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HYDROGEN PRODUCTION FROM HIGH-MOISTURE CONTENT BIOMASS IN SUPERCRITICAL WATER

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Abstract

Feedstocks studied in this work include potato wastes, wood sawdust mixed in a starch gel, and various starch gels. These feedstocks were delivered to various supercritical flow reactors by means of a cement pump. When rapidly heated in a flow reactor at pressures above the critical pressure of water (22 MPa), these feedstocks vaporized. A packed bed of carbon catalyst in the reactor operating at 650 °C or above caused the tarry vapors to react with water, producing hydrogen, carbon dioxide, and some methane with a trace of carbon monoxide. The water effluent of the reactor was essentially free of organic material. The gas composition was strongly influenced by the peak temperature of the reactor. Irrespective of the reactor geometry and method of heating, each reactor plugged after 1 to 2 hr of use with feedstocks that contain 15 wt% organic material. Lower loadings of organic material lengthened the time before plugging occurred. The plug results from small amounts of char formed at high temperatures by coking reactions involving the biomass vapors.

Introduction

When biomass is heated in water at pressures above the critical pressure of water ($P_c = 22$ MPa), the carbohydrates (cellulose, starch, and hemicellulose), and lignin react to form organic vapors (i.e. char is not a primary product in water). If the water and reaction products are further heated to 600 °C or more, the vapors crack and steam reform over a carbon catalyst, producing a hydrogen rich gas and clean water. The gas is available at high pressure without expensive compression costs. An overall, idealized reaction for the process is:

$$C_6H_{10}O_5 + 7\ H_2O \rightarrow 6\ CO_2 + 12\ H_2.$$

In this idealized, stoichiometric equation, cellulose (represented as $C_6H_{10}O_5$) reacts with water to produce hydrogen and carbon dioxide, mimicking the commercial manufacture of hydrogen from methane by catalytic steam reforming chemistry.

This annual report summarizes our progress during the past year towards the goal of developing a practical reactor for steam reforming biomass in supercritical water.

Apparatus and Experimental Procedures

Six different reactors (see Figures 1 – 6) were fabricated and operated during the past year to study the effects of reaction conditions (i.e. reaction temperature, weight hourly space velocity, gas phase residence time, etc.) on gas composition, and char formation. These reactors all employed similar operating procedures. For the sake of brevity, we limit our description to the operation of reactor #6 below.

The flow reactor (see Figure 6) is fabricated from Hastelloy C276 tubing with 9.53 mm OD x 6.22 mm ID x 1.016 m length. The reactant flow is quickly heated by an annulus heater (located along the reactor's centerline) and an entrance heater outside the reactor. The annulus heater (3.18 mm OD x 15.2 cm heated length) delivers all its heat directly to the feed. The entrance heater is made from a split stainless steel tube that is held in good thermal contact with the reactor, and an electrical heater which is coiled around the outer surface of the stainless steel tube. Downstream of the entrance heater, the reactor's temperature is maintained in an isothermal condition by the furnace. The chief purpose of the furnace is to prevent heat loss: most of the heat required to lift the reactant flow to reaction temperature is provided by the entrance heater and the annulus heater. Carbon catalyst is usually packed in about 60% of the heated zone of the reactor, as well as the downstream cold section of the reactor. The reactor's temperature profile is monitored by 12 fixed, type K thermocouples held in good thermal contact with the reactor along its outer wall. Also, the reactant temperature is measured by a fixed, internal, annulus thermocouple which is located at 12.7 cm from the entrance of the reactor. Pressure in the reactor is measured by an Omega PX302 pressure transducer. A Grove Mity-Mite model 91 back-pressure regulator reduces the pressure of the cold, two phase, product effluent from 28 to 0.1 MPa. After leaving the back-pressure regulator, the reaction products pass through a gas-liquid separator. The liquid product is collected over a measured time period to calculate the liquid outlet flow rate. The gas flow rate is measured using a wet test meter.

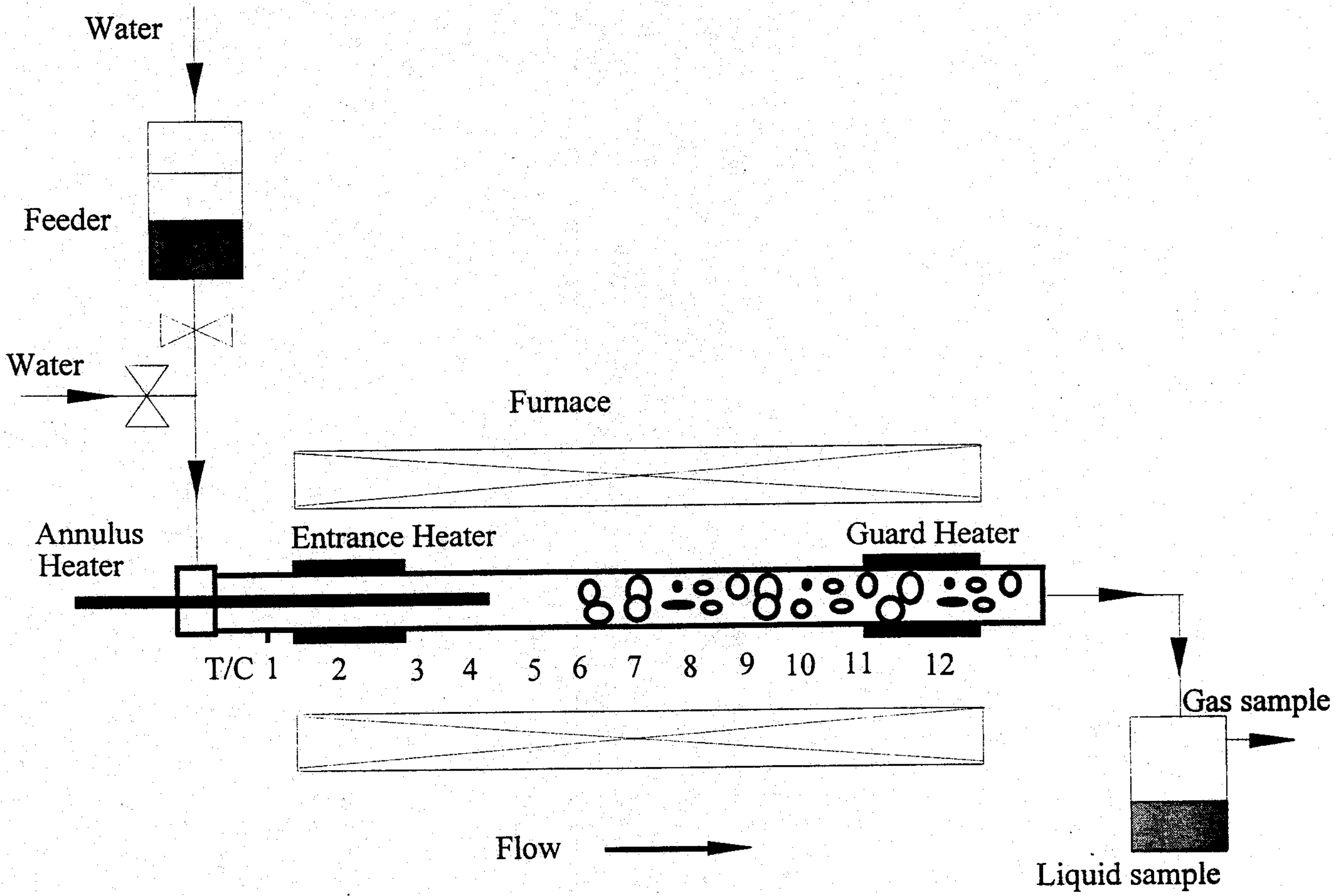

Figure 1. Gasification reactor #1 (1997)

Three different types of feedstocks are used in this work: gels made from corn and other starches, poplar wood sawdust mixed into one of these gels, and potato wastes obtained from Lamb Weston Corporation. The poplar sawdust was ground with a Wiley mill (Thomas Scientific) to 40 mesh before they are mixed with the paste. Table 1 gives elemental analyses of the feedstocks.

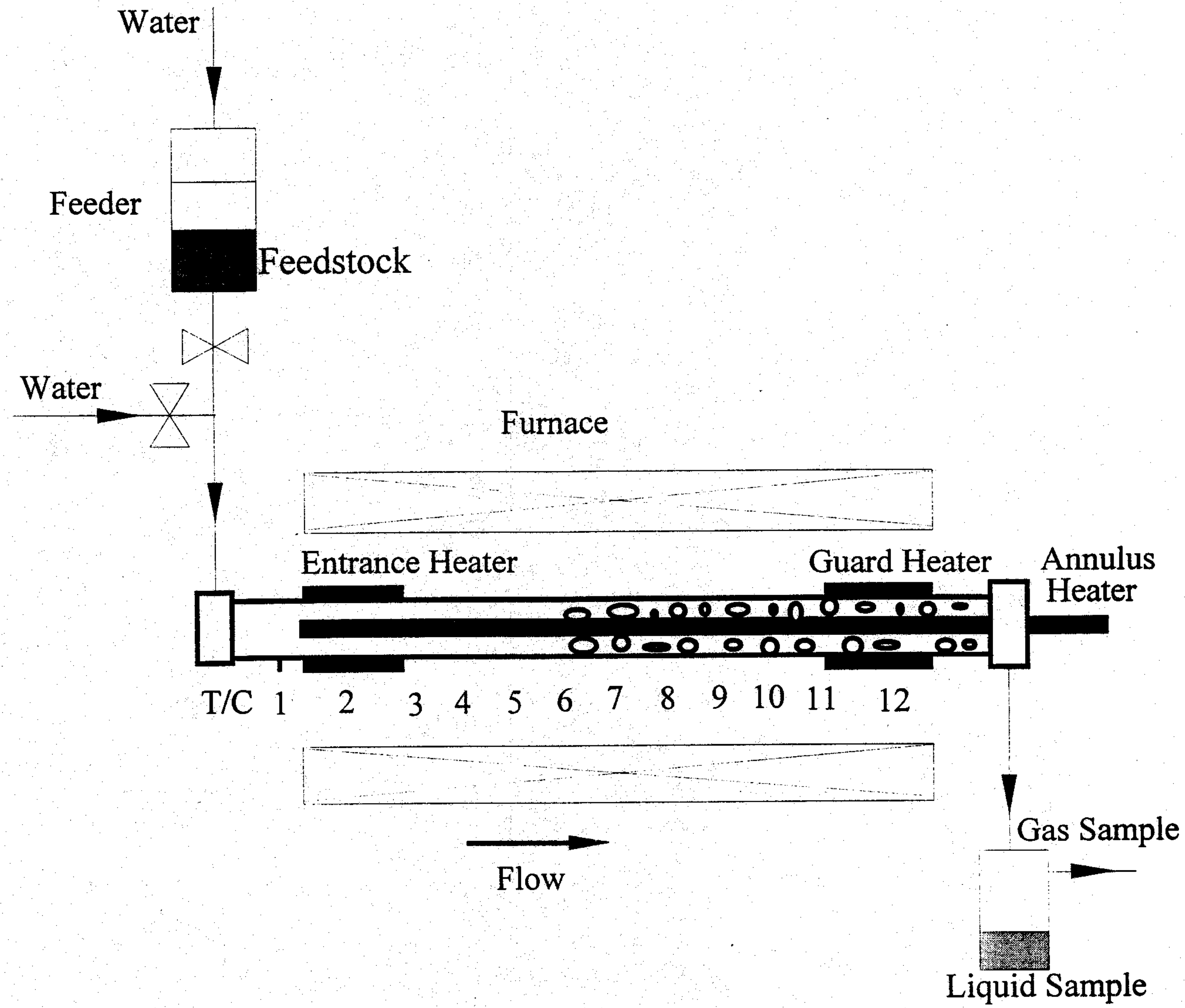

Figure 2. Gasification reactor #2 (1998)

The feeder consists of a cylinder, a movable piston, and two end-caps (High Pressure Equipment). The piston is first moved to the center of the cylinder. The top portion is then filled with water and its endcap secured. After inverting the cylinder, the feed material is loaded into the remaining chamber and the top endcap installed. Both the feeder and the reactor are pressurized separately to 28 MPa at the beginning of a run. During the time that the system is being brought up to temperature, water is pumped into the reactor by a Waters 510 HPLC pump. When the main body of the reactor reaches the desired temperature (usually 600-650 °C), the feeder is connected to the reactor. Thereafter, water flow to the reactor is terminated, and water flow to the feeder is initiated, displacing the paste feedstock into the reactor. Because the thermophysical properties of the paste are considerably different than those of water, and possibly also because of exothermic pyrolysis reactions associated with the decomposition of the paste, the temperature of the feed rises very rapidly in the entrance region of the reactor. To avoid excessively high temperatures, usually it is necessary to reduce the heat input to the feed from the annulus heater and the entrance heater.

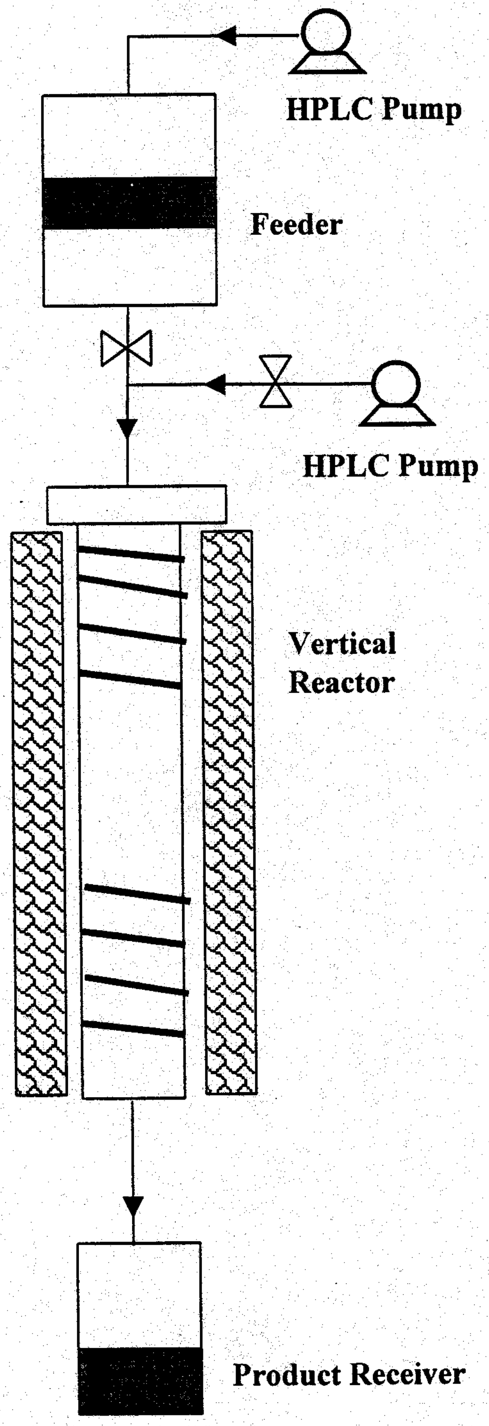

Figure 3: Gasification reactor #3 with downward flow (1999)

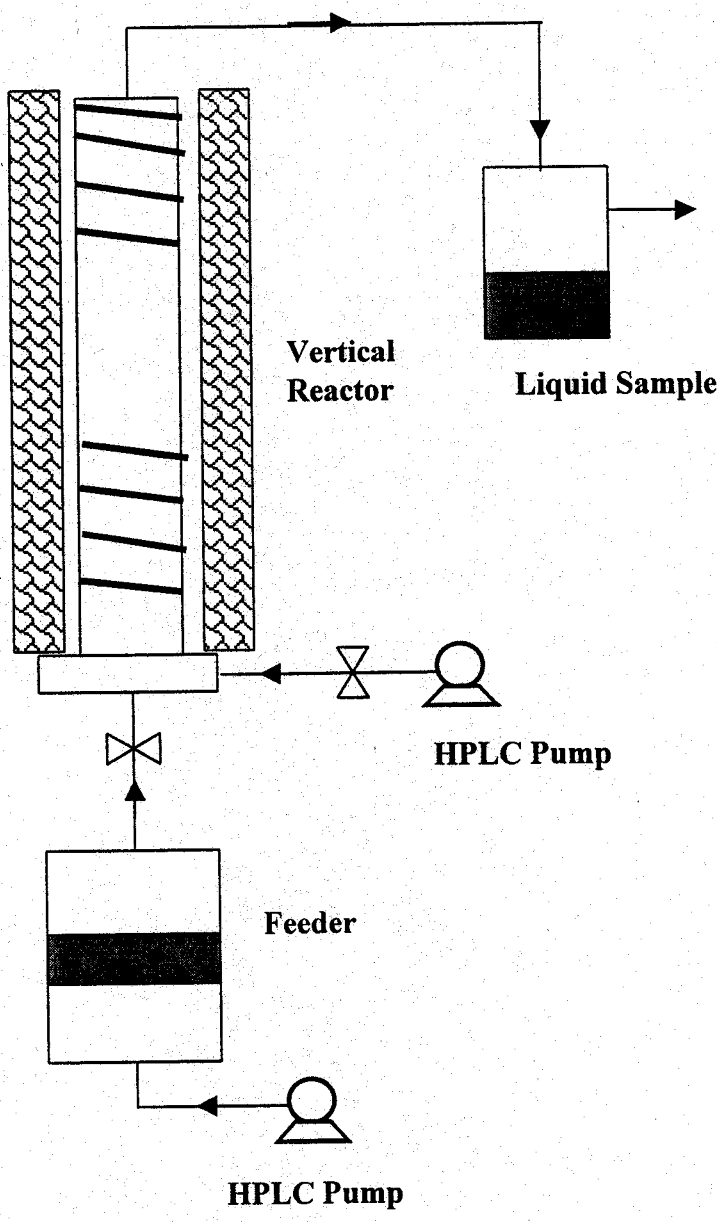

Figure 4: Gasification reactor #4 with upward flow (1999)

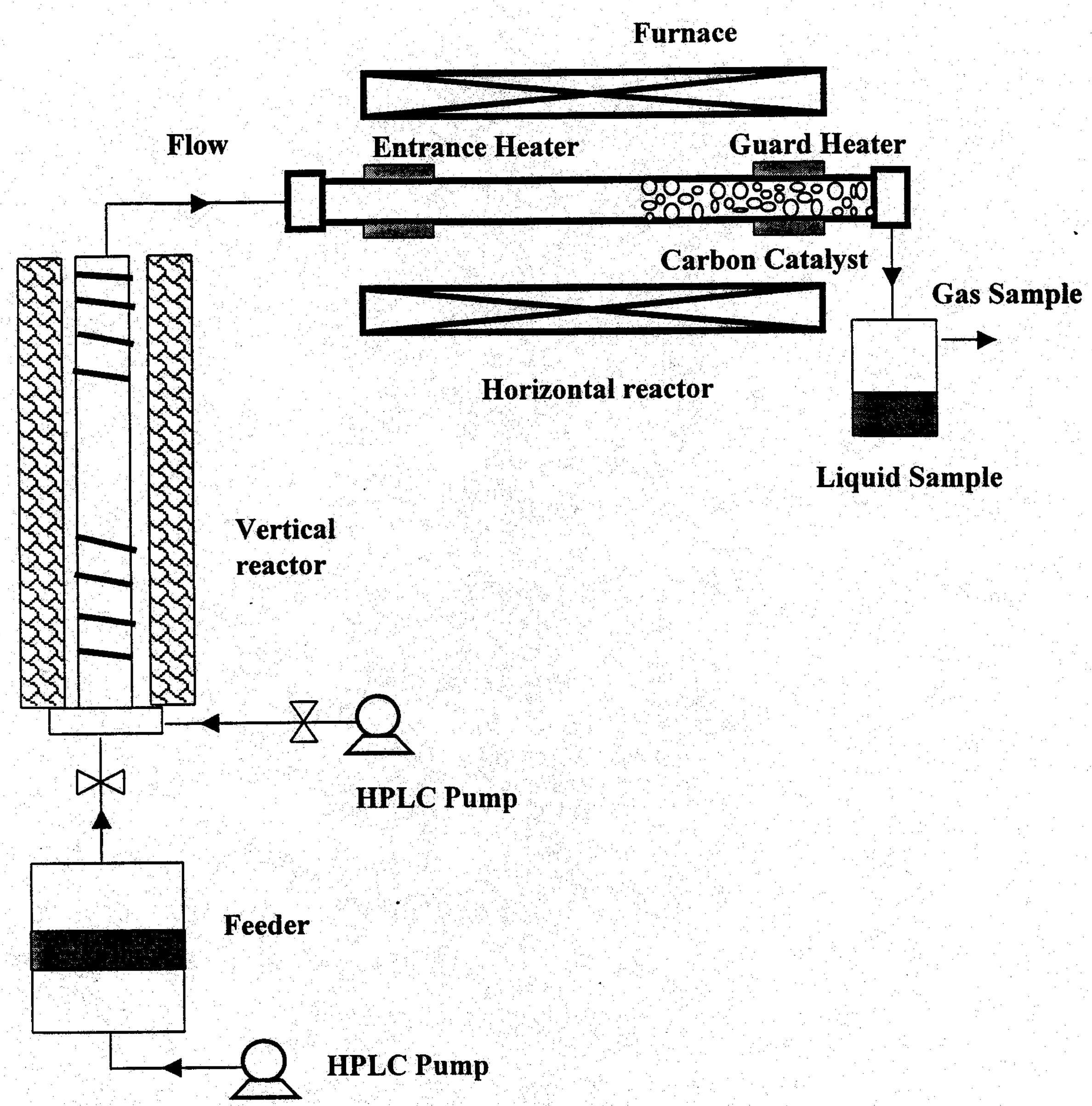

Figure 5. Gasification reactor #5: combined vertical and horizontal reactor (1999)

Gas samples are taken by gas-tight syringes from the gas sample outlet of the separator. Analysis of the gas is conducted using a Hewlett-Packard model 5890 gas chromatograph equipped with flame ionization and thermal conductivity detectors. A 80/100 mesh carbosphere molecular sieve packed column is used, operating at 35 °C for 4.1 min, followed by a 25 °C/min ramp to 350 °C, and a 1.4 min hold at 350 °C. The carrier gas is a mixture of 8% hydrogen in helium. A standard gas mixture obtained from Air Liquide is used for day-to-day calibration. The COD in the liquid effluent is determined by a Hach model 45600 COD reactor.

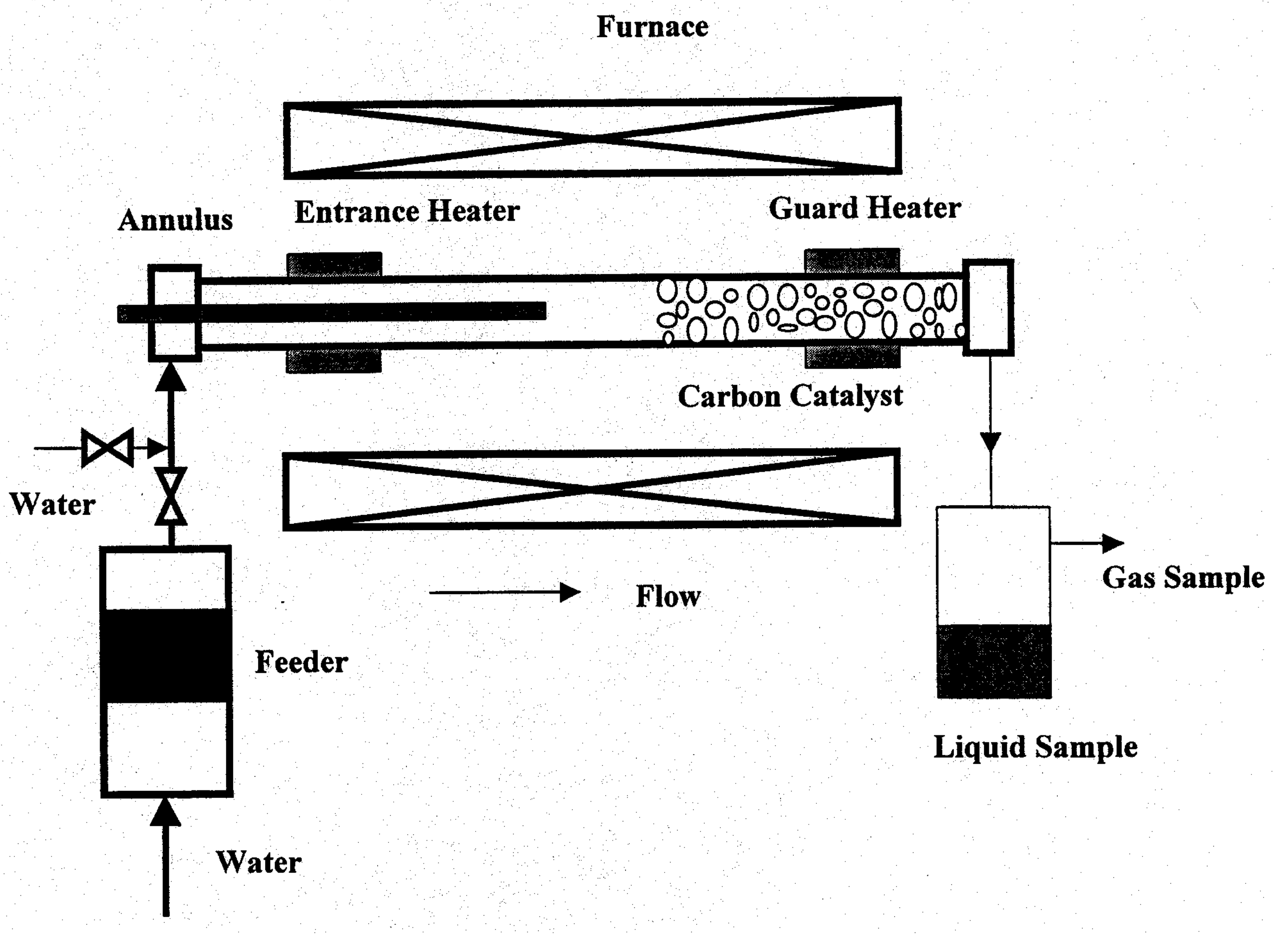

Figure 6. Gasification reactor #6 (1999)

Results

Typical "low temperature" results from the gasification of Poplar wood sawdust in a corn starch gel are displayed in Table 2. We emphasize that the indicated "Reactor Peak Temperature" in Table 2 (and the other Tables in this report) is measured on the reactor's outer wall and is significantly higher than the actual temperature of the reactant flow in the entrance region of the reactor. We believe that the reactant temperature approaches the indicated "Catalyst Bed Temperature" (also measured on the reactor's outer wall) within the packed bed of carbon catalyst. Note that the reproducibility of the gasification results is good. Also note that the carbon efficiency (which is the carbon in the gas divided by the carbon in the feed) is near 100%, indicating complete gasification of the organics in the feed. As evidenced in Table 2, complete gasification is usually accompanied by high gas yields (i.e. > 1 L/g). Corroborating this result, the water effluent of the reactor is clean (see Table 3). Finally, note that the gas composition is dominated by carbon dioxide (46%), hydrogen (27%), and methane (24%).

Table 1. Elemental Analysis of Feedstocks

	Corn Starch[1]	Poplar Wood Sawdust[2]	Sugar Cane Bagasse	Banagrass
Elemental Analysis (wt% Dry Basis)				
C	41.1%	49.4%	48.2%	48.8%
H	6.5%	6.0%	5.7%	5.6%
O	52.4%	45.1%	42.4%	42.6%
N	N/A	0.06%	N/A	N/A
S	N/A	N/A	N/A	N/A
Volatile Matter	N/A	N/A	N/A	N/A
Fixed Carbon	N/A	N/A	N/A	N/A
Ash	N/A	0.16%	N/A	N/A
Moisture Content[3]	12.8%	8.5%	21.9%	7.1%

1. The C, H, and O data were obtained from the Merck Index (5th edition, 1983).
2. The elemental analysis was conducted by Huffman Laboratories, Inc.
3. Moisture content was measured by placing the samples in an oven at 110°C for 8 hours.

Table 4 displays typical "low temperature" results obtained from other feedstocks. The gas yields are somewhat lower than those of the Poplar wood sawdust, which may in part reflect the higher ash content of these feeds and the catalytic effect of the ash on char formation. Nevertheless, these yields are quite high relative to those realized from conventional gasifiers.

Table 2. Gasification of Poplar Wood Sawdust /Corn Starch in Supercritical Water with Coconut Shell Activated Carbon Catalyst

Experiment Date	12/17/97	4/21/98
Feedstocks (Dry Basis)	Sawdust 9.47 wt% + Corn Starch 3.55 wt%	Sawdust 10.64 wt% + Corn Starch 3.88 wt%
Reactor Peak Temp / Catalyst Bed Temp	750°C/ 700°C	739°C/ 710°C
Flow Rate (g/min)	2.0	
Time on Stream (hr)	1.37	1.95
Product	Mole Fraction	
H_2	0.27	0.26
CO	0.02	0.02
CO_2	0.46	0.46
CH_4	0.24	0.23
Total Gas Yield		
(L/g of solid in feed)	1.36	1.15
(g/ g of solid in feed)	1.34	1.21
C efficiency	0.98	0.96
Global mass balance	0.95	1.00

Table 3. COD (Chemical Oxygen Demand)
Measurement of Liquid Effluent from the Reactor

Exp. date	Feedstock	COD in liquid effluent
4/21/98	Poplar sawdust /corn starch	56 mg/L
6/24/98	Onion / corn starch	64 mg/L
8/10/98	Tap water	Mineral concentration 250 mg/L

Effects of Operating Conditions on Gas Composition

Table 5 displays gasification results obtained with increasing flow rates of 10.4 wt% corn starch gel feed. In order to deliver sufficient heat to the reactant at the higher flow rates, the reactor peak temperature was increased from 690 to 805 °C. This increase in temperature influences both the gas yield and the gas composition. The higher temperatures drive the methane steam reforming reaction to increase hydrogen yields at the expense of methane. Because the methane steam reforming reaction creates 5 moles of product gas from 3 moles of reactant, the carbon dioxide mole fraction of the gas product also decreases. Note that the gas yield reaches 1.7 L/g at the highest peak temperature. The gas composition and gas yield at this temperature (805 °C) typifies a "high temperature" gasification result.

Table 6 presents a more extreme "high temperature" gasification result. The gas yield (2 L/g) and gas composition (55% hydrogen, 35% carbon dioxide, and 6% methane) realized in this experiment are extraordinary. Unfortunately, our equipment did not permit an accurate measurement of the peak temperature in this experiment. After the experiment was completed and the reactor was disassembled, we detected a slight bulge in the reactor tube under the entrance heater. This bulge suggests that the entrance temperature was considerably higher than the registered peak temperature.

Table 7 displays the effects of total pressure on the gasification of sugar cane bagasse. The increase in pressure from 28 to 34.5 MPa has no significant effect on the gasification results.

Table 4. Gasification of Agricultural Residues and Wastes in Supercritical Water with Coconut Shell Activated Carbon Catalyst

Experiment date	5/6/98	6/3/98	6/24/98
Feedstock (dry basis)	Sugar cane bagasse 10.70 wt% + Corn starch 4.28 wt%	Banagrass 11.70 wt% + Corn starch 4.60 wt%	Onion 11.10 wt% + Corn starch 4.20 wt%
Pressure (psi)	4000	4000	4000
Flow rate (g/min)	2.0		
Reactor peak temp / Catalyst bed temp	749°C/ 716°C	751°C/ 717°C	750°C/ 716°C
Time on stream (hr)	1.23	0.73	0.96
Product	Mole fraction		
H_2	0.28	0.30	0.28
CO	0.02	0.02	0.02
CO_2	0.44	0.44	0.44
CH_4	0.23	0.24	0.25
Gas yield			
L gas / g solid in feed	1.16	1.02	1.06
g gas / g solid in feed	1.22	1.02	1.02
C efficiency	0.97	0.72	0.80
Global mass balance	1.02	0.93	0.92

Table 5. Gasification of Corn Starch in Supercritical Water with Coconut Shell Activated Carbon Catalyst at 28 MPa (Exp. Date: 2/20/97)

Flow rate (g/min)	1.0	2.0	4.0
Reactor peak temp / Catalyst bed temp	690°C/ 650°C	715°C/ 650°C	805°C/ 650°C
Time on stream (hr)	2.18	4.57	5.70
Product	Mole fraction		
H_2	0.28	0.30	0.28
CO	0.02	0.02	0.02
CO_2	0.44	0.44	0.44
CH_4	0.23	0.24	0.25
Gas yield			
L gas / g solid in feed	1.28	1.38	1.70
g gas / g solid in feed	1.14	1.22	1.34
C efficiency	0.97	1.01	1.0
Global mass balance	1.01	1.01	0.99

Table 6. Gasification of Corn Starch in Supercritical Water at 4000 psi Using Reactor #6 with an Annulus Heater[1]

Feedstock (dry basis)	13.7 wt% Corn starch		
Flow rate	2 g/min		
$T_{max}/T_{catalyst}$	≥745°C/715°C		
Time on stream (hr)	0.45	0.73	1.00
Product	Mole fraction		
H_2	0.55	0.57	0.55
CO	0.03	0.03	0.03
CO_2	0.35	0.34	0.35
CH_4	0.07	0.06	0.06
C_2H_6	0.00	0.00	0.00
Gas yield			
L gas / g of solid in feed	2.05	2.05	2.05
g gas / g of solid in feed	1.56	1.55	1.57
C efficiency	1.07	1.05	1.07
Global mass balance	1.06	1.06	1.06

1. No heat was delivered to the reactor by the annulus heater as it was not turned on.

Table 7. Pressure Effect on the Gasification of Sugar Cane Bagasse / Corn Starch in Supercritical Water with Coconut Shell Activated Carbon Catalyst

Experiment date	5/6/98	5/22/98
Feedstock (dry basis)	Sugar cane bagasse 10.70 wt% + Corn starch 4.28 wt%	Sugar cane bagasse 10.64 wt% + Corn starch 4.25 wt%
Pressure (psi)	4000	5000
Flow rate (g/min)	2.0	
Reactor peak temp / Catalyst bed temp	749°C/ 716°C	748°C/ 711°C
Time on stream (hr)	1.23	1.0
Product	Mole fraction	
H_2	0.28	0.28
CO	0.02	0.02
CO_2	0.44	0.45
CH_4	0.23	0.25
Gas yield		
L gas / g solid in feed	1.16	1.13
g gas / g solid in feed	1.22	1.20
C efficiency	0.97	0.90
Global mass balance	1.02	0.95

We also executed experiments to examine the effects of the gas phase residence and the size of the catalytic packed bed (i.e. the weight hourly space velocity WHSV) on the gas composition and carbon efficiency. Results indicated that these parameters have little affect on the performance of the reactor relative to the effect of temperature. We plan to study the effects of these two parameters more carefully next year.

Wall Effects

Hastelloy C-276 is composed of Ni (52.4 – 60.9 wt%), as well as Mo (15 – 17 wt%), Cr (14.5 – 16.5 wt%), Co (2.5 wt%) and other metals (Fe, and W) which can exert a catalytic influence on the gasification chemistry. One approach to studying the catalytic role of the reactor's wall is to run a sequence of feedstocks, such as glycerol in water; followed by glucose in water; followed by glycerol in water. Glycerol is easily gasified, and the gas composition is affected by the condition of the reactor's wall. This approach is illustrated in Table 8, which shows that the gasification of 22.5 wt% glucose for 3.68 hr does not alter the gas composition derived from glycerol. On the other hand, the gasification of Avicel cellulose (see Table 9) and lignin (see Table 10) reduced the role of the steam reforming reaction as evidenced by the decrease in hydrogen and the increase in methane in the gas composition from glycerol. These results suggest that the wall can play a significant role in catalyzing the gasification chemistry.

Table 8. Reactor Wall Effect Shown in the Gasification of Glycerol and Glucose Feedstocks in Supercritical Water at 4000 psi Using Reactor #2 (Feedstock Sequence: Glycerol → Glucose → Glycerol)

Feedstocks	18.71 wt% glycerol	22.52 wt% glucose	18.71 wt% glycerol
T_{peak} / $T_{catalyst}$	746 °C/ 710 °C	745 °C/ 707 °C	744 °C/ 707 °C
Time on stream (hr)	1.79	3.68	5.01
Product	Mole fraction		
H_2	0.52	0.46	0.52
CO	0.04	0.04	0.04
CO_2	0.32	0.36	0.31
CH_4	0.12	0.13	0.12
Gas yield			
L gas/g of solids in feed	1.58	1.42	1.63
g gas/g of solids in feed	1.17	1.20	1.16
C efficiency	0.96	0.97	0.96
Global mass balance	0.94	1.03	0.98

Table 9. Reactor Wall Effect Shown in the Gasification of Glycerol and Avicel/ Corn Starch Feedstocks in Supercritical Water at 4000 psi Using Reactor #2 (Feedstock Sequence: Glycerol → Avicel/Corn Starch → Glycerol)

Feedstocks	18.71 wt% glycerol	11.43 wt% Avicel/ 4.57 wt% cornstarch	18.71 wt% glycerol
T_{peak} / $T_{catalyst}$	748 °C/ 718 °C	756 °C/ 715 °C	756 °C/ 715 °C
Time on stream (hr)	1.62	2.70	4.24
Product	Mole fraction		
H_2	0.51	0.30	0.45
CO	0.04	0.02	0.03
CO_2	0.31	0.45	0.32
CH_4	0.13	0.21	0.18
Gas yield			
L gas/g of solids in feed	1.47	1.09	1.38
g gas/g of solids in feed	1.19	1.19	1.19
C efficiency	1.01	0.95	1.07
Global mass balance	1.04	1.02	1.00

Effects of Operating Conditions on Plugging

In nearly all of the experiments with feedstock loadings of 15 wt% discussed above, plugging occurred after one or two hours on-stream (see Table 11, and note that 18.5 wt% glycerol did not plug). To gain insight into this problem, we ask the question: "How much carbon is formed from a typical feedstock in thermochemical equilibrium at 200 °C and 4000 psi?" Figure 7 displays Stanjan equilibrium calculations that predict the solid carbon yield for different feedstock loadings at 200 °C and 4000 psi. No solid carbon is formed for feedstock loadings below 30 wt% organics. Note that higher temperatures decrease carbon formation, and the rates of the reactions are negligible below 200 °C. In light of these calculations, it is mildly surprising that coke (carbon) forms within the reactor. We presume that the small amounts of carbon that cause plugging are formed because the feed is not homogeneous, and local loadings of organics may exceed 30 wt%.

Table 10. Reactor Wall Effect Shown in the Gasification of Glycerol and Lignin /Corn Starch Feedstocks in Supercritical Water at 4000 psi Using Reactor #2 (Feedstock Sequence: Glycerol → Lignin/Corn Starch → Glycerol)

Feedstocks	18.71 wt% glycerol	10.76 wt% lignin/ 4.25 wt% cornstarch[1]	18.71 wt% glycerol
T_{peak} / $T_{catalyst}$	758 °C/ 710 °C	757 °C/ 710 °C	758 °C/ 710 °C
Time on stream (hr)	1.17	1.77	3.02
Product	Mole fraction		
H_2	0.49	0.48	0.39
CO	0.03	0.02	0.03
CO_2	0.35	0.47	0.36
CH_4	0.13	0.02	0.21
Gas yield			
L gas/g of solids in feed	1.45	0.39	1.30
g gas/g of solids in feed	1.21	0.34	1.10
C efficiency	1.00	0.16	0.99
Global mass balance	1.00	N/A	0.98

1. Using lignin/ cornstarch feedstock, the reactor plugged in 10 minutes. The liquid sample was unable to collect, as a result, mass balance was available.

Reactors #3, #4, and #5 were assembled to study the plugging problem. We were amazed when Reactor #3 plugged after one hour at 220 °C and 1000 psi (see Table 12). No carbon (coke) was formed in this situation. The plug occurred because the gel broke down and water separated from the sawdust/starch mixture. Somehow, the moist sawdust/starch solid was able to adhere to the wall of the reactor and stop flow. This phenomenon was reproducible. It illustrates the importance of operating the reactor in either a horizontal or up-flow mode to avoid separation of water from the organics.

Table 11. Time to Plug with Different Feedstocks Using Reactors #1 and #2 (1997- 1998)

Feedstock	Time to plug	Experiment date
18.5 wt% Glycerol	no plug	5/28/98
10.4 wt% Corn starch	no plug	2/20/97
4.9 wt% Poplar sawdust + 5.5 wt% Corn starch	4 hr	4/23/97
11.5 wt% Poplar sawdust + 4.2 wt% Corn starch	1 - 2.5 hr	7/3/97- 9/15/97
10.7 wt% Poplar sawdust + 3.9 wt% Corn starch + 9.81 wt% Glycerol	2.6 hr	2/26/98
10.5 wt% Poplar sawdust + 4.0 wt% Potato starch	2 hr	12/29/97
11.7 wt% Banagrass + 4.6 wt% Corn starch	1 hr	6/3/98
10.5 wt% Sugarcane bagasse + 4.2 wt% Corn starch	1 hr	8/4/98
11.1 wt% Onion + 4.2 wt% Corn starch	1 hr	6/24/98
21.6 wt% Glucose	1 hr	9/8/98

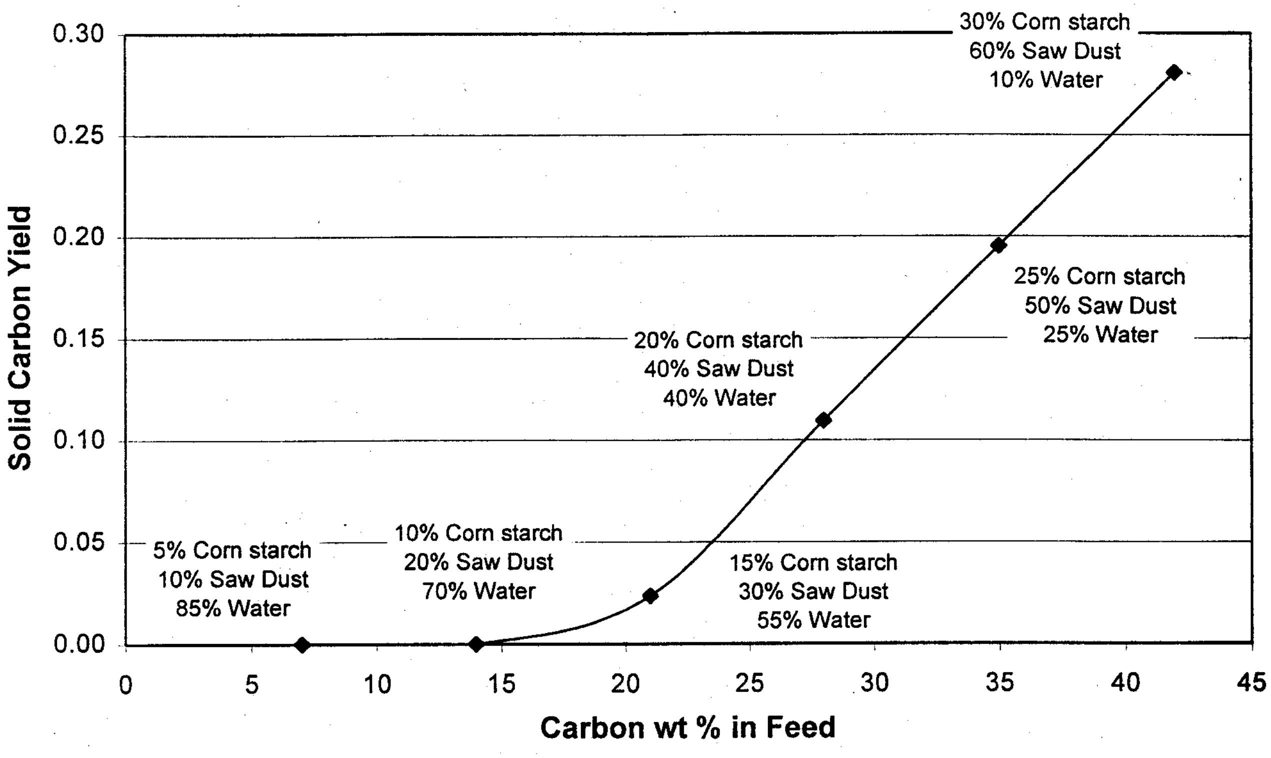

Figure 7. Stanjan Equilibrium Calculations at 200°C and 4000 psi

Reactors #4 and #5 were operated in an up-flow mode at both sub-critical and supercritical pressures. We remark that even glycerol plugged Reactor #5 when the vertical section was operated as a boiler at sub-critical pressures (see Table 12). Other experiments confirmed the observation that plugging was not a result of the high-pressure. At sub-critical pressures when the vertical section served as a boiler, heavy organics with low vapor pressures accumulated in the liquid phase and eventually formed tar and char that plugged the reactor. Because we found no advantages associated with the vertical reactor configuration or sub-critical pressures, we returned to our original reactor configuration (Reactor #6) and executed a series of experiments to detail the onset of plugging. As shown in Table 13, plugging occurs with corn starch when the loading exceeds about 11 wt%. Plugging occurs with potato wastes at a loading of about 8.5 wt%.

Table 12. Time to plug with different reactor configurations (1997- 1999)

Feedstock	Reactor 1	Reactor 2	Reactor 3	Reactor 4	Reactor 5	Reactor 6
18.5 wt% Glycerol	N/A	no plug	N/A	N/A	3.5 hr	N/A
21.6 wt% Glucose	N/A	1 hr	N/A	N/A	1 hr	N/A
8.9 wt% Corn starch	no plug	N/A	N/A	N/A	2 hr	no plug
10.1 wt% Poplar sawdust + 3.9 wt% Corn starch	1.5 hr	1.5 hr	1 hr at 220°C 1000 psi	1.5 hr	N/A	N/A

Note:
Reactor 1: Annulus heater at the entrance, 1997;
Reactor 2: Annulus heater at the exit, 1998;
Reactor 3: Vertical reactor with downward flow, 1999;
Reactor 4: Vertical reactor with upward flow, 1999;
Reactor 5: Combined vertical and horizontal reactor with an annulus heater at the exit, 1999;
Reactor 6: Annulus at the entrance, 1999.

Table 13. Time to Plug Using Reactor #6 (1999)

Feedstock	Concentration	Flow rate (g/min)	Time to plug	Experiment date
Corn starch	8.9 wt%	1,2,4	4 hr run, no plug	3/8/99
Corn starch[1]	10.4 wt%	1,2,4	6 hr run, no plug	2/10/97
Corn starch	13.7 wt%	2	1.5 hr, plug	4/5/99
Potato starch	11.9 wt%	2	1.5 hr, plug	3/30/99
Potato waste	8.48 wt%	2,4	3.5 hr, plug	3/10/99
Potato waste	13.4 wt%	2	1.3 hr, plug	3/16/99

Because it is not cost-effective to heat and cool large quantities of water, feedstock loadings should be as high as possible. Very preliminary economic projections by Air Products Corporation indicate that loadings of 15 wt% or more may be required. In light of this and the results above, we believe it is essential to design and operate a reactor that can be cleaned of carbon (coke) buildup and restarted. This goal is a focus of our current work.

Gasification of Potato Wastes

Tables 14 and 15 compare results from the gasification of commercial potato waste, potato starch, and corn starch using reactor #6 with an annulus heater, and with a short thermocouple well annulus (not an annulus heater). As expected, slightly higher gas yields are obtained with the annulus heater, since it is probable that the reactant reached higher temperatures with it. Nevertheless, the gas compositions and gas yields are nearly identical, and the differences may simply reflect the non-homogeneous nature of the potato waste feed. We remark that the potato waste contains protein and ash. The disposition of nitrogen (from the protein) as well as the ash needs to be quantified in our future work.

Table 14. Gasification of Corn Starch, Potato Starch, and Potato Waste in Supercritical Water at 4000 psi Using Reactor #6 with an Annulus Heater

Experiment Date	3/8/99	3/30/99	3/16/99
Feedstocks	8.9 wt% Corn starch	11.9 wt% Potato starch	13.4 wt% Potato waste
T_{max} / $T_{catalyst}$	711°C/708°C	714 °C/ 715 °C	719 °C/ 724 °C
Time on stream (hr)	3.25	0.85	0.58
Product	Mole fraction		
H_2	0.29	0.31	0.32
CO	0.02	0.01	0.01
CO_2	0.49	0.47	0.44
CH_4	0.18	0.21	0.21
C_2H_6	0.02	0.01	0.01
Gas yield			
L gas/g organics in feed	1.08	1.12	1.07
g gas/g organics in feed	1.17	1.18	1.03
C efficiency	0.93	0.93	0.84
Global mass balance	1.01	1.01	0.97

Table 15. Gasification of Corn Starch, Potato Starch, and Potato Waste in Supercritical Water at 4000 psi Using Reactor #6 with an Annulus Thermocouple Well[1]

Experiment Date	4/13/99	4/15/99	4/20/99
Feedstocks	13.1 wt% Corn starch	12.8 wt% Potato starch	13.74 wt% Potato waste
T_{max} / $T_{catalyst}$	713 °C/ 717 °C	700 °C/ 717 °C	705 °C/ 718 °C
Time on stream (hr)	1.35	0.98	1.15
Product	Mole fraction		
H_2	0.29	0.31	0.33
CO	0.03	0.01	0.01
CO_2	0.47	0.49	0.45
CH_4	0.18	0.17	0.19
C_2H_6	0.03	0.02	0.03
Gas yield			
L gas/g organics in feed	1.04	0.91	1.00
g gas/g organics in feed	1.13	0.94	0.99
C efficiency	0.91	0.73	0.78
Global mass balance	1.02	0.97	0.98

[1] Annulus thermocouple well: 1/8" OD x 5" in the heated section of the reactor.

Conclusions

1. A semi-solid gel can be made from 4 wt % (or less) starch in water. Wood sawdust and other particulate biomass can be mixed into this gel and suspended therein for a period of days. This suspension is easily and reliably delivered to a supercritical flow reactor by a cement pump.
2. Above the critical pressure of water, wood sawdust and other biomass can be steam reformed over a carbon catalyst to a gas composed almost entirely of hydrogen, carbon dioxide, methane, and a trace of carbon monoxide. There are effectively no tar or char byproducts. The liquid water effluent from the reactor has a low COD value, a neutral pH, and no color.
3. The gas composition and gas yield are strongly affected by the reaction temperature. Other parameters, such as pressure, gas phase residence time, and WHSV exert a lesser influence on the reactor's performance.

4. The reactor's wall influences the gas composition. Some reactants appear to poison the wall and reduce its favorable influence on gasification; whereas others do not.
5. Thermochemical equilibrium calculations indicate that carbon plugs (coking) should not form in the reactor. Nevertheless, coking does occur, and is strongly influenced by the configuration of the reactor, as well as the organic loading of the feed. Future work will emphasize practical methods of removing coke from the reactor.

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