SUPERCRITICAL WATER PARTIAL OXIDATION

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Abstract

General Atomics is developing Supercritical Water Partial Oxidation (SWPO), a gasification process involving oxidative reactions in a supercritical water environment – akin to high-pressure steam – in the presence of substoichiometric quantities of oxidant. The key potential advantage of the SWPO process is the use of partial oxidation in-situ to rapidly heat the gasification medium, resulting in less char formation and improved hydrogen yield. Another major advantage is that the high-pressure, high-density aqueous environment is ideal for reacting and gasifying organics. The high water content of the medium should encourage formation of hydrogen and hydrogen-rich products and is highly compatible with high water content feeds such as biomass materials. By the same token, the high water content of the medium is effective for gasification of hydrogen-poor materials such as coal. A versatile pilot plant for exploring gasification in supercritical water has been established at the General Atomics' facility in San Diego. Preliminary testing of the SWPO process has found hydrogen yields of about 10 grams per 100 grams of feed, comparable to those found in prior laboratory-scale work carried out at the University of Hawaii. As in that prior work, a significant amount of the hydrogen found in the gas phase products is derived from the water/steam matrix.

Introduction

General Atomics is developing Supercritical Water Partial Oxidation (SWPO) for the efficient and environmentally advantageous gasification and hydrogen production from low-grade fuels such as biomass, municipal/solid waste (MSW) and high-sulfur coal.

SWPO involves carrying out oxidative reactions in a supercritical water environment – akin to high-pressure steam – in the presence of substoichiometric quantities of oxidant, typically pure oxygen or air. The key potential advantage of the SWPO process is the use of partial oxidation in-situ to rapidly heat the gasification medium, resulting in less char formation and improved hydrogen yield. Another major advantage is that the high-pressure, high-density aqueous environment is ideal for reacting and gasifying organics. The high water content of the medium should encourage formation of hydrogen and hydrogen-rich products and is highly compatible with high water content feeds such as biomass materials. By the same token, the high water content of the medium is effective for gasification of hydrogen-poor materials such as coal.

The pressurized nature of the SWPO process naturally lends itself to the liquefaction and sequestration of CO_2. The combination of high pressure and the cold sink available with a liquid

oxygen oxidant enables ready liquefaction of CO_2. It may then be recycled, injected for oil recovery or otherwise handled to reduce greenhouse effects.

The overall goals and objectives of the program are to develop and commercialize SWPO technology to convert biomass, MSW and high-sulfur coal to hydrogen. Development phases include:

I. Pilot-scale preliminary testing / feasibility studies
II. Technology development
III. System integration and design
IV. Pilot-scale demonstration
V. Engineering-scale demonstration
VI. Commercial-scale SWPO

The program is currently nearing the end of Phase I, in which the specific tasks are:

Task 1: Pilot-Scale Preliminary Testing/Feasibility
- Perform SWPO testing on cornstarch, followed by biomass fuels and coal.

Task 2: Pilot-scale Design and Analysis
- Perform pilot-scale conceptual design of SWPO system for Phase II development.
- Perform system engineering evaluation to predict when and how hydrogen production goals can be met.

Task 3: Development Plan
- Prepare a SWPO development plan, including cost and schedule estimate.
- Prepare a business plan to identify SWPO market potential.
- Define follow-on activities from preliminary testing through pilot-scale demonstration of an integrated SWPO system, including follow-on proposal.

This paper focuses on Task 1, the Pilot-Scale Preliminary Testing, which has recently been completed.

Background

Supercritical water (SCW) gasification and partial oxidation technology is based on the unique properties of water at conditions near and beyond its thermodynamic critical point of 705°F and 3206 psia. At typical SCW reactor conditions of 1200°F and 3400 psi densities are only one-tenth that of normal liquid water. Hydrogen bonding is almost entirely disrupted, so that the water molecules lose the ordering responsible for many of liquid water's characteristic properties. In particular, solubility behavior is closer to that of high-pressure steam than to liquid water. The loss of bulk polarity by the water phase has striking effects on normally water-soluble salts. No longer readily solvated by water molecules, they frequently precipitate out as solids.

Small polar and nonpolar organic compounds, with relatively high volatility, will exist as vapors at typical SCW conditions, and hence will be completely miscible with supercritical water. Gases such as N_2, O_2, and CO_2 show similar complete miscibility. Larger organic compounds and polymers will hydrolyze to smaller molecules at typical SCW conditions, thus resulting in

solubilization via chemical reaction. Figure 1 summarizes the density and typical solubility behavior of water at 3400 psi as a function of temperature. Figures 1a and 1b show the rapid drop in density in the vicinity of the critical temperature, with a concomitant increase in the solubility of nonpolar organics and gases. As shown in Fig. 1c, high-salt solutions may persist well beyond the critical temperature. This is due to salt stabilization of the dense liquid phase, much as salt raises the boiling temperature of water on a kitchen stove.

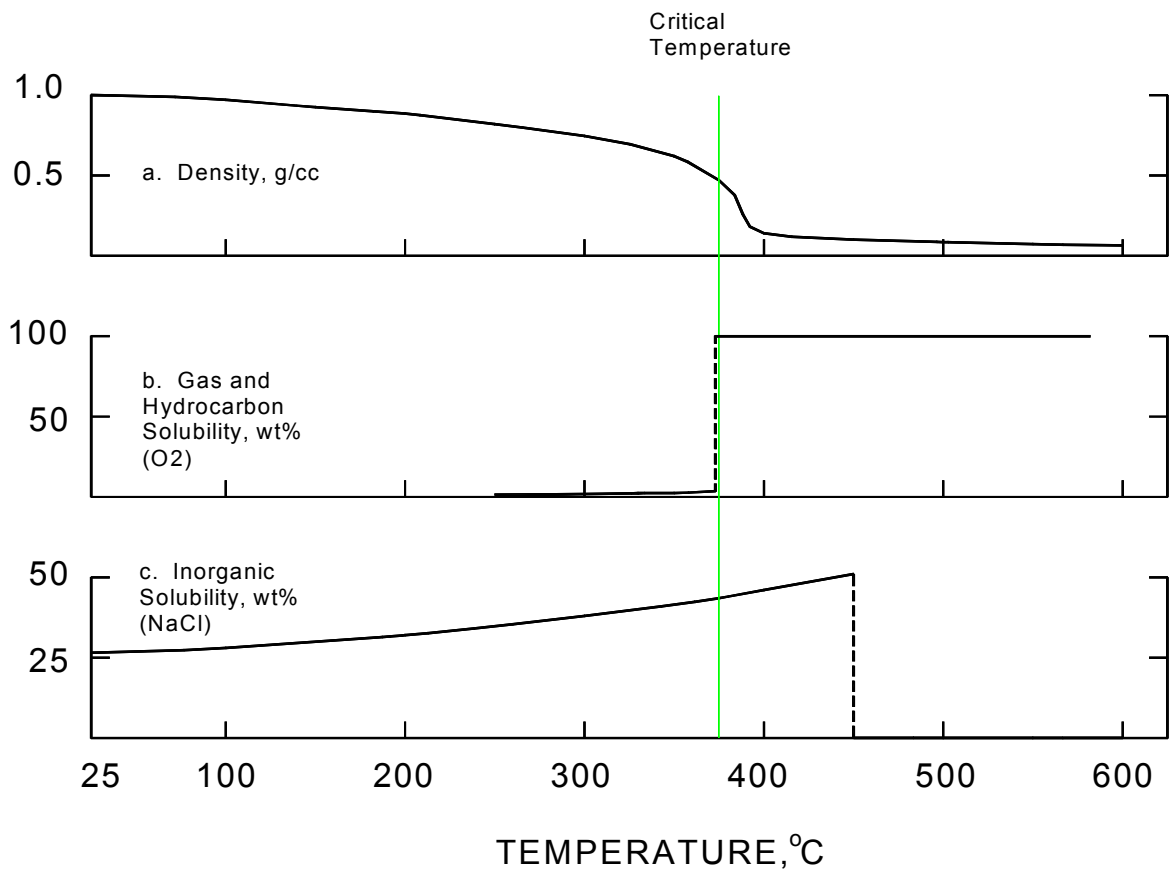

Fig. 1. Characteristics of water at 3400 psi as a function of temperature. a. Density. b. Solubility of nonpolar organics and permanent gases. c. Solubility of sodium chloride.

The earliest tests on gasification in supercritical water were carried out by Modell and coworkers at the Massachusetts Institute of Technology (MIT) in the late 1970's (Modell et al., 1978). These tests utilized residence times of at least 30 minutes with temperature and pressure conditions essentially at water's critical point. Various metallic catalysts were employed. Table 1 summarizes some of these results along with representative data from more recent testing. Dramatically improved results have been achieved through the use of higher temperatures and activated carbon catalyst, with reactor residence times of less than a minute. A number of results have been reported in which the yield of hydrogen in the gas (including primarily H_2 and CH_4) is higher than the mass of hydrogen in the organic feed. This situation arises when water is consumed in gas-forming reactions.

Table 1. Prior Laboratory-Scale SCWG Test Results

Reference	Feedstock	T, °C	P, psi	Catalyst	Reaction Time, min	%C Gasified	g H gas/ 100 g feed
Modell et al., 1978	Glucose Cellulose	374	3200	Mixed metallic	30	23 18	1.4 0.3
Woerner, 1976	Maple sawdust	374	3200	None	30	88	2.3
Whitlock, 1978	Glucose	380	4750	Mixed metallic	13	36	0.8
Sealock and Elliott, 1991	Cellulose Holocellulose Lignin Wood	400	4000	Ni/Cs_2CO_3	15	76 70 37 74	6.5 5.1 4.1 7.6
Yu et al., 1993	Glucose	600	5140	None	0.5	86	11.3
Xu et al., 1996	Glucose Bagasse Glycerol	600	5140	Activated carbon Activated carbon None	0.3 1.4 0.75	99 100 100	8.1 3.3 11.8
Antal, 1996	Cellobiose Water hyacinth	600	5140	Activated carbon	0.3	100 100	5.2 9.4
Antal and Xu, 1998	Corn starch (CS) Sewage sludge + CS Sawdust + CS	650	4170	Activated carbon	0.25	100 94 100	9.1 8.8 9.6

The preponderance of data in Table 1 indicates that activated carbon catalyst is conducive to high gas yields. It is also clear, however, that this catalyst is not universally required. Furthermore, Antal (1996) reports that the carbon becomes deactivated over the course of several hours. Due to the complexities involved in maintaining an active carbon catalyst bed, it is considered worthwhile to evaluate any given feedstock for yield without carbon catalyst to establish what tradeoffs are involved.

An advantage of the SCWG process, which is expected to extend to the SWPO process, is the general lack of char formation. It is known that the formation of high molecular weight hydrocarbons (tar and char) is a function of feed heat-up time (Xu et al., 1996), with longer heat-up times yielding higher amounts of these products.

SWPO involves carrying out oxidative reactions in the SCW environment in the presence of sub-stoichiometric quantities of an oxidant, typically pure oxygen or air, and as such is related to the technology of supercritical water oxidation (SCWO). The SCWO process has been under development since the early 1980's. Applications of SCWO technology have thus far been primarily targeted at waste destruction applications, where the high destruction efficiencies attainable in compact equipment are very desirable. The process has the capability of operating on a wide range of feed materials, including wet or dirty fuels such as sewage sludge, MSW, or high-sulfur coal.

The molecular dispersion of the organic and oxidant reactants within a single phase, in conjunction with the high diffusivity, low viscosity, and relatively dense SCW reaction medium, is conducive to rapid oxidation reactions. Furthermore, the temperature is sufficiently high that reaction completion is usually attained within seconds to tens of seconds. Rapid reaction rates have been demonstrated for virtually all types of organic materials, including solids.

SCWO has proven to be a robust method for the complete oxidation and mineralization of a wide spectrum of materials. It is particularly suited to feedstocks with a high water content, such as biomass-derived materials, as well as dirty fuels such as high-sulfur coal. It is a natural complement to the process of SCWG, with the matched pressures of the processes facilitating heat interchange.

SCWO arose as an outgrowth of the gasification work at MIT in combination with the well-known process of wet oxidation. The key concepts were formulated by Modell (1982) in the early 1980s. Experimentation quickly established that temperatures considerably higher than the critical temperature of water (374 °C), in the range of 600 °C, were desirable to achieve rapid and complete oxidation. In contrast, the pressure functionality was more ambiguous, with good oxidation result being reported at pressures both considerably below and above the critical pressure of 3206 psi (Hong, 1992; Buelow et al, 1990). (For simplicity, the process is still referred to as SCWO, even though the operating pressure may be somewhat subcritical.)

The low temperature of SCWO in comparison to normal combustion has the advantage of reducing NOx and SOx formation. Typical effluent levels for these gases, even with nitrogen-containing feeds and air oxidant, is less than 1 ppm. Residence times for complete oxidation are typically less than a minute and can be as little as several seconds for liquid or gaseous feeds. The short reaction time and relatively dense process medium results in reactors that are highly compact as compared to conventional combustors.

The effectiveness of SCWO has been demonstrated at the laboratory and pilot scale on hundreds of feedstocks. Feedstocks of interest to the current program that have been treated

by SCWO include sewage sludge (General Atomics, 1997), black and gray water (Elliott et al., 2000), coal slurry (Modar, Inc. unpublished results), pig manure (Rulkens et al., 1989), various biomass slurries including pulp mill sludge (Modell, 1990), pulverized wood with ground plastic, rubber, and charcoal (General Atomics, 1999), fermentation waste (Johnston, et al., 1988) and ground cereal (Hong, et al., 1996). Complete oxidation of virtually any organic material, including highly refractory hazardous wastes such as hexachlorobenzene, has been demonstrated. Regardless of the particular feedstock, the heat of combustion is captured directly within the high-pressure aqueous stream without the need for intervening heat transfer surfaces.

Like SCWO, SWPO has an inherent advantage over external heating in that the high-temperature, high-pressure steam resulting from the reaction is generated in situ, without the need for any intervening heat transfer surfaces. Thus, the problems of scaling heat transfer surfaces and limited metal strength at high temperatures are largely avoided. Use of pure oxygen or highly enriched air as the process oxidant minimizes the noncondensable gas content of the steam.

Exothermic energy derived from the SWPO process is an excellent heat source for gasification processes that may be carried out in SCW. Gasification is typically operated at conditions of 1200 °F and 3400 psi. Complete gasification has been reported in the laboratory for some biomass feedstocks in the presence of an activated carbon catalyst. A complete absence of char has also been reported in most cases. Should char or other organic residues remain in the effluent, however, it can be recycled back through the SWPO system. Rapid reaction times and a relatively dense medium make for compact, heat-efficient equipment in the SWPO process. Following purification and hydrogen separation, the SWPO effluent fuel gas may be supplied to a combustion turbine, or burned to raise steam.

The use of LOX as the oxidant supply is expected to improve hydrogen yields. The cost of LOX is an added operational expense, but may be more than offset by the improvements in gasifier performance in the absence of large amounts of nitrogen from air.

As described above, the supercritical water gasification process developed by Antal and coworkers at the University of Hawaii (1998) indicates that it is possible to produce an enriched hydrogen gas stream by reacting wet biomass with water at temperatures and pressures above the critical point of water, with minimal formation of char. While promising, the University of Hawaii testing was carried out at a very small scale, with a reactor volume of about 30 mL. One of the objectives of the GA testing is to demonstrate a SCW gasification process at pilot scale to obtain data more representative of a full-scale application.

An important finding of Antal's work is that a significant amount of hydrogen in the gaseous products (primarily H_2 and CH_4) is contributed by the water. Similar observations have also been reported for supercritical water gasification of coal (Lin et al., 1999a,b; Wang and Takarada, 2001). Thus the gaseous products may contain significantly more hydrogen than is present in the feed material. Given the high water partial pressure in a supercritical water process this is to be expected as the carbon-steam gasification (1) and water gas shift (2) reactions are encouraged:

$$C + H_2O \Leftrightarrow CO + H_2 \qquad (1)$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad (2)$$

For a given feedstock a theoretical maximum yield of hydrogen in the gas may be calculated by converting all feed carbon to carbon dioxide, with the oxygen supplied from water. Thus, for ideal cellulose we have:

$$C_6H_{10}O_5 + 7H_2O \Leftrightarrow 6CO_2 + 12H_2 \qquad (3)$$

The maximum hydrogen yield for cellulose is thus 24/162, or 14.8 g per 100 g of dry feed. Table 2 shows several other feed stocks and their maximum hydrogen yields. The table includes values for ethanol and wood, which are of particular relevance for the pilot scale testing to be described later.

Table 2. Maximum Gaseous Hydrogen Yield

Material	Formula	Maximum gaseous g Hydrogen per 100 g dry feed
Polyethylene	CH_2	42.9
Ethanol	C_2H_6O	26.1
GA Wood	$CH_{1.26}O_{0.62}$	17.3
Antal Wood	$CH_{1.46}O_{0.68}$	16.7
Cellulose	$C_6H_{10}O_5$	14.8
Corn starch	$C_6H_{11.4}O_{5.7}$	13.7

Test Description

Figure 2 provides a representative process flow diagram (PFD) for the gasification tests carried out. A number of different configurations were tested over the course of the project. The particular configuration shown is that used in conjunction with the “large” reactor vessel. This reactor has a volume of about 10 liters and at the flow rates tested provides a residence time of about 75 seconds at 650°C operating temperature and about 60 seconds at 800°C operating temperature.

Dual syringe pumps to deliver high pressure slurry to the system. Pressurized slurry (or water during startup and shutdown) is fed to the preheater where it is preheated to a temperature of 250°C, or other suitable temperature depending on the feed material. It was found during testing that slurry preheating had to be limited to avoid char formation and plugging of the preheater. In addition, the pumpable concentration of biomass slurry was limited, for example to about 10-15 wt% for wood flour. Due to limited resources for advancing solutions to these limitations during the Phase I effort, it was decided to utilize a liquid fuel to help attain the desired reactor operating temperature. Thus, as shown in Figure 2, high-pressure auxiliary fuel (ethanol) and oxygen are combined with the preheated slurry at the reactor inlet. Oxidation of the organics results in a nominal reactor temperature of 650°C. In the reactor, the feed is converted primarily to CO_2, H_2O, H_2, CH_4 and CO.

The reactor effluent is cooled to near ambient temperature by a series of annular heat exchangers. Pressure control water is introduced and the stream passes through a capillary to be depressurized to slightly above atmospheric pressure. The flow of the pressure control water is varied to maintain the reactor at the desired pressure of 3400 psi. Following depressurization, the effluent is phase separated in a low pressure gas-liquid separator. Level control in the phase separator is aided by the introduction of a low flow of air from an air

cylinder. Liquid effluent pH and conductivity are measured on-line in the effluent line. The liquid effluent is then collected in a tank, while the gases are vented through the facility carbon filter and released to the atmosphere. Liquid effluent samples are collected either just downstream of the cooldown heat exchanger or from the drain line of the effluent collection tank. The effluent gas is monitored online upstream of the carbon filters for CO_2, H_2, CH_4, CO, and O_2 content.

Table 3 provides a synopsis of the Phase I pilot-scale testing carried out.

Several runs with composted MSW were carried out with a pipe reactor in the absence of oxidant, i.e., they were indirectly heated and did not utilize partial oxidation. The pipe reactor had an ID of 0.815 in. and a length of about 90 feet.

In the large vessel tests, an appurtenance known as a "J-screen" was frequently utilized. A J-screen is essentially a rugged filter plate or grate made from two layers of bars at right angles to one another. The J-screens were used as a method of retaining larger particles in a desired zone in the reactor while allowing the process fluid and smaller particles to pass through.

Test Results and Discussion

Slurry Pumping

Significant effort was required to obtain reliable operation of a dual syringe pump for pumping thick slurries to high pressure. A number of improvements over the basic design were implemented, including magnetic sensing of the position of the driving pistons. The pump is now operating in highly reliable fashion.

The maximum pumpable concentration of wood dust slurries is in the range of 10-15 wt% dry basis. The maximum pumpable concentration of composted municipal solid waste is in the range of 30 wt% dry basis. 10 wt% wood + 10 wt% coal (wet basis) is readily pumpable. To attain higher biomass content, alternate methods such as auger feeding are being considered.

Feed Heatup

The pilot plant was initially set up with a mixing tee to rapidly heat incoming biomass by mixing with supercritical water. This proved to be problematic because a relatively large amount of supercritical water was required. This diluted the biomass slurry and required oxidation of most of the biomass to attain the desired final temperature of about 650°C. It was also found that feed could not be preheated to near reactor temperature in a heat exchanger without charring and plugging. Thus, a combination of preheat and partial oxidation was utilized to attain gasification temperatures. Preheat temperatures in excess of about 250°C are conducive to charring with wood slurry feeds. Preheating of corn starch is even more limited as it thickens and plugs quickly above about 60°C.

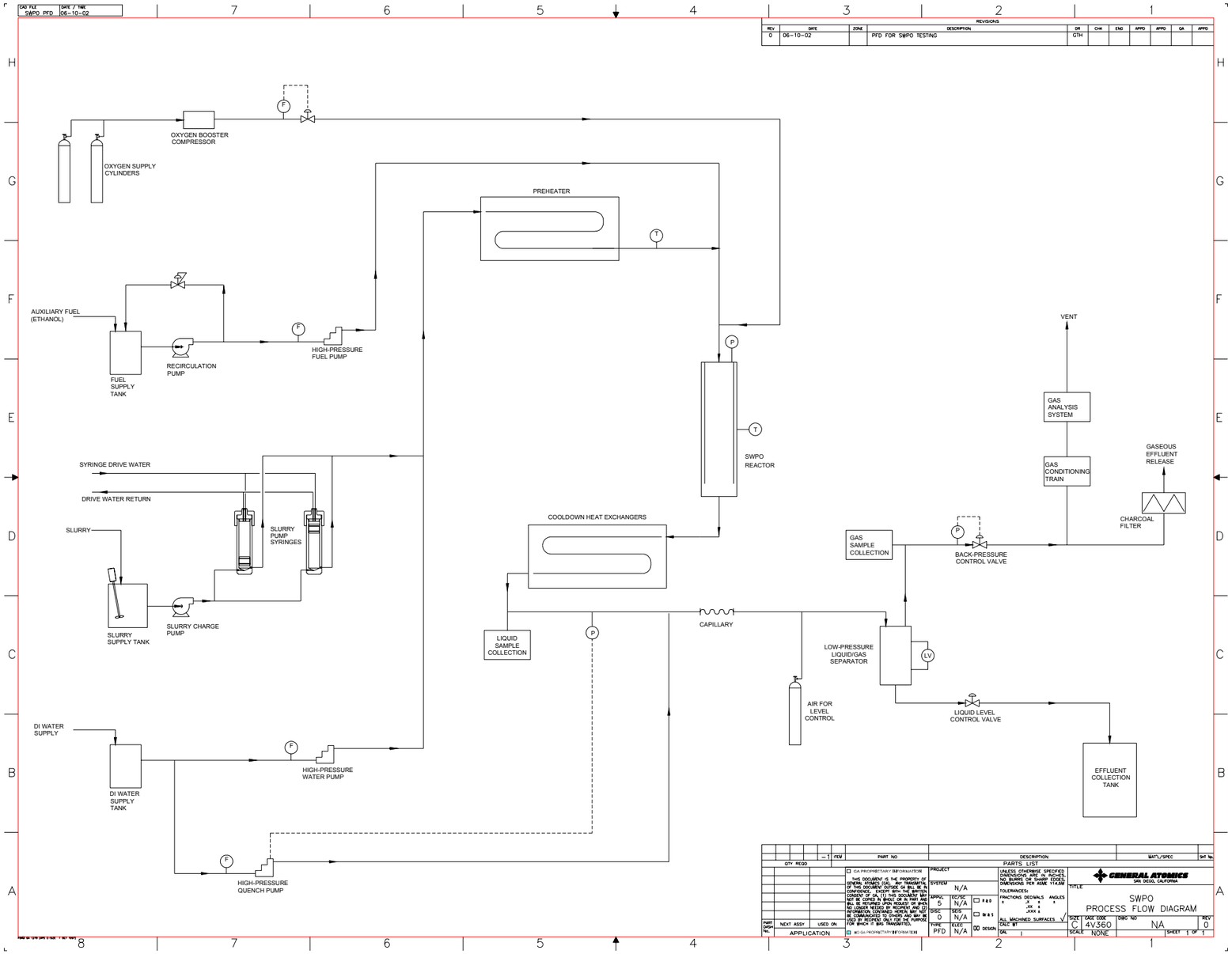

Figure 2. GA SWPO pilot plant process flow diagram (PFD).

Table 3. Summary of Gasification Runs

Feed	Run Dates	Reactor Type	System Configuration[1]	Run Conditions[2]	Results
40% corn starch	6/19/01	Small vessel (volume ~4L)	Mixing tee	605°C	Significant char
40% coal	6/28/01; 7/2/01	Small vessel	Mixing tee	530°C; 620°C	Poor gasification of coal
30-40% MSW compost[3]	8/16/01	Small vessel	Mixing tee	570°C	Mixing tee requires too much hot dilution water
30-40% MSW compost[3]	10/12/01; 10/31/01; 11/8/01; 11/19/01; 1/3/02	Pipe (volume ~9L)	Pipe preheater, no oxidant	620°C-650°C	Preheat T < 400°C necessary to avoid charring
30% corn starch	1/30/02	Pipe	Pipe preheater, air oxidant	650°C, 300°C preheat	Preheat T < 300°C necessary to avoid charring
10% wood + 10% coal	3/18/02; 3/21/02	Large vessel (volume ~10L)	Reactor baffle; reactor mid-screen	800°C, 250°C preheat, EtOH fuel[4]	Poor gasification of coal, rapid buildup of char
10% wood	4/10/02; 4/12/02; 4/23/02	Large vessel	Various J-screen positions	650°C, 250°C preheat, EtOH fuel[4]	H gasification yield ~10 g/100 g dry feed, <10% char
10% wood	4/17/02; 4/18/02; 4/24/02	Large vessel	Various J-screen positions	800°C, 250°C preheat, EtOH fuel[4]	H gasification yield ~11 g/100 g dry feed, <10% char
10% corn starch	4/25/02; 4/26/02; 4/30/02; 5/3/02	Large vessel	Various J-screen positions	650°C, EtOH fuel[4]	Corn starch can only be preheated to 70°C to avoid thickening and preheater plugging.
40% corn starch	5/8/02; 5/14/02	Large vessel	J-screen at reactor bottom	650°C, EtOH fuel	40% corn starch plugs preheater at 70°C. Poor nozzle dispersion leads to char buildup and plugging at reactor bottom.
15% wood	5/15/02;5/16/02	Large vessel	J-screen at reactor bottom	650°C, EtOH fuel	Suspect new suspending agent (commercial gum) leads to pumping problems.
20% MSW compost[3]	5/17/02	Large vessel	J-screen at reactor bottom	650°C, EtOH fuel	Poor nozzle dispersion leads to char buildup and plugging at reactor bottom.

Notes:
1. Commas denote same run, semicolons denotes separate runs. Oxidant is oxygen unless noted.
2. All tests are at 3400 psi.
3. MSW is municipal solid waste.
4. Ethanol (EtOH) is oxidized with stoichiometric oxygen in the reactor to bring the preheated stream up to the target reactor temperature.

Reactor Type

As noted in Table 3, both vessel and pipe reactors have been tested. Based on these tests and other information, we now feel that a vessel reactor is preferable to a pipe reactor. A vessel reactor allows better temperature control and better heat conservation, and is amenable to the use of a corrosion resistant thermal sleeve. With such a thermal sleeve the reaction zone can be maintained at a temperature considerably above the allowable temperature of the pressure vessel. A thermal sleeve allowed us to conduct tests at 800°C. Even higher temperatures are possible with this reactor type.

One area of potential improvement is in the design of the feed injector nozzle. In the Phase I tests, a relatively large nozzle orifice was used to minimize the chance of nozzle plugging. This results in a relatively slow velocity and poor dispersion of the feed entering the reactor. Based on test observations, it is now believed that the feed nozzle was overly large in orifice size, and that as a result relatively large globules of feed material were able to fall through the reactor with insufficient opportunity to disperse and react.

Another potential improvement is the incorporation of baffles within the reactor to allow larger feed particles sufficient time in the reactor to achieve complete gasification.

Feed Type

Sewage sludge (SS) is a good target biomass feed for generating H_2 because it is negative value and abundant near population centers. However, it is relatively limited in quantity, so economies of scale are limited. Adding municipal solid waste (MSW) to sewage sludge increases the potential negative value biomass feed stock near population centers by about a factor of 10, and overcomes the limit on economies of scale. Composted SS/MSW available from the Bedminster Process (and other similar composting processes) is a good source of size-reduced feed for supercritical water gasification, minimizing front end processing (shredding, grinding, etc.). Composted MSW/SS can be pumped at over 30 wt% (dry basis), sufficient to support partial oxidation and gasification without the addition of coal or other fuel. The ability to pump a >30 wt% compost slurry may be due to either the depleted organic content and concentrated ash, or breakup of cell structure. By contrast, concentrated sewage sludge and uncomposted sawdust or wood flour can only be pumped at concentrations between 10-15 wt% (dry basis) maximum.

The advantages of composted MSW/SS are offset by several factors. During composting, the organic material becomes depleted in hydrogen and heating value due to microbial action. This works against high hydrogen production. Compost also has a fairly high content of minerals and grit from soil, complicating grinding, pumping, heat exchange and pressure letdown in a SCWG system. We have also found that a composter front end is expensive, adversely affecting the economics of a SCWG/SWPO process, unless a composter already exists at the site.

Although coal can readily be oxidized at 650°C, it does not gasify well at 3400 psi and temperatures up to 800°C.

On balance, we now feel it is preferable to focus on uncomposted MSW, the largest constituent of which is cellulosic materials. This is also consistent with the target feeds for energy crops. For materials such as wood, paper, and vegetation, a series of shredding/grinding/slurrying steps are needed to prepare a slurry feed for SCWG/SWPO. As mentioned, finely ground wood

can only be pumped at concentrations between 10-15 wt% (dry basis) maximum. This concentration of cellulosic feed is too low for efficient gasification. Therefore as mentioned above we are considering means for auger-feeding of higher biomass-content materials. This approach will ultimately require development of pressurized feed and discharge lock-hoppers.

Char Formation

Unlike the laboratory results (which used a carbon catalyst), our tests without catalysts thus far have produced significant char, about 10% or less of the feed carbon. Char reduction/ transport methods are being explored. If the char cannot be reduced, GA has existing solids removal methods that are expected to be effective in removing the char. Thus, it may be possible to recycle the char in a fully developed process.

SWPO of Wood Slurries

For the reasons discussed, testing was focused on SWPO of wood slurries. Table 4 summarizes the tests carried out. Again, it is important to bear in mind that auxiliary fuel in the form of ethanol was used in these tests.

Gaseous effluent from the system was monitored by online gas meters as usual, but grab samples were also checked by gas chromatography (GC) in the laboratory. In general the results of the GC and online meters were within 10% of one another, the only significant difference being that CO from the online infrared meter is erroneously high due to interference from CO_2 and CH_4. The GC results have been used for Table 4. The presence of nitrogen in the effluent gas is primarily due to the diluting air stream used to aid in level control at the low pressure gas-liquid separator.

Hydrogen yields are expressed on two different bases in order to allow comparison with both indirectly heated and directly heated gasifiers. The first of these, relevant to indirectly heated gasifiers, expresses hydrogen yield assuming only the wood flour and excess ethanol is available for gasification. This is essentially assuming that the oxygen feed stoichiometrically oxidizes a quantity of ethanol fuel, allowing the reactor to reach operating temperature and providing a background of carbon dioxide and additional steam. For comparison to directly heated gasifiers, all of the wood and ethanol are included in the yield calculations.

Conversion of carbon to gaseous products was incomplete, as indicated by the liquid (tar) and solid (char) products shown in Table 4. Much of this incomplete conversion is believed to be due to insufficient dispersion at the feed injection nozzle. This explanation is consistent with the finding of unused O_2 in the gaseous effluent from reactor. About 1/3 of the oxygen in the effluent gas is residual oxidant, while the remainder is from the air introduced at the gas-liquid separator.

Mass balances are fairly good, in the range of 90%. At least some of the missing mass is likely due to residual tar or char that was distributed in different parts of the system and difficult to collect.

Comparison of SWPO with Other Gasifiers

Table 5 compares the results of the SWPO wood slurry tests with those of other gasifiers. Comparisons are given with both indirectly heated and directly heated (partial oxidation) gasifiers. When comparing with indirectly heated gasifiers, only the wood and excess ethanol is

assumed to be available for gasifying. When comparing with directly heated gasifiers, all of the wood and ethanol are included in the calculations.

In comparison to indirectly heated gasifiers, the GA hydrogen yields are similar to those obtained by Antal. As may be noted from both Tables 2 and 5, the presence of excess ethanol does give the GA feed somewhat more potential for hydrogen formation than wood or cellulose alone. It is also of interest to note the relatively high H_2O to feed ratio for the supercritical processes (both GA and University of Hawaii) as compared to the other processes. The highest hydrogen yields are shown by the Wright-Malta (WM) and Manufacturing and Technology Conversion International (MTCI) gasifiers. GA is not aware of the current status of these gasifiers. However, it is noted that the MTCI hydrogen yield actually exceeds the theoretical maximum, so the data must be considered suspect.

In comparison to directly heated gasifiers, the GA hydrogen yields are close to those obtained from the Shell gasifier and significantly less than those reported for the Institute of Gas Technology (IGT) gasifier. The primary contributors to the lower GA hydrogen yields are believed to be inefficient heat recovery (feed slurry only preheated to 250°C) and the relatively small size and attendant heat loss of the GA pilot plant. The low degree of preheat is manifested as a need to oxidize a relatively large amount of ethanol fuel. This is reflected in the high oxygen to feed ratio shown for SWPO in Table 5. GA anticipates that significant gains in hydrogen yield will be attained as SWPO is further developed. As mentioned previously for example, an improved feed injection nozzle should substantially reduce tar and char formation.

Table 5 includes results from the Dutch company TNO and an economic study by Craig and Mann (1996). While hydrogen yields from these references are not available, they still serve as useful references for product gas composition.

Table 4. Summary of 9% Wood Gasification Runs

Run Date:	**4/10/2002**	**4/12/2002**	**4/17/2002**	**4/18/2002**	**4/23/2002**	**4/24/2002**
Feed (dry basis)	9% wood	9% wood	9% wood	9% wood	9% wood	9% wood
Setup	2 J-screens	1 J-screen	1 J-screen	No J-screen	No J-screen	No J-screen
Reactor T, C	650	650	800	800	650	800
Input						
Run time min	105	250	242	195	128	132
Oxygen g/min	109	104	110	112	86	113
Stoich. EtOH g/min	52.2	49.8	52.7	53.7	41.2	54.1
Excess EtOH g/min	16.8	22.2	10.3	3.3	17.8	7.4
Feed g/min	367	345	350	336	330	347
CMC %	2.5	2.5	2.5	2.5	2.5	2.5
Output						
Gas SCFM	4.5	5.1	4.6	4.7	4.3	4.9
H_2 %	18.6	21.1	17.0	18.8	25.3	16.9
CH_4 %	16.3	16.7	13.6	14.9	15.7	13.3
C_2H_6 %	0.1	0.1	0.1	0.1	0.2	0.1
CO %	2.7	2.9	1.9	2.2	4.1	1.7
CO_2 %	48.6	48.6	54.5	48.7	43.7	54.9
N_2 %	10.4	8.0	9.5	11.2	8.1	9.7
O_2 %	3.5	2.7	3.5	4.1	3.0	3.5
H-gas yield, g/100 g feed, excess fuel only	9.1	10.5	9.4	12.7	10.3	10.4
H-gas yield, g/100 g feed, all fuel	4.8	5.8	4.6	5.6	5.9	4.8
% Feed C in solid	6.9	2.7	3.5	2.7	0.5	0.2
% Feed C in liquid	2.3	2.9	6.0	0.0	8.7	5.0
Carbon balance %	79	88	90	90	83	94

Table 5. Comparison of Gasifiers

Indirectly heated-type						Product gas mol%					H gas yield		
Organization	**Feed**	**T, °C**	**P, psi**	**H_2O: Feed**	**O_2: Feed**	**H_2**	**CH_4**	**C_2+**	**CO**	**CO_2**	**g/ 100g feed**	**Max g/ 100g feed**	**Notes**
GA	9% wood + CMC[1,2]	650	3400	5.2	-	44	33	0.3	7	16	9.9	19.7	Excess fuel only included
GA	9% wood + CMC[1,2]	800	3400	6.6	-	38	30	0.2	4	28	10.8	18.1	Excess fuel only included
U Hawaii	10.4% corn starch[3]	650	4061	8.6	-	45	14	0.0	2	35	9.1	13.7	Antal and Xu, 1998
U Hawaii	5% wood + 5.5% corn starch[3]	650	4061	8.5	-	34	23	0.2	3	45	8.2	15.2	Antal and Xu, 1998
U Hawaii	5% wood + 5.6% corn starch[3]	650	4061	8.5	-	50	10	0.0	4	39	11.4	15.2	Antal and Xu, 1998
U Hawaii	5% wood + 6.1% corn starch[3]	650	4061	8.0	-	43	14	0.2	3	37	9.3	15.1	Antal and Xu, 1998
U Hawaii	11.5% wood + 4.2% corn starch[3]	650	4061	5.4	-	57	6	NA	4	33	12.2	15.9	Xu and Antal, 1997
TNO	Waste biomass	600	4351	NA	-	54	9	NA	3	34	NA	NA	Company fact sheet
BCL	Wood	826	25	0.5	-	21	16	5.8	43	13	NA	NA	Craig and Mann, 1996
BCL	Wood	927	15	0.3	-	21	15	6.0	47	11	7.4	18.5	Katofsky, 1993
WM	Wood	600	218	0.0	-	21	35	NA	7	38	16.2	17.2	Katofsky, 1993
MTCI	Wood	697	15	1.37	-	50	8	0.4	22	19	18.5	17.8	Katofsky, 1993
Directly heated-type						**Product gas mol%**					**H gas yield**		
Organization	**Feed**	**T, °C**	**P, psi**	**H_2O: Feed**	**O_2: Feed**	**H_2**	**CH_4**	**C_2+**	**CO**	**CO_2**	**g/ 100g feed**	**Max g/ 100g feed**	**Notes**
GA	9% wood + CMC[1,2]	650	3400	2.9	0.9	22	16	0.1	3	47	5.5	21.8	All fuel included
GA	9% wood + CMC[1,2]	800	3400	3.0	1.1	17	13	0.1	2	55	5.0	22.1	All fuel included
IGT	Wood, air-blown[4]	830	460	0.3	0.3	25	18	0.2	19	38	NA	NA	Craig and Mann, 1996
IGT	Wood, oxygen-blown	982	500	0.3	0.3	31	12	0.5	22	35	9.1	17.0	Katofsky, 1993
TPS	Wood, air-blown[4]	870	20	0.0	0.5	37	0	NA	46	16	NA	NA	Craig and Mann, 1996
Shell-bio	Wood, oxygen-blown	1085	352	0.03	0.5	38	0	NA	48	14	6.0	17.0	Katofsky, 1993

Notes:
1. CMC is carboxymethyl cellulose suspension agent.
2. Average of 3 runs
3. Activated carbon catalyst.
4. Nitrogen-free basis.

Other Phase I Tasks

While progress has been slower than anticipated, the current Phase I program has actually made progress against the primary objectives originally planned for the Phase II effort, i.e., pilot scale design, fabrication and testing. Thus from this perspective the program is ahead of plan. Contribution to progress from synergistic programs has also been significant.

Pilot-Scale Design and Analysis

Task 1 involves pilot-scale testing and development, so the pilot-scale design is being carried out in the normal course of operations. Many of the lessons learned apply directly to the pilot scale design. Completion of pilot scale design and analysis will be completed in July and August of 2002.

Development Plan

This task will be carried out in July and August of 2002. Highlights of the Development Plan are given below.

Phase II – Technology Development: (1/03 – 12/04)
- Design, fabricate and test second generation pilot-scale SWPO reactor
- Optimize SWPO operating parameters and hydrogen yields
- Demonstrate feasibility and provide data for evaluations and scale-up

Phase III – System Integration and Design: (1/05 – 12/05)
- Safety, reliability and maintainability analyses
- Life-cycle cost analyses
- Process design and long-lead procurement for Phase IV

Phase IV – Demonstration Plant: (1/06 – 12/08)
- Implement Phase III studies
- Integrate pilot-scale SWPO with industrial H_2 separation and storage systems

Summary and Conclusions

A versatile pilot plant for exploring gasification in supercritical water has been established at the General Atomics' facility in San Diego. Preliminary testing of the SWPO process has found hydrogen yields of about 10 grams per 100 grams of feed, comparable to those found in prior laboratory-scale work carried out at the University of Hawaii. As in that prior work, a significant amount of the hydrogen found in the gas phase products is derived from the water/steam matrix. Potential improvements to the SWPO process include higher energy feed injector nozzles for the reactor to achieve better dispersion of the incoming feed, second-generation reactor designs, and means for feeding more concentrated slurries or dry feed.

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