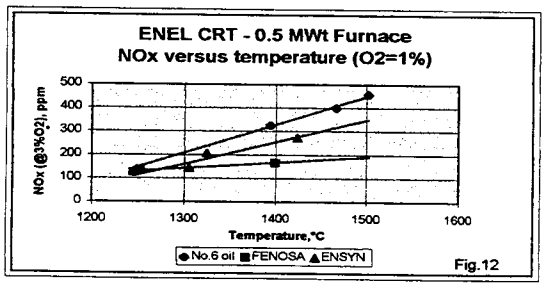


Fig. 9 **Maximum thermal load - NOx emissions**

Fig. 10. **Maximum thermal load - Solid particles**

Fig. 11. **Temperature profile at max thermal load**

Fig. 12. **NOx vs. temperature (O2=1%)**