Alcohol Fuel Activities at the Solar Energy Research Institute

Biomass Program Office
Solar Energy Research Institute

Solar Energy Research Institute
A Division of Midwest Research Institute
1617 Cole Boulevard
Golden, Colorado 80401

Operated for the U.S. Department of Energy
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SOLAR ENERGY RESEARCH INSTITUTE
Solar Energy Information Center

JUL 31 1981

GOLDEN, COLORADO 80401

ALCOHOL FUEL ACTIVITIES AT THE
SOLAR ENERGY RESEARCH INSTITUTE

BIOMASS PROGRAM OFFICE
SOLAR ENERGY RESEARCH INSTITUTE

APRIL 1980

PREPARED UNDER TASK NO. 3320.20

Solar Energy Research Institute
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PREFACE

Our nation's energy problems have been aggravated because we obtain a substantial portion of our petroleum supplies from relatively unstable foreign sources. Large price increases imposed by these foreign sources and threats of discontinued supply have been detrimental to our international trade balance and, consequently, our economy.

Alcohol fuels derived from biomass can make a significant contribution to our nation's energy pool and thus reduce our dependence on foreign petroleum suppliers. The Solar Energy Research Institute (SERI) is sponsoring in-house and subcontracted research into the production of alcohol fuels from biomass. This report describes that research for anyone interested in alcohol fuel activities at SERI.

Approved for:

SOLAR ENERGY RESEARCH INSTITUTE

Clayton Smith, Division Manager
Chemical and Biological Division
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SECTION 1.0

INTRODUCTION

Petroleum annually supplies approximately 47% (37 quads) of our energy, and about half of this petroleum is imported. Liquid fuels derived from petroleum are used to supply energy for transportation, electric power generation, residential and commercial heating, and industrial process heat.

To reduce our dependence on foreign petroleum suppliers, our government has introduced measures that encourage energy conservation, such as mandating that new cars get better gasoline mileage and providing tax incentives for home insulation and solar heating. Domestic production of petroleum has been encouraged by deregulating the petroleum obtained through new wells and through secondary and tertiary recoveries from old wells. Legislation to promote synthetic liquid fuel production from coal and biomass has been introduced in Congress. In addition, Congress and some states have taken action to advance the use of synthetic fuels, such as ethanol, made from grain and other biomass resources.

In general, the processes for making synthetic fuels from biomass can be grouped into two categories: bioconversion and thermal conversion. Bioconversion uses the enzymes produced by microorganisms such as yeasts and bacteria to ferment liquids and gases from biomass. For example, the glucose found in starches and sugars is fermented into ethyl alcohol (ethanol) through bioconversion. Thermal conversion uses heat rather than microorganisms to convert biomass into useable energy. In the presence of air or oxygen, the products of thermal conversion are oil, char, and hydrocarbon gases. In the absence of air or oxygen, the products are fuel gas mixtures that can be converted into products such as methanol.

The conversion techniques for these processes do not represent new technology. Ethanol has been produced as a beverage from grain and sugar for centuries, and the Germans had a large synthetic fuel industry during World War II. Although technically well-developed, these fuels have been unable to compete with petroleum without significant subsidies.

A major objective in any research and development effort to produce liquid fuels from biomass should be to decrease the cost of the product. This objective can be achieved by using low-cost feed materials and improving process efficiency through low capital and operating costs.

A task force from the Department of Energy conducted an intensive review to explore the potential of alcohol fuels. The task force concluded that:

Alcohol fuels (both ethanol and methanol) can contribute to U.S. Energy resources by using domestic, renewable resources and coal to extend supplies of high-quality liquid fuels. Indeed, ethanol is the only alternative fuel commercially available from renewable resources now, and the only one likely to be available in quantity before 1985. Methanol can be made from coal using commercially available technology, and could be produced in large quantities in the mid-to-late 1980s when plants—if begun soon—could be completed and begin operating. Maximizing ethanol's contribution will require minimizing the use of oil and gas in producing feedstocks and converting them to alcohol.
Through 1985, the contribution of alcohol fuels is expected to be modest nationally—perhaps displacing as many as 40,000 barrels of oil per day once recent presidential initiatives are put into practice. Production will be limited by the capacity to convert agricultural and waste material into alcohol. The impact is likely to be much greater regionally, however.

In agricultural states, alcohol fuels may become significant sources of local supply. The potential beyond 1985 may be quite large—especially if major new ethanol and methanol facilities are developed during the early 1980s and if fuel users adapt to take advantage of alcohol fuels' properties.

It is important to note that no one energy source can solve our national energy problems. Though alcohol fuels cannot be a total or, in the near term, even a major solution to our national energy needs, they do represent an important energy component and building block for the longer term. Our national energy needs must be met by actively conserving and by aggressively developing contributions from a large number of energy supplies, building on the nation's abundant resources. Alcohol fuels represent important supplies based on the American agricultural system and on the potential of U.S. coal.*

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SECTION 2.0
SERI PROGRAM

The U.S. Government, through the Biomass Energy Systems Branch of the Department of Energy, is supporting programs to produce alcohol and liquid fuels from various biomass feedstocks.

The Solar Energy Research Institute conducts and/or manages a major portion of this effort. SERI's activities in this area come under the direction of Dr. Clayton Smith, Manager, Chemical and Biological Division.

The alcohol and liquid fuels activities at the Solar Energy Research Institute are in five general areas:

- research,
- process development,
- analysis,
- technology dissemination, and
- contract management.

The various efforts are being conducted in several different parts of the SERI organization as follows:

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<td>Dr. Ruxton Villet</td>
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<td>Dr. Tom Reed</td>
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<td>Biopolicy Analysis and Alcohol Crops</td>
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<td>Mr. Joe Finegold</td>
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<td>Biomass Refining</td>
<td>Biomass Program Office</td>
<td>Dr. Larry Douglas</td>
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<td>Mr. Dan Jantzen</td>
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All alcohol fuel efforts are part of a broader program for development and use of biomass. The objectives of SERI's Biomass Program include:
development of more efficient systems for producing and collecting biomass;
• development of more effective methods of processing and utilizing biomass resources;
• development through analytical techniques of a better understanding of the economic and social effects of various scenarios for the production and utilization of biomass;
• organization and dissemination of available information to various national audiences; and
• utilization of the tools of contract management to achieve major parts of these objectives.

The bioconversion research is directed toward efficient, economic production of liquid fuels and chemical feedstocks from inexpensive biomass materials. Biological conversion research will include investigations of novel bioreactor systems and improved existing and novel separation processes. Strains of microorganisms for hydrocarbon production will be identified, and genetic engineering experiments on these strains will be performed. Enzymes will be identified and purified, and enzyme degradation of lignocellulose will be studied. Fermentation research will develop economical and energy-efficient processes for bioconversion of lignocellulosic biomass to ethanol and other energy-intensive chemicals such as acetic acid, butanol, and acetone.

Thermal conversion research is attempting to develop novel thermochemical and thermoelectrochemical processes that convert biomass to gaseous or liquid fuels and chemicals. In addition, the mechanisms and kinetics of biomass pyrolysis and gasification are under investigation, as is electrochemical conversion of biomass to electricity or chemicals.

Process development work will include improvement and optimization of available technologies in biomass feedstock product pretreatments (acid hydrolysis, enzymatic hydrolysis, fermentation) and product separation and recovery. A process development unit (PDU) will be constructed and operated.

The systems analysis efforts are oriented toward integration of current technology and identification of optimal areas for future work. Policy analysis studies will determine potential contributions of unconventional agricultural crops, and the impact increased production of these crops will have on farm income, food prices, foreign trade, etc.

The biomass technology dissemination group will prepare and distribute pamphlets, brochures, reports, audio visual presentations, magazine articles, etc. to accelerate the commercialization of biomass production and conversion technologies.

Summaries of each of the projects are presented on the following pages.
Title
Biological Conversion of Biomass

Principal Investigator
Dr. Ruxton Villet

Fiscal Year 1980 Funds
$756,000

Lead Group
Biotechnology Research Branch

Fiscal Year 1980 Funds for Subcontracts
$50,000

Task Number
3370.10

Fiscal Year 1980 Manpower
10 person years

SUMMARY
The objective of this bioconversion research is to devise biotechnological processes for converting biomass to fuels and chemical feedstocks. Research and development work within an integrated triple set of disciplines (namely, biochemical engineering, genetics, and biochemistry) is a necessary prerequisite to the rational process engineering design of effective bioconversion systems.

An improved process design base for biotechnological conversion of biomass to fuels and chemical feedstocks gradually will be established.

Active integrated R&D in the following three disciplines will be pursued.

- Biochemical engineering:
  - investigate novel bioreactor systems;
  - study ways to improve chemical engineering separations processes;
  - investigate the dynamic regulation of biotechnology processes; and
  - perform process engineering systems analysis and economic evaluations.

- Genetics:
  - examine the hydrocarbon production of various strains of microorganisms;
  - study methane-metabolizing microorganisms; and
  - initiate gene-transfer experiments.

- Biochemistry:
  - investigate enzymes in bioconversion systems;
  - study enzyme degradation of lignocellulose; and
  - investigate the stabilization of microbial cells to products.
Title
SERI Pressurized Oxygen Gasifier for Methanol/Ammonia Production

Principal Investigator
Dr. Tom Reed

Fiscal Year 1980 Funds
$236,000

Lead Group
Biomass Thermal Conversion
Research Branch

Fiscal Year 1980 Funds for Subcontracts
$0

Task Number
3356.20

Fiscal Year 1980 Manpower
2 person years

SUMMARY

The objective of this research is to develop and demonstrate a practical process for converting biomass into methanol and/or ammonia. A gasifier suitable for production of the syn-gas (CO+H₂) needed to make methanol or ammonia from biomass has been designed and is being fabricated and installed in Golden, Colorado.

The first "proof of concept" model will be tested in late 1980 using about 1 ton/day. Information obtained on this gasifier will be used to design a larger system in 1981.
### Title

**Applied R&D in Fast Pyrolysis to Produce Olefins for Alcohol Synthesis**

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<tr>
<td>Mr. Jim Diebold</td>
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<td>3356.30</td>
<td>1 person year</td>
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### SUMMARY

The project objective is to expand the basic understanding of fast pyrolysis mechanisms as related to the conversion of biomass to gases containing olefins such as ethylene and propylene. One of numerous potential uses for these olefins is to convert them to alcohols by the use of state-of-the-art petrochemical processes.

A new type of fast pyrolysis reactor is being designed and will be fabricated and checked out in FY80. Extensive process variable evaluation is planned for FY81. This reactor has the unique potential to fast pyrolyze chip-sized biomass particles, and data from it will be used to design a larger system in FY81.
Title

Methanol/Hydrogen Automobile System Demonstration

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<tr>
<td>3510</td>
<td>2.1 person years</td>
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SUMMARY

The objective of this task is to successfully demonstrate the dissociation of methanol in an automobile, and to burn the products of dissociation in the car's modified 4-cylinder engine. The dissociation reaction is highly endothermic, requiring 22% of the lower heating value of methane. This energy comes from the engine exhaust. Thus, the dissociated fuel, hydrogen and carbon monoxide, has 22% more energy than the original methanol.

The hydrogen-rich gases will be burned in a modified internal combustion engine. The major modifications consist of a much higher compression ratio (≈14:1) and excess air combustion (up to 100% excess air beyond the stoichiometrically correct amount). Both of these effects result in increased engine efficiency: ≈15% for the higher compression ratio and typically 25% to 100% for the excess air combustion.

If these fuel economy increases were independent, the vehicle would be expected to have approximately double the efficiency of a baseline gasoline vehicle. While this is unrealistic in the short term, it is probably a good goal for this type of system.

The amount of exhaust emission is expected to be much less than the amounts from gasoline or traditional methanol combustion, especially in terms of particulates and aldehydes.

Our current schedule calls for catalyst testing and engine dynamometer testing in spring 1980, system integration in summer 1980, and vehicle demonstration before the end of fiscal 1980.
SUMMARY

The subcontractor will design, build, and test a catalytic reactor to decompose gaseous methanol into hydrogen and carbon monoxide. This reactor then will be installed in an automobile by SERI as part of the Methanol/Hydrogen Automobile System Demonstration.

The reactor is designed to decompose 0-5 gal/hr of methanol at a minimum conversion of 80%. The catalyst will be easily replaced. The unit will be able to operate at a reaction working pressure of 0 - 1.0 MPa above atmospheric.

JPL will test this unit with a methanol vaporizer (to be supplied by SERI) over the ranges of:

- methanol flow rate: 0-7.5 gal
- reaction pressure (above atmospheric): 0-1.0 MPa
- simulated exhaust temperature: 200°-540°C
- equivalence ratio: 0.5-1.0

JPL will also run a transient performance test to simulate a step function in engine throttle setting from closed throttle to wide open throttle.

The deliverables are one tested catalytic reactor (with three extra charges of catalyst) by May 1, 1980, and one final report by August 1, 1980.
Title
Alcohol/Gasoline Blends Systems Study

Principal Investigator
Mr. Joe Finegold

Fiscal Year 1980 Funds
$100,000

Lead Group
Systems Development Branch

Fiscal Year 1980 Funds for Subcontracts
$0

Task Number
3510

Fiscal Year 1980 Manpower
1.3 person years

SUMMARY

The objective of this element of Systems Analysis Research is to rank various biomass-to-alcohol systems for automotive gasoline/alcohol blends. Important considerations include potential supply, competing markets, harvest, collection, processing, distribution, and utilization. Net energy, economic, and supply analyses will be performed.

The utilization study will include such subjects as materials compatibility, vapor pressure considerations, phase separation problems, and evaporative and driving exhaust emissions. Special consideration will be given to analysis of self-compensating air-fuel metering systems to tolerate variable alcohol/gasoline blends without undue exhaust emissions and fuel economy penalties.
Title
Bio-Policy Analysis and Alcohol Crops

Principal Investigator
Mr. Don Hertzmark

Fiscal Year 1980 Funds
$200,000

Lead Group
Agriculture and Transportation Group

Fiscal Year 1980 Funds for Subcontracts
$55,000

Task Number
3346.10, -.50

Fiscal Year 1980 Manpower
1.5 person years

SUMMARY

Technical objectives:
- study the impacts of growing alcohol/sugar crops for energy production;
- assess state and federal biomass policies;
- assess nonfuel potentials for alcohol; and
- determine the environmental impacts from growing exotic hydrocarbon species on arid lands.

Scope of work:
- modify the agricultural sector model to include alcohol crops;
- construct an interfuel substitution model for nonfuel uses; and
- environmental research on exotic crops and use of marginal/arid lands.
Subcontractor and Address
Northwest Economic Associates
Vancouver, Washington 98663

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<tr>
<td>Pacific Northwest Resource Assessment</td>
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<td>Mr. Robert McKusick</td>
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SUMMARY
The subcontractor will:

- assess the potentials for sunflower and other crops to produce energy;
- estimate the available land in certain regions for energy production; and
- estimate the energy potential of processing and field wastes.
Title
National Alcohol Fuels Information Center

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<th>Principal Investigator</th>
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<td>Mr. Pete Mourning</td>
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<td>8620</td>
<td>8 person years</td>
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**SUMMARY**

This program provides manpower, facilities, and all necessary materials to establish and operate an alcohol fuels information center. The center, named the National Alcohol Fuels Information Center (NAFIC) is operated as part of the Solar Energy Information Data Bank (SEIDB). SERI, as lead center for the SEIDB, is solely responsible for management of NAFIC. The four DOE Regional Centers, as the principal members of the SEIDB, will provide alcohol fuels information outreach services on a local basis, as will other government-funded activities.

This program includes six major tasks:

- management and network support;
- information development and dissemination;
- inquiry and referral service;
- data base development and maintenance;
- document collection, reference, and loan service; and
- computer programming support.

The principal features of this program are the establishment of an in-WATS line especially for alcohol fuel inquiries (with the necessary staffing to respond to these inquiries), the development and printing of various publications to meet anticipated information demands, production of TV media spots and training materials, the tie-in of various USDA, State Energy, and other public outreach offices with a central data bank via on-line computer terminals, and the creation of a central repository for direct access to, or loan of, various reference materials.
**Title**

Biomass Technical Information Dissemination Program

**Principal Investigator**  
Mr. William Corcoran

**Fiscal Year 1980 Funds**  
$350,000

**Lead Group**  
Industrial Applications and Policy Branch

**Fiscal Year 1980 Funds for Subcontracts**  
$180,000

**Task Number**  
6722.14

**Fiscal Year 1980 Manpower**  
1.25 person years

**SUMMARY**

The objective of this task is to establish effective biomass technology information transfer mechanisms to facilitate early commercialization of biomass solar energy.

Through the use of various information transfer media such as pamphlets, brochures, reports, slide shows, and workshops, the information generated by the DOE research and development effort will be disseminated to several target audiences including organizations and individuals directly involved in DOE-sponsored biomass R&D programs, organizations and individuals who will manufacture, service, and/or install biomass solar technologies, organizations and individuals interested in fostering biomass solar technology use through legislation, regulation, financing, etc., and the interested general public.

Informational material prepared for small-scale ethanol plants will include a small, fold-out pamphlet, a 15-page brochure, case studies of 10 small-scale ethanol plants, and a 12-min slide-tape presentation.
Title
Biomass Refining

Principal Investigator
Dr. Larry Douglas
Mr. Dan Jantzen

Fiscal Year 1980 Funds
$3,950,300

Task Number
3336.01

Fiscal Year 1980 Funds for Subcontracts
$3,950,000

Fiscal Year 1980 Manpower
2.5 person years

SUMMARY

This task will manage subcontracted research that is aimed at improving the technical aspects and economies of converting biomass to ethyl alcohol and other energy-intensive chemicals. The feedstocks studied will include soft and hard woods, corn stovers and other agricultural residues, and some aquatic biomass. The current subcontracts, in addition to a basic research effort, are providing a strong support function for development of a process development unit (PDU) by Georgia Tech and Gulf Research. Research is directed to the following general areas:

- feedstock pretreatment;
- acid and enzymatic hydrolysis;
- enzymatic conversion of glucose to alcohol;
- methods for using the hemicellulose fraction;
- methods for using lignin, thus producing a byproduct credit; and
- methods for separating EtOH/water mixtures.

The task complements the SERI in-house bioconversion program. Present subcontracts are described in Section 3.0.
SECTION 3.0

BIOMASS REFINING:
SUBCONTRACTS MANAGED BY SERI

The subcontracted research described in this section is managed by the Biomass Program Office of the Solar Energy Research Institute.
**SUMMARY**

The University of Pennsylvania has a broad program studying biomass conversion to liquid fuels. The butanol delignification process is one of the top three competitive pretreatments now being developed. The following is a general description of the program at Penn:

- Solvent delignification and lignin slurry fuel production:
  - investigate solvent delignification as a pretreatment scheme for the production of a readily degradable cellulose and useable byproduct streams and measure lignin slurry recovery for use as a fuel.

- Hemicellulose utilization:
  - define the kinetic character of the *Thermoactinomyces* cellulase system for optimal enzyme production and cellulose hydrolysis.

- Production of concentrated glucose syrups:
  - define an enzymatic system for production of concentrated glucose (20%) syrups for ultimate use in existing alcohol fermentation processes.

- Enhanced *Thermoactinomyces* mutants:
  - develop *Thermoactinomyces* mutants producing cellulase with high unit activity and low product inhibition characteristics.

- Use of ethanol-tolerant *Clostridium thermocellum* [S-4] in combined saccharification and vacuum fermentation for ethanol production:
  - investigate the feasibility of combining, at high temperatures, enzymatic saccharification, *Clostridium thermocellum* fermentation, and alcohol recovery by vacuum techniques into a single processing step.

- Combine saccharification and extractive fermentation:
  - investigate the feasibility of combining enzymatic saccharification, *Clostridium acetobutylicum* fermentation, and butanol extraction by solvent and/or solid absorption into a single processing step.

- Increase the efficiency of ethanol fermentation:
- utilize extractive fermentation to increase the efficiency of ethanol production by yeast.

- Economic analysis:
  - perform economic analysis of the integrated process and its intermediate steps for the purpose of identifying cost-sensitive steps and reasonable alternatives.
SUMMARY

The major objective of this effort is to examine the direct microbiological conversion of cellulosic biomass to a liquid fuel (ethanol). The study includes microbiological, genetic, and engineering aspects of cellulose degradation and ethanol production. In addition, the production of chemical feedstocks using degradation products from biomass will also be examined. These include the production of acrylic acid, acetone/butanol and acetic acid. The following is a general description of the program at MIT.

- Enhance degradation of biomass and utilization of the cellulosic fraction for ethanol production by *Clostridium thermocellum*:
  - increase the rate of biomass degradation through genetic, environmental, and engineering manipulations;
  - increase rate of product (ethanol) formation;
  - increase tolerance of the organism to the end product (ethanol); and
  - utilize directed catabolism to produce a single fermentation product (ethanol).
- Achieve complete utilization of biomass including the hemicellulose fraction, for the production of ethanol by strain HG-2, a thermophilic anaerobic microorganism:
  - kinetic and stoichiometric characterization of HG-2 using xylose as a fermentation substrate;
  - increase the concentration and rate of ethanol production by strain HG-2;
  - utilize directed catabolism to produce a single fermentation product (ethanol); and
  - provide mixed culture application of *C1. thermocellum* and HG-2 for complete biomass conversion to ethanol.
- Develop improved technology for the direct fermentation of cellulosic biomass to ethanol:
  - characterization of a packed bed fermenter for biomass utilization and ethanol production; and
  - process synthesis, design, and economics for the production of liquid fuel (ethanol) from biomass.
• Explore the production of liquid fuels via the microbial utilization of lignin residues:
  - define the kinetics and stoichiometry of lignin degradation by a defined mixed culture; and
  - characterize the soluble organic products resulting from lignin degradation and assess their fuel potential.
• Investigate utilization of degraded biomass for the production of chemical feedstocks:
  - acrylic acid production through fermentation technology that uses direct fermentation of cellulosic biomass to lactic acid (which is the substrate for acrylic acid production)
    a. utilize both hexoses and pentoses for lactate production, and
    b. use immobilized cells of *Clostridium propionicum* to produce acrylate from propionate;
  - acetone/butanol production by improvement through increased productivity and increased solvent concentration (extractive fermentation using solvents extraction during fermentation to overcome product toxicity); and
  - acetic acid production using *Clostridium thermaceticium*.
SUMMARY

One of the responsibilities given LBL at the onset of this subcontract was testing processes and materials under development by other DOE subcontractors at the pilot-plant scale. This was designed to provide scale-up data for design of the Process Development Unit (PDU) and larger applications. The other charge was to pursue process development studies initiated at LBL. The four main areas of LBL work are described below.

- Ethanol fermentation studies:
  - media development and growth factors
    a. vitamins and amino acid can increase growth rate, and
    b. biotin is a critical vitamin in synthetic media;
  - process development studies
    a. rapid fermentations are done in a continuous, high cell-density, atmospheric pressure fermenter, and
    b. an improved experimental design. Fermentation is carried out in continuous, high cell-density, atmospheric pressure fermenter. Fermenter beer is cycled to a flash-pot where an equilibrium ethanol/water vapor mixture is boiled away.

- Utilization of hemicellulose sugars:
  - xylanase production
    a. both shaker flask and controlled fermenter experiments were run, and
    b. the enzyme concentration was higher in the fermenter, mainly due to pH control;
  - xylose fermentation
    a. fermented using *Bacillus macerans*,
    b. yields ethanol, acetone, and acetic acid, and
    c. high conversions at 2.3% xylose in both.

- Raw material and process evaluation:
- Dartmouth pretreated corn stover subjected to enzymatic hydrolysis: yielded 97% conversion of cellulose to glucose in less than 20 hours;
- corn stover treatment: 194°C for 12 secs. with 0.5% acid; and
- high pressure HCl conversion of wood: gas phase HCl under pressure renders cellulosic material more susceptible to enzymatic or dilute acid hydrolysis.

- Enzyme fermentation studies:
  - cellulose production
    a. continuous cellulose production, and
    b. batch fermentation—found optimum temperature to be 25°C which gave a three-fold increase in B-glucosidase. This reduces cellulose concentration in fermenter broth and, therefore, results in less inhibition of the $c_1$ enzyme, giving an increase in the depolymerization of cellulose.
  - composition of cellulose enzyme
    a. analytical and preparative separation techniques were used to isolate the components of the cellulose complex—present work indicates a total of 12 components.
  - xylan hydrolysis
    a. purpose is to hydrolyze hemicellulose to xylose using xyranase.
SUMMARY

The current program to convert biomass into liquid hydrocarbon fuels is an extension of the previous program to ferment marine algae to acetic acid. In that study, it was found that marine algae could be converted to higher aliphatic organic acids and that these acids could be readily removed from the fermentation broth by membrane or liquid-liquid extraction. It was then proposed to convert these higher organic acids to aliphatic hydrocarbons via Kolbe Electrolysis, which may be used as a diesel fuel. The following are the specific goals at Dynatech.

- Establish conditions under which substrates other than marine algae may be converted in good yield to organic acids. The primary task in this regard is methane suppression.
- Modify the current 300-liter fixed packed bed batch fermenter to operate in a continuous mode.
- Change from membrane extraction of organic acids to liquid-liquid extraction.
- Optimize the energy balance of the electrolytic oxidation process. The primary task in this regard is to reduce the working potential required for the electrolysis while maintaining an adequate current density.
- Scale the entire process up to match the output of the 300-liter fermenter.

These goals have been attained and the net energy balance for the whole process has been calculated to be $5.48/MMBtu assuming a feedstock cost of $30.00/ODT. The data used to generate this figure were obtained mainly for a computer optimization procedure for plant scaling and some preliminary mass balance data. These data are being reviewed and updated where necessary, to verify the accuracy of the $5.48/MMBtu figure. If this number is even close, Dynatech has a real winner.
**Subcontractor and Address**

Auburn University  
Auburn, Alabama 36830

**Title**

Liquid Fuel and Chemical Production from Cellulosic Biomass—Hemicellulose Recovery and Pentose Utilization in a Biomass Processing Complex

**Subcontract No.**

DOE/23051

**Period of Performance**

2/80 - 2/81

**Principal Investigators**

Dr. R. P. Chambers  
Dr. Y. Y. Lee

**Fiscal Year 1980 Funding**

$260,000

**SUMMARY**

The primary thrust of the Auburn research program is directed toward utilization of the hemicellulose fraction of lignocellulosic biomass, which may account for as much as 40% of the total material. To a great extent, the development of an economically viable ethanol-from-biomass process depends on utilization of lignin and hemicellulose, either as part of the process or as a valuable byproduct. The Auburn research is directed toward using the hemicellulose to make ethanol, butanol, and butanediol.

There are four tasks in the program:

- hemicellulose conversion to xylose by selective acid hydrolysis;
- equipment selection for hydrolysis and solid-liquid separation;
- fermentation of hemicellulose hydrolyzates; and
- screening and characterization of wood hydrolyzate fermenting bacteria.
SUMMARY

The objective of this program is to show that the conversion of cellulose to glucose can be significantly increased by enzymatically removing the inhibitory cellobiose from the reaction system using immobilized B-glucosidase (B-G). When an enzymatic catalyst was prepared and used in a fluidized bed with cellobiose as the substrate, only a 10% loss of activity was observed during a 500-hour period. Cellulose was hydrolyzed in two batch reactors operated side-by-side, with one reactor containing immobilized B-G and cellulose and the other reactor containing an equal amount of cellulose only. The reactor containing the immobilized B-G had 100% more glucose, indicating that the catalytic removal of the cellobiose had a significant effect upon the production of glucose.

This important result should effect the development of some mid-term biomass refining technology.
SUMMARY

The Iotech Corporation has developed a pretreatment process for producing a fermentation substrate from wood, straw, and other lignocellulosic materials. The Iotech process achieves high enzyme accessibility by heating the materials at high pressure to the point of structural softening, then releasing the pressure quickly, thereby exploding the materials to open the cellulose fiber bundles and render them accessible to enzymatic attack by microorganisms.

Iotech is conducting a wide-ranging program to optimize the process parameters for steam explosion of biomass in terms of its digestibility. They are currently evaluating:

- mapping; i.e., time, temperature, and pressure vs. digestibility;
- analysis of total sugars;
- analysis of hemicellulose fraction;
- growing protein on hemicellulose for animal feed;
- material balance for the process;
- energy balance for the process; and
- use of lignin as a phenolic resin.

The best value for hydrolysis of cellulose is 97% and Iotech can control the process above 90%. Electron microscope studies and enzymatic hydrolysis studies are being performed. Lignin from the Kraft and Sulfite processes is being used for making a bonded composite board for wood chips. It is felt that lignin from clean biomass will be a superior bonding agent and, more importantly, will have a market value in excess of $11/1b and a market large enough to absorb the output from several ethanol plants.
Subcontractor and Address
Purdue University
West Lafayette, Indiana 47907

Title
Selective Solvents Extraction in Utilization of Stored Solar Energy in Cellulosic Biomass

Subcontract No.
DOE/4298

Period of Performance
1/80 - 1/81

Principal Investigators
Dr. G. Tsao
Dr. M. Flickinger
Dr. M. Ladisch

Fiscal Year 1980 Funding
$325,000

SUMMARY
The University of Purdue, Laboratory of Renewable Resources Engineering is a large multidisciplined research organization. The program covers much of the biotechnology involved in fermentation. Most of their research is standard, mainstream, and well done; however, in several areas they have produced results that are outstanding:

- separation techniques for polysaccharides, hexosans, and pentosans using special column techniques developed at LORRE;
- recycled, dilute acid system for removing hemicellulose from corn stover;
- concentrated sulfuric acid used as a cellulose solvent followed by precipitation with methanol;
- development of mutant strains of microorganisms to produce ethanol and butanediols from xylose; and
- development of a vapor phase concentration system to produce 99+% ethanol without using large energy input; e.g., 8,000-10,000 Btu/gal total energy input.
SUMMARY

The objective of the Rutgers research program is to improve the economics of enzymatically converting cellulose to glucose and eventually to ethanol and/or other energy-intensive chemicals. These improvements are sought through the use of microbial genetics to give a cellulase enzyme offering greater yields and more effective use of cellulose.

The current program is focused on producing improved strains of Trichoderma reesei by use of specialized screening techniques developed at Rutgers. Over a million strains have been screened during the course of this research and several improved strains have been isolated. In particular, the RUT-30 strain gave a 3- to 4-fold improvement over the best Natick microorganism. Other organisms have been isolated that are superior to RUT-30.

The Rutgers research program is expanding and will now include:

- enhancement of the saccharification of cellulose by modifying biochemistry and yields of cellulase in T. reesei;
- isolation of other potentially useful microorganisms for cellulose degradation (in particular, thermophilic microorganisms); and
- application of genetic engineering techniques to develop microbial strains capable of digesting cellulose and fermenting it to ethanol.
SUMMARY

The research program at Dartmouth College is centered on the development of a plug flow reactor that is designed to operate at steady-state isothermal conditions. This mode of operation will allow development of kinetic data on the hydrolysis of cellulosic materials and decomposition of sugars. The kinetic data to date show a good fit to the Saeman model and, more importantly, do not depend on slurry concentration in the range of 5% to 13%.

The experimental conditions employed were:

- temperature: 180°-240°C
- pressure: 400-600 psi
- acid concentration: 0-2%
- residence time: 0.1-2 min

The plug flow reactor can serve two valuable functions in biomass refining: (1) as a pretreatment for lignocellulosic materials, and (2) as a high-rate acid hydrolysis system.

The advantage of the Dartmouth plug flow system as a pretreatment is that it renders biomass degradable by acid or enzyme at high yields. Enzymatic hydrolysis is completed in 20 hours at quantitative yields.

The greatest value of the plug flow reactor may be as a pretreatment step for future process development units (PDUs) and ethanol production plants. This process warrants a strong evaluation and comparison with the Iotech steam explosion technology on the basis of energy consumption, product degradability, etc.
The G.E. thermophilic wood fermentation process is set up so that relatively coarse hardwood (and/or softwood, if amenable) chips are steamed for a brief time at low pressure in the presence of supplemental amounts of sulfur dioxide (or equivalent reagent) and then rapidly decompressed (similar to Iotech). The partially defibrated wood is neutralized with ammonia gas and fed directly into a fermenter which operates at approximately 60°C. A mixed culture of Clostridium thermocellum and thermosaccharolyticum are employed to ferment the readily digestible substrate to ethanol. C. thermocellum is used primarily to solubilize cellulose and secondarily to convert cellobiose to ethanol. C. thermosaccharolyticum is employed to ferment the pentose sugars (produced during pretreatment but not utilized by C. thermocellum) to ethanol. Product recovery and cell recycle are accomplished by continuous withdrawal of the broth to a vacuum distillation chamber (modified vacuum ferment) and subsequent distillation to produce 95% ethanol.
Subcontractor and Address
Columbia University
New York, New York 10027

Title
Permselective Membrane Control of Algol and Wood Digesters

Subcontract No.
SERI/8161

Period of Performance
6/79 - 6/80

Principal Investigator
Dr. H. Gregor

Fiscal Year 1980 Funding
$166,000

SUMMARY
Professor Gregor is working in membrane development technology. The potential application of membranes in biomass refining falls into three general areas.

- **Tight structures for concentrating HCl.**
  - Concentrated HCl is a fast, efficient medium for hydrolyzing cellulose to glucose; however, HCl is expensive. A method to economically concentrate and recycle the acid-using membranes would make this technology viable.

- **Ultrafiltration for separating cellobiose and glucose.**
  - In the enzymatic hydrolysis of cellulose to glucose, glucose acts as an inhibiting agent. As the glucose concentration increases, it shuts down the production of cellobiose. Continuous separation of glucose would prevent this inhibition.

- **Separation of water/alcohol solutions.**
  - Using membranes to concentrate dilute ethanol/water solutions is an inexpensive method compared to distillation.
  - Membranes can potentially separate ethanol/water mixtures past the azeotrope.
**Subcontractor and Address**  
Colorado State University  
Fort Collins, Colorado 80523

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**Title**  
Anaerobic Digestion of Ethanol Plant Stillage

### SUMMARY

The technical objective of this research is to determine the biodegradability and kinetic constants for anaerobic digestion of grain alcohol stillage, and assess the value of the digester effluent as a cattle feed.

Corn stillage from an alcohol plant will be digested to determine the methane yield, biodegradability, and rate constants under both mesophillic and thermophillic conditions. The composition of the effluent from the digesters will be analyzed to provide an indication of the potential value of the effluent as a cattle feed. An economic analysis will be performed to test the hypothesis that it is more economical for the alcohol plant to use the methane produced from stillage to fuel part of the alcohol operation and feed the effluent to cattle, rather than feeding the stillage directly to cattle without first removing some energy.

If the process of digestion of the stillage prior to feeding it to cattle is shown to be economical, then potential gasohol plants would be able to obtain a higher value for their stillage. If the methane produced in the digestion process turns out to be a significant portion of the energy required to run the alcohol plant, it would provide additional flexibility in locating and operating the plant.
Subcontractor and Address
Gulf Oil Chemicals Company
P.O. Box 2900
Shawnee Mission, Kansas 66201

Title
Operation of Pilot Plant Facility for Conversion of Cellulose to Ethanol

Subcontract No. Period of Performance
12 months

Principal Investigator Fiscal Year 1980 Funding
Mr. Charles Wessel $450,000

SUMMARY
The objective of the experimental program is to:

- obtain data for evaluating scale-up of processes developed by various research teams under the biomass refining program;
- demonstrate the technical feasibility of biological conversion of biomass to ethanol on a commercial scale;
- identify areas where further research is most needed; and
- provide a preliminary integration of technical approaches currently under investigation.

Gulf built the subject pilot plant in 1975 to support their internal research and development program which had the objective of producing ethanol and other chemicals from biomass and municipal solid waste (MSW). The pilot plant consists of four basic units: (1) substrate pretreatment, (2) enzyme/biomass production, (3) saccharification/fermentation, and (4) distillation. These units can be used individually or sequentially as needed. This facility offers a previously unavailable capability to perform experiments on a larger-than-bench scale. Current plants call for the construction and operation of a three-ooven-dry-ton-per-day process development unit (PDU) having an anticipated start-up in the spring of 1981.

The methodology to be followed will include the development of a base case conversion scheme for transforming biomass feedstocks to ethanol using selected feedstocks, pretreatments, enzymatic hydrolysis, fermentation, and alcohol recovery. The initial program will investigate: corn stover and poplar as feedstocks; Iotech-type, comminution, and chemical pretreatments; Trichoderma reesei for enzymatic hydrolysis; and glucose-to-ethanol, xylose-to-ethanol, and glucose + xylose-to-ethanol fermentations. The initial phase of operation will last six months, during which additional specific experiments will be identified and integrated into the program as deemed appropriate. The program will consist of runs lasting two weeks, each having ten days of operation.
Subcontractor and Address | Title
---|---
Argonne National Lab Argonne, Illinois | Ethanol Production Via Fungal Decomposition and Fermentation of Biomass

Subcontract No. | Period of Performance
---|---
SERI/9042 | 3/80 - 3/81

Principal Investigator | Fiscal Year 1980 Funding
---|---
Dr. A. A. Antonopolis | $165,000

SUMMARY

Several strains of Fusarium species decompose cellulose, hemicelluloses, pectic substances, and lignin, as well as ferment both hexoses and pentoses to ethanol (yeasts can ferment only hexoses). In addition, members of the genus Fusarium stimulate ethylene production during their interactions with biomass. Ethylene seems to increase polysaccharide hydrolysis. Research indicates that delignification and saccharification of biomass are the key factors in obtaining the stored energy in the plant tissues. Ethanol is a potential substitution (partially or totally) for gasoline. Therefore, utilizing selected Fusarium strains to decompose and convert biomass to ethyl alcohol is well justified. The purpose of this investigation is:

- to isolate and develop Fusarium strains by exploring their parasexuality and mutagenic reactions that potentially delignify, saccharify, and ferment biomass to ethanol;
- to optimize the parameters that dictate maximum ethanol production via biomass decomposition and fermentation by the selected Fusarium strains;
- to identify the type and quantity of enzymes released by the strains, as well as to explore the use of stimulants (ethylene, indoleacetic acid, etc.) that could increase and accelerate the enzyme yield;
- to investigate the synergistic action of Fusarium strains with other fungal and bacterial isolates that are also known to degrade and ferment biomass; and
- to make comparative economic studies of this process and other known processes for obtaining ethanol.
SUMMARY

On June 9, 1978 a contract for the design, construction, and operation of a process development unit (PDU) that utilizes three dry tons of feedstock per day was negotiated with Georgia Institute of Technology.

The work to date has utilized laboratory-scale units. There is now a need to have a PDU through which the technical feasibility of the conversion processes can be evaluated and scale-up and economic/cost factors can be estimated. The purpose of this experimental program is to determine the technical and economic feasibility of using fermentation to convert cellulosic biomass to ethanol. The PDU will include pretreatment of the cellulosic biomass to separate the cellulose from hemicellulose and lignin; acid hydrolysis of the cellulose to glucose or other simple sugars; fermentation of the sugar to ethanol; and recovery of the ethanol.

The major specific objectives of the experimental program are:

- evaluation of a number of promising fermentation processes for the conversion of various types of biomass to ethanol;
- testing of various pretreatment processes that prepare the biomass feedstock for breakdown by hydrolysis;
- determination of the costs of producing ethanol from various forms of biomass;
- determination of the energy balance for the conversion of biomass to ethanol; and
- establishment of the technologies and economic bases for commercial utilization.
SUMMARY

A technological problem common to many fermentations is the relatively dilute aqueous product streams. Concentrations of ethanol above 60 g/l cause the rate of yeast reproduction to drop and the metabolism of Clostridium thermocellum to stop. Likewise, less than 12 g/l of butanol is toxic to Clostridium acetobutylicum. Selection and adaptation, fermentation manipulation, and improved separation techniques have increased yields very little.

The basic cause of alcohol toxicity in microorganisms is unknown. It is known that membrane structure is altered by concentrations noted above as being toxic. The objective of the proposed work is to demonstrate that membrane functionality in transporting sugars is destroyed by aliphatic alcohols at low concentrations. Further, it is proposed to define characteristics of membranes more stable in structure and function to alcohols and to attempt to modify the cellular membranes of Cl. thermocellum and Cl. acetobutylicum to contain desirable properties that impart tolerance to higher concentrations of the respective alcohols.
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<td>The Georgia Institute of Technology</td>
<td>Fuel-grade Ethanol Recovery By Solvent Extraction</td>
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<td>Dr. D. W. Tedder</td>
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**SUMMARY**

The principal objective of this research is to develop a solvent extraction process that can economically remove fuel-grade ethanol from dilute fermentation broths. The program is set up to provide a commercial-ready system in two years, complete with energy balance, engineering design, and economics.
SUMMARY

The initial results from this study indicated that wet-oxidation reaction of biomass may be valuable both as a pretreatment and as a direct process for converting wood into low-molecular acids such as formic, acetic, and glycolic acids. The present study will be concentrated on these two processes.

The wet-oxidation process is relatively inexpensive. The only chemicals required are oxygen, water, and the biomass material. The amount of energy required is low since the wet-oxidation reaction is very exothermic. The exact amounts of energy used during the wet-oxidation reaction is not known but will be determined during the next research period.

The effects of time, temperature, and oxygen pressure on the yields of formic, acetic, and glycolic acid will be determined. The objective of this study will be to maximize the yield of these valuable commercial products. Concurrent with this study, researchers at SERI will be evaluating the possibility of electrochemical conversion of these products into other potentially useful organic chemicals. Preliminary studies have shown that metal catalysis (ferrous and ferric salts, copper and nickel salts) led to a large increase in the acidic component during wet oxidation, with the major product increase being acetic and glycolic acid.