

Carbon-Catalyzed Gasification of Organic Feedstocks in Supercritical Water[†]

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Spruce wood charcoal, macadamia shell charcoal, coal activated carbon, and coconut shell activated carbon catalyze the gasification of organic compounds in supercritical water. Feedstocks studied in this paper include glycerol, glucose, cellobiose, whole biomass feedstocks (depithed bagasse liquid extract and sewage sludge), and representative Department of Defense (DoD) wastes (methanol, methyl ethyl ketone, ethylene glycol, acetic acid, and phenol). The effects of temperature, pressure, reactant concentration, weight hourly space velocity, and the type of catalyst on the gasification of glucose are reported. Complete conversion of glucose (22% by weight in water) to a hydrogen-rich synthesis gas was realized at a weight hourly space velocity (WHSV) of 22.2 h⁻¹ in supercritical water at 600 °C, 34.5 MPa. Complete conversions of the whole biomass feeds were also achieved at the same temperature and pressure. The destruction efficiencies for the representative DoD wastes were also high. Deactivation of the carbon catalyst was observed after 4 h of operation without swirl in the entrance region of the reactor, but the carbon gasification efficiency remained near 100% for more than 6 h when a swirl generator was employed in the entrance of the reactor.

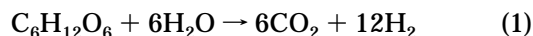
Introduction

Wet biomass (water hyacinth, cattails, banana tree stem, kelp, green algae, etc.) grows rapidly and abundantly around the world. For example, water hyacinth (*Eichhornia crassipes*) produces over 150 tons/ha/yr of dry organic matter, and cattails (*Typha* sp.) can deliver 97 tons/ha over a 7 month growing season (Wolverton and McDonald, 1980). Nevertheless, wet biomass is not regarded as a promising feedstock for conventional thermochemical gasification processes because the cost of drying the material is too high. This problem can be circumvented by employing water as the reaction medium.

When biomass is heated in liquid water, solvolysis of hemicellulose and lignin macromolecules begins to occur at temperatures above 190 °C (Bobleter and Binder, 1980; Bouchard et al., 1990, 1991; Mok and Antal, 1992; Allen et al., 1996). After only 2 min at 220 °C, all of the hemicellulose and much of the lignin dissolves in the water. Solvolysis and pyrolysis of the remaining lignocellulosic solid occurs at somewhat higher temperatures (Bobleter and Concinn, 1979). These hydrothermolysis reactions evolve an extraordinary variety of isomerization, dehydration, fragmentation, and condensation products, many of which participate in subsequent reaction chemistries (Antal et al., 1990a,b; Antal et al., 1991; Holgate et al., 1995). Exploiting this unusual ability of water to attack biomass materials, Modell (1985) found that wood (maple sawdust) can be completely solubilized in supercritical water. But only limited gasification was observed at temperatures below 380 °C: less than 40% of the feedstock carbon was converted to gas. Moreover, catalysts (including Ni, Co/Mo on alumina, and Pt on alumina) had little effect on the reaction chemistry. Related experiments (Amin et al., 1975) involving glucose as a reactant in supercritical water evidenced conversions near 100%; but again, the gas yield was very low. Less than 20% of the carbon in

the glucose was converted to gas; while the rest remained associated with organic compounds dissolved in the liquid phase.

More recently, Elliott and his colleagues (Elliott et al., 1993; 1994a,b; see also Minowa et al., 1995) employed nickel and ruthenium catalysts to gasify the organic matter (ca. 2 wt %) in wastewater at 350 °C and 20 MPa. For example, 85% of the carbon contained in a 5% sucrose in water feed was converted to methane and carbon dioxide in their system (Elliott et al., 1994b). We view Elliott's work to hold promise for the destruction of organic waste streams, but much higher concentrations of biomass in water must be gasified if the renewable feedstock is to be an economical source of fuel. To achieve high carbon gasification efficiencies (ca. 99%) with concentrated feedstocks (ca. 20 wt % organics in water), we have explored gasification in supercritical water at higher temperatures than those studied by Elliott and his co-workers. In supercritical water, pyrolysis, hydrolysis, steam reforming, water-gas shift, methanation, and other reactions all play a role in the gasification chemistry (Aznar et al., 1993). The foci of our interest (Antal, 1983; Antal et al., 1993; Yu et al., 1993) are the steam reforming reactions which convert biomass to hydrogen and carbon dioxide. Using glucose as a model compound for complex biomass feeds, the steam reforming stoichiometry is given by



Prior work in this laboratory (Manarungson, 1991; Antal et al., 1991; Yu, 1993; Yu et al., 1993) showed that low concentrations of glucose and various wet biomass species (water hyacinth, algae) can be completely gasified in supercritical water at 600 °C and 34.5 MPa after a 30 s residence time. But higher concentrations of glucose evidenced incomplete gasification. In these studies both the extent of conversion to gas and the gas composition were observed to depend upon the chemical composition and condition of the reactor's wall (Yu et al., 1993). These results suggested that heterogeneous catalysis might be employed to increase the extent of gasification of concentrated feeds. Conse-

[†] We dedicate this paper to the memory of Dr. Melvin G. Bowman, Associate Division Leader of CMB Division, Los Alamos National Laboratory.

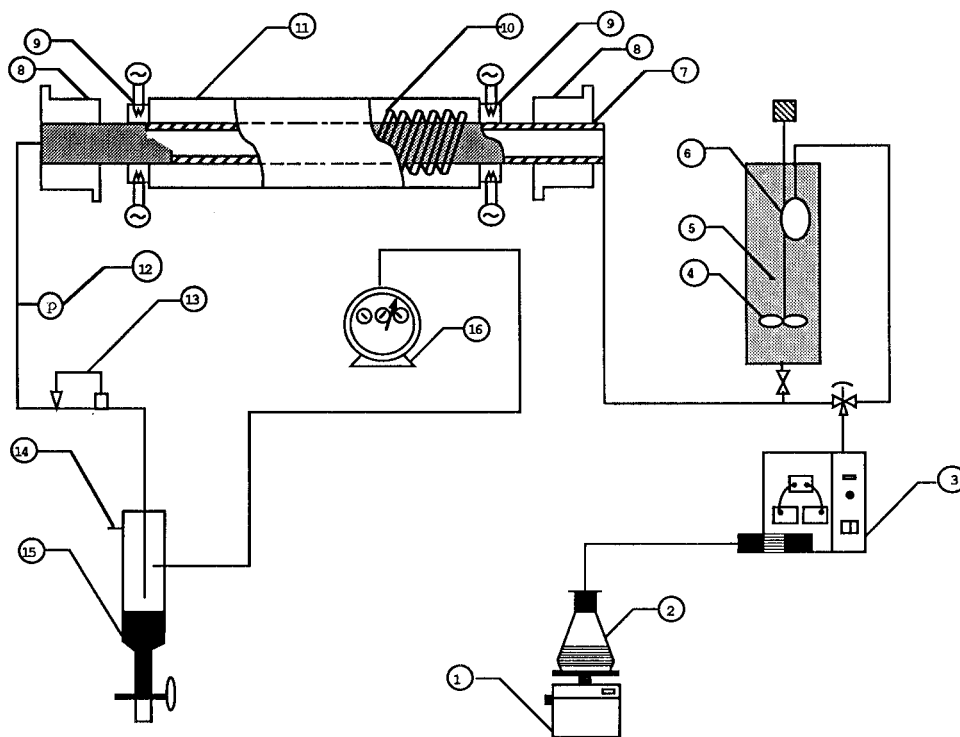


Figure 1. Supercritical flow reactor schematic: (1) balance; (2) flask with reactant; (3) HPLC pump; (4) feeding vessel with agitator; (5) wet-biomass slurry; (6) balloon; (7) Inconel 625 tube; (8) cooling jacket; (9) heater; (10) furnace; (11) furnace shell; (12) pressure transducer; (13) back-pressure regulator; (14) gas sample outlet; (15) liquid-gas separator; (16) wet test meter.

quently, reactors were fabricated which could accommodate packed beds of catalysts and research was initiated on heterogeneous catalysis of the steam reforming reactions of biomass materials in supercritical water. In the field of biomass gasification, downdraft gasifiers (Reed, 1981; Chern and Walawender, 1989) are known for their ability to produce a tar-free gas product. This desirable result is achieved by passing tar vapors through a red-hot bed of charcoal. Consequently, we anticipated that carbon could play the role of an active gasification catalyst in supercritical water. This paper records the results of our investigation of the activity of carbon as a gasification catalyst in supercritical water.

Apparatus and Experimental Procedures

A schematic of the apparatus is shown in Figure 1. The reactor is made of Inconel 625 tubing with 9.53 mm o.d. and 4.75 mm i.d. The temperature of the reactant flow is abruptly raised to the desired value by an entry heater/cooling water jacket combination. The reactor is maintained at isothermal conditions by a furnace and a downstream heater. Product flow is rapidly quenched by a cooling water jacket at the exit of the reactor. A unique feature of this reactor is its ability to accommodate annuli of different diameters and lengths. These annuli enable wide variations in residence times within the reactor. For some experiments, two stainless steel wires (1 mm o.d.) are wrapped around a 1.6 mm o.d., 38 cm long, stainless steel, tubular annulus to create swirl flow in the entrance region of the reactor, thus improving heat transfer to the reactant. Different amounts of solid catalyst are packed within the reactor in order to vary the WHSV (weight hourly space velocity). Usually, about two-thirds of the heated zone of the reactor is packed with carbon catalyst. The remainder of the downstream heated zone and the downstream cold section of the reactor is filled with

sintered aluminum oxide (Aldrich Chemical Co.). Blank experiments with only the aluminum oxide present in the reactor proved it to be inert within the context of this work. The axial temperature profile along the reactor's functional length of approximately 0.41 m is measured by 15 fixed, type K thermocouples mounted on the reactor's outer wall. Furthermore, a movable type K thermocouple inside the annulus provides a temperature profile inside the reactor. Pressure in the reactor system is measured by an Omega PX302 pressure transducer. A Grove Mity-Mite model 91 back-pressure regulator reduces the pressure of the cold products exiting the reactor from 34.5 MPa to ambient. After leaving the back-pressure regulator, the reactor effluent passes through an in-house fabricated glass gas-liquid separator. The gas flow rate is measured using a wet test meter.

A diaphragm-type pump was employed to feed sewage sludge (from the Japan National Institute for Resources and Environment) into the reactor. The sludge was first ground with a Speed blender (Hamilton Beach, Inc.) and then with a Brinkmann homogenizer. The heterogeneous sewage sludge slurry filled a 500 mL pressure vessel equipped with a Parr-A1120HC magnetic drive. A 10 g weather measure balloon was placed in the vessel together with the slurry. Water was pumped into the balloon, and the balloon's expansion forced the sewage sludge slurry into the reactor. Other feeds, including a depithed bagasse liquid extract, were pumped directly into the reactor using a Waters 510 HPLC pump.

Gas samples were taken by a gas-tight syringe from the gas sample outlet of the separator, and liquid samples were collected at the bottom of the separator. For the representative DoD wastes, which have lower gas generation rates, a ten-port sampling system was employed to collect the liquid and gaseous samples. Interested readers should refer to an earlier publication (Xu, 1992) for details.

Table 1. Effect of Various Carbon Catalysts on 1.2 M Glucose Gasification in Supercritical Water at 600 °C, 34.5 MPa

catalyst type	coal activated carbon	coconut shell activated carbon	macadamia shell charcoal	spruce wood charcoal
WHSV, h ⁻¹	19.9	22.2	25.7	12.6
exp date	4/11/94	4/18/94	4/22/94	7/21/95
product	gas yield (mol of gas/mol of feed)			
H ₂	1.48	2.24	2.71	3.86
CO	2.34	0.79	0.54	0.34
CO ₂	1.45	3.09	1.09	3.72
CH ₄	1.04	1.23	3.18	1.36
C ₂ H ₄	0.002	0.0	0.002	0.0
C ₂ H ₆	0.39	0.35	0.27	0.23
C ₃ H ₆	0.002	0.0	0.003	0.0
C ₃ H ₈	0.13	0.13	0.11	0.01
carbon gasification efficiency, %	97	103	95	99
unconverted TOC, %	N/A	N/A	N/A	0.9
pH of liquid effluent	4	5	4	4

All feedstocks were prepared using degassed, deionized water. Glucose, glycerol, cellobiose, methyl ethyl ketone, and ethylene glycol from Sigma Chemical Co.; acetic acid and methanol from Fisher Scientific; and phenol and benzene from J. T. Baker Chemical Co. were used either as reactants or as calibration reagents. No impurities were detected in these compounds by HPLC analysis. Coconut shell activated carbon and coal activated carbon from Barnebey & Sutcliffe Corp. and high yield spruce wood charcoal and high yield macadamia shell charcoal produced in-house were used as catalysts.

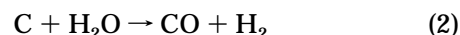
Analysis of the gaseous products was accomplished by use of a Hewlett-Packard model 5890 gas chromatograph (GC) equipped with flame ionization and thermal conductivity detectors. A 800/100 mesh carbosphere molecular sieve packed column was used, operating at 35 °C for 4.2 min, followed by a 15 °C/min ramp to 227 °C, a 70 °C/min ramp to 350 °C, and a 5.3 min hold at 350 °C. A mixture of 8% hydrogen in helium from AIRCO was used as a carrier gas. A standard gas mixture used for calibration was also obtained from AIRCO. Qualitative analysis of the liquid effluents was conducted using a Hewlett-Packard model 5790A GC coupled to a Hewlett-Packard model 5970A mass-selective detector. Quantification of the liquid products (except phenol) was accomplished using a high-performance liquid chromatograph (Waters 510 HPLC pump, Perkin-Elmer LC 600 autosampler, Waters 410 differential refractometer, Millipore Millennium software). A BIO-RAD HPX-87H column and a BIO-RAD cation H guard column were employed with degassed 0.01 M trifluoroacetic acid as the solvent at a flow rate of 0.6 mL/min. The liquid effluent of the phenol experiment was analyzed by GC with a J&W DB-1 capillary column, operating at 40 °C for 5 min, followed by a 12 °C/min ramp to 150 °C, and a 1.3 min hold at 150 °C. TOC analysis was performed using a Shimadzu model TOC-5000 total organic carbon analyzer.

Results and Discussion

Catalytic Properties of Various Carbon Substrates. Table 1 displays the catalytic effects of four different carbon substrates on the gasification of 1.2 M glucose. In all cases the carbon gasification efficiency was high (carbon gasification efficiency = total moles of carbon in the gaseous products/moles of carbon in the feed), the water effluent was clear, and its pH was 4 or higher. The TOC analysis (unconverted TOC = grams of TOC in the liquid effluent/grams of TOC in the feed) of the liquid product from the spruce wood charcoal

experiment confirmed the nearly complete gasification of the glucose feed. TOC values for the other feeds are missing because a TOC instrument was not available (N/A) to us in 1994 when these experiments were conducted. Table 1 offers several important insights into the role of these carbons as gasification catalysts. Since the coconut shell activated carbon has an iodine number of 1050, whereas the spruce wood charcoal has an iodine number below 50, it is evident that the surface area of the carbon does not strongly influence its catalytic activity. Likewise, the diversity of carbons represented suggests an equal diversity in mineral matter content, leading to the tentative conclusion that carbon is the active gasification catalyst, and not one of the inorganic species present in the ash. Currently, this assumption is being examined in ongoing work. Gas yields (defined as moles of gas/moles of feed) associated with the different carbons are similar, except that the coal activated carbon does not appear to catalyze the water-gas shift reaction; consequently, the yield of CO is higher (and the yields of H₂ and CO₂ lower) than those obtained with the other carbons. Also, the yield of methane associated with the macadamia shell charcoal is inexplicably high. All these results were obtained with weight hourly space velocities (WHSV) in excess of 10 h⁻¹ (WHSV = $C_0 V/W$, where C_0 is the reactant concentration at NTP [g/cm³], V is the volumetric flow rate of the feed at NTP [cm³/h], and W is the weight of the catalyst [g]). Because the coconut shell activated carbon is commercially available, and bulk samples of the material are homogeneous, reproducible, and well characterized, we decided to employ it in our subsequent work. It is noteworthy that other, less expensive carbons are as catalytically active as the coconut shell activated carbon.

The skeptical reader may wonder what contribution the water-gas reaction



makes to the gaseous product slate. To determine the effects of this reaction, water (alone) was passed through a bed of coconut shell activated carbon at 600 °C and 34.5 MPa. The measured gas generation rate under these conditions was 1.0×10^{-4} mol/min with 3.6 g of carbon in the bed. Gasification of 1.2 M glucose at 4 mL/min produces 3.6×10^{-2} mol/min (with a carbon gasification efficiency of 100%), and gasification of 0.235 M cellobiose (see below) results in a gas generation rate of 4.5×10^{-3} mol/min under the same conditions. Thus, even with the low concentration cellobiose feed, the contribution of reaction 2 to the gas yield is small (<3%).

Table 2. Gasification of 1.2 M Glucose in Supercritical Water at 600 °C, 34.5 MPa with and without Coconut Shell Activated Carbon Catalyst

amt of catalyst, g	0.60	none
WHSV = 22.2 h ⁻¹		res time = 34 s
exp date	4/18/94	12/4/92
product	gas yield (mol of gas/mol of feed)	
H ₂	2.24	0.56
CO	0.79	3.18
CO ₂	3.09	0.29
CH ₄	1.23	0.84
C ₂ H ₄	0.00	0.03
C ₂ H ₆	0.35	0.20
C ₃ H ₆	0.00	0.00
C ₃ H ₈	0.13	0.00
carbon gasification efficiency, %	103	80

Table 3. Effect of Temperature on 1.0 M Glucose Gasification in Supercritical Water with Coconut Shell Activated Carbon Catalyst at 34.5 MPa (WHSV = 13.5 h⁻¹)

temp, °C	600	550	500
exp date	3/10/94	3/10/94	3/10/94
product	gas yield (mol of gas/mol of feed)		
H ₂	1.97	0.62	0.46
CO	2.57	1.67	1.57
CO ₂	1.54	0.73	0.85
CH ₄	0.90	0.37	0.25
C ₂ H ₄	0.008	0.01	0.016
C ₂ H ₆	0.25	0.10	0.07
C ₃ H ₆	0.009	0.03	0.04
C ₃ H ₈	0.11	0.05	0.036
carbon gasification efficiency, %	98	54	51
tar yield, %	0.1	0.9	1.3

Some of the other feedstocks studied in this work involved even lower concentrations of reactant than the cellobiose experiment. In these experiments, the water-gas reaction may have contributed significantly to the observed gasification rate (see Tables 7 and 9 below).

Catalyst Performance with Glucose. Results displayed in Table 2 demonstrate the need for heterogeneous catalysis if complete gasification of a concentrated organic feed is desired. In accord with our earlier work (Yu et al., 1993), a carbon gasification efficiency of only 80% is realized without catalyst. In Table 2, the residence time is given by the volume of the reactor at the chosen reaction temperature divided by the volumetric flow rate of water at the reaction temperature and pressure. Note that the carbon catalyst dramatically increased the carbon gasification efficiency while reducing the CO content of the gaseous products, evidently by enhancing the rates of both the water-gas shift reaction and the methanation reactions.

The effect of temperature on the gasification of glucose is shown in Table 3. Complete carbon conversion was achieved at 600 °C, but as the reaction temperature fell below 580 °C, the color of the liquid effluent from the reactor became yellow and a thin layer of a dark brown, oil-like tar was observed on its surface. Small (<10 mL) samples of the liquid product stream from the reactor were dried in beakers in an oven at 100 °C and the weight gain due to the tar residue was measured. At 600 °C virtually no tar was detected, but at the lower temperatures a dark tar deposit remained on the bottoms of the beakers. In Table 3 the tar yield is defined as grams of tar in the liquid effluent/grams of organic feed. Note that this tar yield is a measure of nonvolatile organic species. Volatile organic species (sometimes also called "tars") are lost during the drying

Table 4. Effect of Pressure on 1.2 M Glucose Gasification in Supercritical Water at 600 °C with Coconut Shell Activated Carbon Catalyst

pressure, MPa	34.5	25.5
WHSV, h ⁻¹	16	16.1
exp date	3/16/94	7/18/95
product	gas yield (mol of gas/mol of feed)	
H ₂	2.15	1.74
CO	2.32	2.84
CO ₂	1.84	1.34
CH ₄	1.01	0.90
C ₂ H ₄	0.0	0.004
C ₂ H ₆	0.23	0.25
C ₃ H ₆	0.0	0.0
C ₃ H ₈	0.10	0.12
carbon gasification efficiency, %	99	99
unconverted TOC, %	3.8	5.3

procedure; consequently the mass balances of the low-temperature experiments are low. Tables 1, 2, and 4–10 do not record the nonvolatile tar yield because it was negligible under the conditions of interest. The drop in gasification efficiency and the increase in tar yield recorded in Table 3 clearly indicate that a reaction temperature of 600 °C or higher is needed to achieve complete gasification of glucose.

Except for differing WHSV, the experiments dated 3/10/94 (Table 3) and 4/18/94 (Table 2) involved similar conditions, and similar carbon gasification efficiencies were observed. Nevertheless, the CO, H₂, and CO₂ yields associated with these two experiments are dramatically different. This lack of reproducibility suggests that the water-gas shift reaction is influenced by experimental conditions in our packed bed reactor that are not well understood at the present time. In related work Tester and his co-workers (Helling and Tester, 1987; Holgate et al., 1992) reported extensive studies of the water-gas shift reaction in supercritical water as part of their research on CO oxidation kinetics. They emphasized the importance of the following two global reaction pathways in the conversion of CO to CO₂:



Their kinetics measurements revealed the direct oxidation reaction to be almost 3 orders of magnitude faster than the shift reaction, which was observed to be slow at temperatures of interest in this paper. Nevertheless, in their recent study of glucose hydrolysis and combustion in supercritical water, Holgate et al. (1995) observed a "fast water-gas-shift-type pathway" at temperatures of 575 °C and above, which was not consistent with their earlier findings. In this paper (see below) we also offer evidence for the sporadic appearance of a fast water-gas shift pathway, whose mechanism remains elusive. We are now focusing our research on this phenomenon and hope to offer insights into it in the near future.

Table 4 reveals that pressure has no measurable effect on the carbon gasification efficiency of 1.2 M glucose but does have some effect on the unconverted TOC value. Also, higher pressure seems to favor the water-gas shift reaction. Consequently, we emphasized operating conditions at 34.5 MPa in this work, which is near the upper limit of the HPLC pump used to feed our reactor.

Table 5. Effect of WHSV on 1.2 M Glucose Gasification in Supercritical Water at 600 °C, 34.5 MPa with Coconut Shell Activated Carbon Catalyst

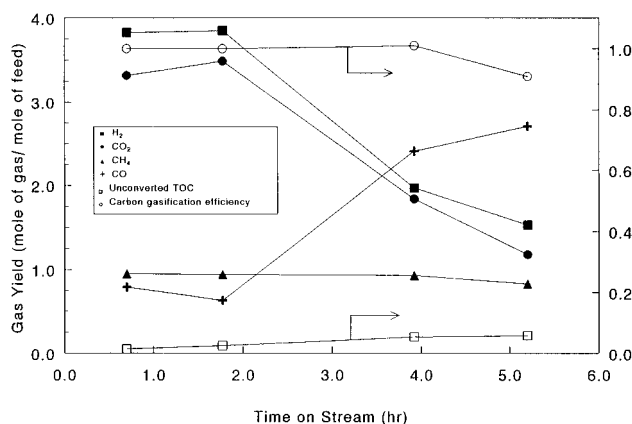
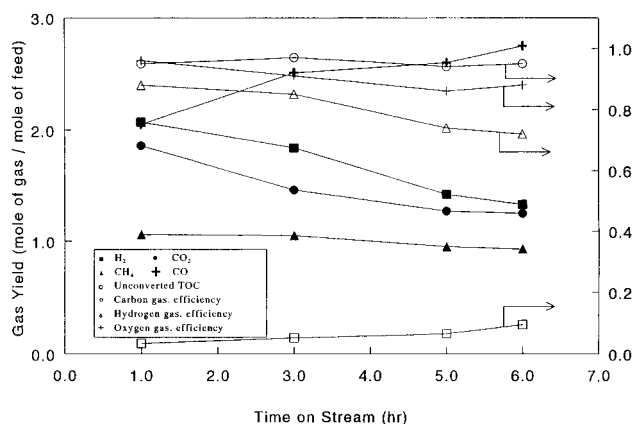
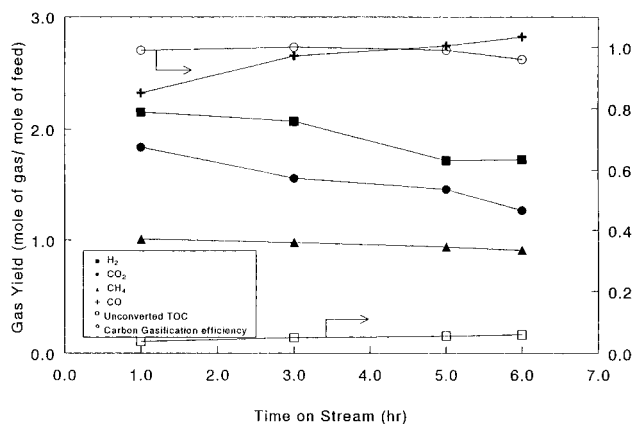
WHSV, h ⁻¹ exp date	14.6 4/27/94	16 7/17/95	22.2 8/11/94
product	gas yield (mol of gas/mol of feed)		
H ₂	2.07	2.07	2.00
CO	1.99	2.65	2.99
CO ₂	2.21	1.56	1.29
CH ₄	1.00	0.98	0.88
C ₂ H ₄	0.0	0.0	0.01
C ₂ H ₆	0.27	0.24	0.23
C ₃ H ₆	0.0	0.0	0.02
C ₃ H ₈	0.12	0.10	0.09
carbon gasification efficiency, %	102	100	100

Table 6. Gasification of 1.2 M Glucose in Supercritical Water at 600 °C, 34.5 MPa with Varying Amounts of Coconut Shell Activated Carbon Catalyst at Constant WHSV

amt of catalyst, g flow rate, mL/min WHSV, h ⁻¹ exp date	0.60 1.0 22.2 4/18/94	1.21 2.0 22.2 8/11/94
product	gas yield (mol of gas/mol of feed)	
H ₂	2.24	2.0
CO	0.79	2.99
CO ₂	3.09	1.29
CH ₄	1.23	0.88
C ₂ H ₄	0.0	0.01
C ₂ H ₆	0.35	0.23
C ₃ H ₆	0.0	0.02
C ₃ H ₈	0.13	0.09
carbon gasification efficiency, %	103	100

Table 5 demonstrates the effect of increasing WHSV on the gasification chemistry. Some decrease in the role of the water-gas shift reaction is evident, accompanied by a small decrease in the formation of methane. Nevertheless, over the wide range of WHSV displayed in Table 5, the carbon gasification efficiency remained high. A classical test for mass transfer limitations in heterogeneous catalysis is to increase the amount of catalyst present while at the same time proportionately increasing the flow rate, thereby maintaining constant WHSV. If mass transfer is unimportant, few changes in the product spectrum should be observed. Table 6 displays such a test with 1.2 M glucose as feed. Although the high-flow experiment evidenced a large increase in the CO yield and a related decrease in the CO₂ yield, as well as smaller decreases in the yields of hydrogen and methane, the carbon gasification efficiency remained high. Consequently, we conclude that the overall gasification rate is not influenced by mass transfer limitations.

Figure 2 shows the product gas yields, the unconverted TOC in the liquid effluent, and the carbon gasification efficiency as a function of time-on-stream during the gasification of 1.2 M glucose when no swirl was present in the entrance region of the reactor. The yields of H₂ and CO₂ remained high for almost 2 h and then decreased sharply; whereas the yield of CO was low initially and then increased with time-on-stream. The gasification efficiency remained high for 4 h before it too began to decrease as a result of the deactivation of the carbon catalyst. Thus the carbon catalyst showed a measurable loss of activity toward carbon gasification after about 4 h on-stream, but its ability to catalyze the shift reaction began to diminish steadily after about 2 h. Figures 3 and 4 display similar data when swirl was

**Figure 2.** Deactivation of coconut shell activated carbon catalyst during 1.2 M glucose gasification in supercritical water at 600 °C, 34.5 MPa without swirl, WHSV = 19.9 h⁻¹ (experiment date: 5/4/94).**Figure 3.** Gasification of 1.2 M glucose using coconut shell activated carbon catalyst in supercritical water at 600 °C, 34.5 MPa with swirl, WHSV = 17.1 h⁻¹ (experiment date: 7/13/95).**Figure 4.** Gasification of 1.2 M glucose using coconut shell activated carbon catalyst in supercritical water at 600 °C, 34.5 MPa with swirl, WHSV = 16 h⁻¹ (experiment date: 7/17/95).

added to the entrance region of the reactor. Note the good reproducibility enjoyed by these two runs. The yield of CO was initially high and increased, whereas the yields of H₂ and CO₂ decreased as the time-on-stream increased. The carbon gasification efficiency was near 100% and remained stable throughout the two runs. Likewise, the TOC value was low, but showed a small increase during the last hour of operation. Figure 3 also displays hydrogen and oxygen gasification efficiencies (defined as total moles of hydrogen (oxygen) in the gas products/moles of hydrogen (oxygen) in the organic feed). The hydrogen gasification efficiency fell

Table 7. Gasification of Whole Biomass Feedstocks in Supercritical Water at 600 °C, 34.5 MPa with Coconut Shell Activated Carbon Catalyst

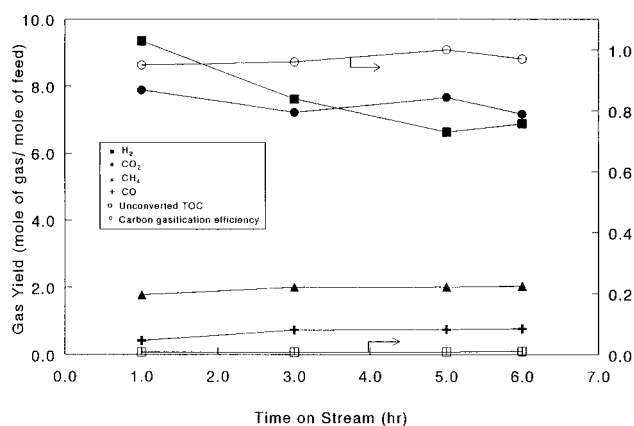
concn, wt % feedstocks	1.52 depithed bagasse liquid extract	2.8 sewage sludge		
WHSV, h ⁻¹	0.32	0.5		
exp date	7/12/94	6/22/94		
product	gas yield (g of gas/g of feed), %			
	raw ^a	corrected ^b	raw	corrected
H ₂	2.4	1.4	2.7	2.2
CO	0.0	0.0	3.5	3.3
CO ₂	90	79	66	61
CH ₄	6.8	6.6	16	1
C ₂ H ₄	0.2	0.2	0.0	0.0
C ₂ H ₆	1	1	7.7	7
C ₃ H ₆	0.0	0.0	0.3	0.3
C ₃ H ₈	0.0	0.0	1.7	1.7
total gas yield, %	101	89	98	77
unconverted TOC, g/L	N/A	N/A	0.28	0.28

^a Gas yield includes the gas generated by the coconut shell activated carbon catalyst. ^b Gas yield does not include the gas generated by the coconut shell activated carbon catalyst.

from 88 to 72%, while the oxygen gasification efficiency declined from 96 to 88%. As expected, these two efficiencies echo the falloff in rate of the water-gas shift reaction. Nevertheless, no obvious deactivation of the coconut shell activated carbon catalyst toward lower gasification efficiencies was observed. These results indicate that swirl in the entrance region, which improves heat transfer and enhances the heating rate of the feed, acts to extend the catalyst life. Tar-forming, condensation reactions are known to be favored by long residence times at lower temperatures. The improved heating rates which result from swirl may inhibit tar formation, and thereby prolong the life of the catalyst and its ability to effect high carbon gasification efficiencies.

Catalyst Performance with Other Feeds. Consider the sequence of events which occurs when a biomass slurry (containing cellulose, hemicellulose, and lignin constituents) is fed to the reactor. As the temperature of the slurry increases above 190 °C, all of the hemicellulose and much of the lignin contained in the biomass dissolve in the water, leaving behind a solid lignocellulosic residue (Mok and Antal, 1992). Related ongoing experimental work in our laboratory (Allen et al., 1996) produces a hemicellulose-rich liquid extract by treating biomass in hot (220 °C) liquid water for about 2 min. Significant quantities of extract from depithed bagasse were available to us; consequently, we decided to examine its gasification behavior in our system. This liquid extract is composed of hemicellulose (typically 60% by weight of the solute content) and lignin (typically 40% by weight) fragments dissolved in water; therefore its gasification chemistry should be representative of the extract from a whole biomass feed that would be formed in the entrance region of the reactor. Likewise, cellobiose is thought to be a good model compound for cellulose. Consequently, we employed it to represent the behavior of the lignocellulosic residue that remains following the low-temperature extraction of the hemicellulose and lignin in the entrance region of the reactor.

As shown in Table 7, complete gasification of the depithed bagasse liquid extract was observed. Note that the gas yields in Table 7 are expressed as mass fractions (grams of gas/grams of feed). Because of the relatively low concentration of the feed in this experiment, two

**Figure 5.** Gasification of 0.235 M cellobiose using coconut shell activated carbon catalyst in supercritical water at 600 °C, 34.5 MPa with swirl, WHSV = 1.35 h⁻¹ (experiment date: 7/24/95).**Table 8. Gasification of 2.0 M Glycerol in Supercritical Water at 600 °C, 34.5 MPa with and without Coconut Shell Activated Carbon Catalyst**

amt of catalyst, g	none	3.12
	res time = 44 s	WHSV = 4.36 h ⁻¹
exp date	2/16/95	2/3/95
product	gas yield (mol of gas/mol of feed)	
H ₂	3.51	3.15
CO	0.13	0.14
CO ₂	1.89	1.90
CH ₄	0.86	0.86
C ₂ H ₄	0.0	0.0
C ₂ H ₆	0.07	0.04
C ₃ H ₆	0.0	0.0
C ₃ H ₈	0.0	0.0
carbon gasification efficiency, %	101	99

values for the gas yield are reported. The "raw" measurement is simply the observed yield as before, whereas the "corrected" value represents the raw measurement less the observed rate of gas species formation (due to the water-gas reaction discussed earlier) in the absence of organic feed. Since reaction products derived from the organic feed may occupy active sites on the carbon and thereby reduce the rate of the water-gas reaction, it is not obvious which of these two yield measurements more accurately represents the gasification chemistry. We view them as representing two extreme situations (either the water-gas reaction contributes fully to the yields, or nothing at all). Remarkably, the carbon monoxide content of the product gas was negligible. Virtually no tar or char products were detected by evaporation of the liquid effluent in sample beakers. Results of the cellobiose experiment are displayed in Figure 5. As was the case with the bagasse liquid extract, complete gasification of cellobiose was achieved. The CO yield was quite low, whereas the H₂ and CO₂ yields were agreeably high. Unfortunately, cellobiose is only marginally soluble in water; consequently, the WHSV achieved in this run was significantly lower than those obtained with glucose as a reactant. Nevertheless, the high gasification efficiencies observed in these experiments cause us to be optimistic about the ability of the carbon catalyst to effectively steam reform concentrated slurries of biomass.

Table 7 also displays gasification results for a low concentration of sewage sludge in water. Complete gasification was achieved, as indicated by the very low unconverted TOC value. Unfortunately, our existing feeding systems have been unable to provide a reproducible, steady flow of higher concentration biomass

Table 9. Catalytic Destruction of Representative DoD Wastes in Supercritical Water at 600 °C, 34.5 MPa with Coconut Shell Activated Carbon Catalyst

concn, M	1.0		0.1		0.1		0.1		0.025	
reactant	methanol		methyl ethyl ketone		ethylene glycol		acetic acid		phenol ^c	
WHSV, h ⁻¹	0.54		0.14		0.11		0.14		0.1	
exp date	8/15/95		8/15/95		8/15/95		8/15/95		7/14/94	
product	gas yield (mol of gas/mol of feed)									
	raw ^a	corrected ^b	raw	corrected	raw	corrected	raw	corrected	raw	corrected
H ₂	2.13	2.04	1.44	0.67	1.41	0.5	1.07	0.16	2.5	0.43
CO	0.04	0.04	0.0	0.0	0.0	0.0	0.0	0.0	0.55	0.17
CO ₂	0.74	0.70	1.96	1.56	1.09	0.62	1.07	0.6	1.06	0.16
CH ₄	0.05	0.04	0.77	0.74	0.35	0.32	0.55	0.53	0.35	0.22
C ₂ H ₄	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ H ₆	0.0	0.0	0.08	0.08	0.02	0.02	0.0	0.0	0.05	0.05
C ₃ H ₆	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₃ H ₈	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
carbon gasification efficiency, %	84	78	72	62	74	49	82	57	35	12
unconverted reactant, %	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	19.2	19.2
unconverted TOC, %	0.2	0.2	0.3	0.3	1.5	1.5	0.5	0.5	N/A	N/A

^a Gas yield includes the gas generated by the coconut shell activated carbon catalyst. ^b Gas yield does not include the gas generated by the coconut shell activated carbon catalyst. ^c Liquid product contains benzene with a yield of 0.075 mol/mol of feed.

Table 10. Destruction of Representative DoD Wastes in Supercritical Water at 600 °C, 34.5 MPa without Catalyst

concn, M reactant res time, s exp date	1.0 methanol 27.7 7/25/95	0.1 methyl ethyl ketone 27.7 7/25/95	0.1 ethylene glycol 27.7 7/25/95	0.1 acetic acid 27.7 7/25/95
product	gas yield (mol of gas/mol of feed)			
H ₂	2.17	0.88	1.24	0.54
CO	0.0	0.36	0.31	0.06
CO ₂	0.76	0.49	0.49	0.41
CH ₄	0.03	0.60	0.39	0.38
C ₂ H ₄	0.0	0.19	0.02	0.0
C ₂ H ₆	0.0	0.25	0.10	0.01
C ₃ H ₆	0.0	0.0	0.0	0.04
carbon gasification efficiency, %	79	58	72	51
unconverted reactant, %	0.2	19	0.0	52
unconverted TOC, %	11	33	16	53

slurries to the reactor. We have begun work to create pumpable biomass pastes which can be fed to a supercritical flow reactor in high concentrations, and we hope to report results from this work in the near future. The remainder of this paper sheds light on the ability of carbon to catalyze the gasification of other organic compounds which could become available as feedstocks for gasification in the near future.

Glycerol is a byproduct of biodiesel fuel production. Increasing demand for biodiesel may create a glut of glycerol, which could become available as a feedstock at low or negative cost. Table 8 shows that glycerol is easily and completely gasified to a hydrogen-rich gas in supercritical water without a catalyst. The presence of the catalyst has little effect on the gas composition. Note the very low yield of CO and the high yield of H₂ in these experiments. These results may be contrasted with those of Stein et al. (1983), who reported a study of glycerol gasification in steam at 0.1 MPa with temperatures ranging from 650 to 700 °C and residence times below 0.13 s. Major gaseous products of the low-pressure work included CO, H₂, C₂H₄, and CH₄ (in decreasing order of yields). Almost no CO₂ was detected by Stein et al. (1983). Evidently, the supercritical condition evokes considerably different gasification chemistry than that observed at atmospheric pressure.

The destruction of chemical wastes is an important societal problem. Because of the large negative cost associated with their disposal, chemical wastes could become a profitable feedstock for hydrogen production. Table 9 portrays the ability of the activated carbon

catalyst to gasify representative Department of Defense wastes (Steeper and Rice, 1993) in supercritical water. Table 10 displays similar results without the catalyst. Essentially complete destruction of all the feeds was realized by the catalyst. The ethylene glycol result is not surprising, since it completely decomposes in supercritical water at 600 °C in the absence of catalyst (see Table 10). Also, glycerol completely decomposes at these conditions without catalyst (see Table 8); consequently, the glycol result might have been anticipated. On the other hand, the complete destruction of methanol without catalyst was unexpected, since its oxidative destruction in supercritical water is sufficiently difficult to have made it the focus of much research (Webley and Tester, 1989; Webley et al., 1991; Steeper et al., 1992; Tester et al., 1993; Boock and Klein, 1993). But the earlier workers emphasized lower temperatures (below 530 °C) where the steam reforming chemistry is slow, so our results are not inconsistent with the earlier findings. Unlike methanol, glycol, and glycerol, acetic acid is known for its refractory nature and has been the subject of many oxidation studies in supercritical water (Wightman 1981; Lee et al., 1990; Steeper and Rice, 1993; Boock and Klein, 1993; Savage and Smith, 1995). The results given in Table 9 plainly indicate the ability of carbon to catalyze the destruction of acetic acid in supercritical water. Table 10 shows that methyl ethyl ketone (MEK) is somewhat less refractory than acetic acid, but considerably more stable than the other feeds. As indicated in Table 9, it also was completely destroyed by contact with the carbon catalyst. Finally, consider-

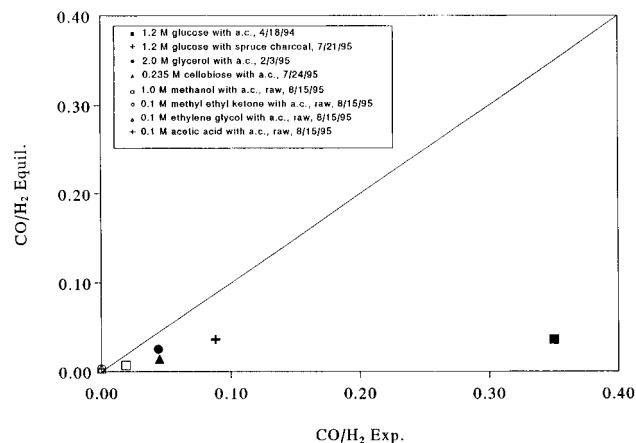


Figure 6. Parity plot of the calculated theoretical equilibrium value of CO/H₂ vs the measured experimental value of CO/H₂ in supercritical water at 600 °C, 34.5 MPa.

able destruction of phenol was achieved (see Table 9), but benzene was detected as a decomposition byproduct. This situation contrasts with supercritical water oxidation, where an extraordinary variety of unwanted byproducts are formed as reaction intermediates (Thornton and Savage, 1990, 1992a,b). The low carbon gasification efficiencies displayed in Table 9 probably reflect carbon deposition on the carbon catalyst, but the amount was much too small to be measured. Carbon deposition may cause a loss of catalytic activity and could therefore be troublesome in an industrial setting; nevertheless the carbon catalyst can ultimately be burned as a fuel. Consequently, we believe this approach to destroying refractory compounds holds much promise for commercial applications.

Figure 6 displays a parity plot of the calculated theoretical equilibrium values of the CO/H₂ molar ratio vs the experimental values reported in this paper. The theoretical values were calculated using STANJAN software (Reynolds, 1987). STANJAN employs the JANAF thermochemical tables to do gas phase chemical equilibrium analysis by the method of element potentials. STANJAN predicts very low yields of CO from organic feeds exposed to supercritical water at 600 °C and 34.5 MPa. This result shows that the high CO product concentrations reported in this paper are far from equilibrium. It offers hope that reaction conditions or catalytic promoters can be identified which will enhance the rate of the water-gas shift reaction and thereby produce a gas composed almost entirely of H₂, CO₂, and methane. Figure 7 displays the calculated theoretical equilibrium yield of methane vs the experimental value. Observed methane yields from the concentrated organic feeds were significantly less than their calculated, equilibrium values. On the other hand, methane yields associated with the DoD wastes were higher than predicted. Again, these results indicate that the system is far from equilibrium.

Conclusion

1. A wide range of carbons effectively catalyze the gasification (steam reforming) reactions of concentrated feeds (22% by weight) of glucose in supercritical water at 600 °C and 34.5 MPa. Carbon gasification efficiencies near 100% are easily achieved. The available surface area of the carbon does not greatly influence its effectiveness as a catalyst.

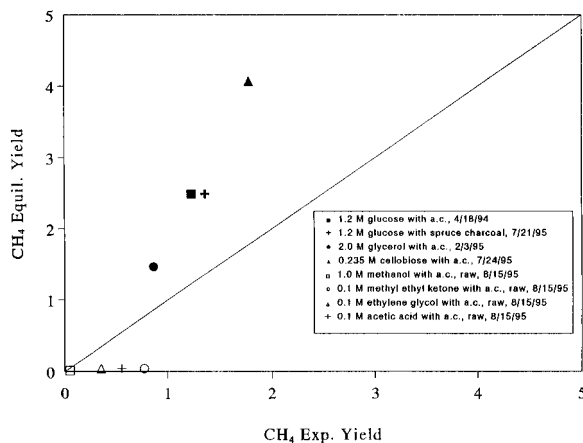


Figure 7. Plot of the calculated equilibrium yield of CH₄ vs the measured experimental yield of CH₄ in supercritical water at 600 °C, 34.5 MPa.

2. In the presence of the carbon catalyst, temperatures above about 600 °C are needed to achieve high gasification efficiencies for concentrated organic feeds in water.

3. Pressures above about 25 MPa are adequate to realize high gasification efficiencies.

4. Mass transfer limitations do not significantly affect the gasification rate but may influence the realization of chemical equilibrium via the water-gas shift reaction.

5. In the presence of coconut shell activated carbon, cellobiose and various whole biomass feeds (including depithed bagasse liquid extract and sewage sludge) are almost completely gasified in supercritical water.

6. Glycerol (a byproduct of biodiesel production) completely decomposes in supercritical water (without a catalyst) to a hydrogen rich synthesis gas containing almost no CO after 44 s at 600 °C and 34.5 MPa.

7. Coconut shell activated carbon effectively catalyzes the destruction of representative Department of Defense wastes in supercritical water at 600 °C.

8. Deactivation of the carbon catalyst toward gasification was observed after less than 4 h of operation without swirl in the entrance region of the reactor; however, the carbon gasification efficiency remained near 100% during runs that lasted for 6 h when swirl was present in the entrance region. Regeneration of spent catalyst will be discussed in a future paper.

9. Thermochemical equilibrium calculations indicate that little CO should be formed from the gasification of organic feeds employed in this work. The fact that significant yields of CO were usually observed, but in isolated instances were not observed, suggests that future work should focus on discovering what experimental conditions affect the rate of the water-gas shift reaction.

10. The above results give cause for optimism that a practical process can be developed for hydrogen production at high pressures by the catalytic steam reforming of abundant wet biomass feedstocks.

Acknowledgment

This work was supported by NREL/DOE, under Contracts DE-FC36-94AL85804 and XCF-5-14326-01, and the Coral Industries Endowment. We thank Dr. Russell Eaton (DOE), Neil Rossmessl (DOE), Dr. Ralph Overend, Dr. Dan Tyndall, and Dr. John Sheenan (all of NREL) and Dr. Patrick Takahashi, Dr. Charles Kinoshita, and Dr. Richard Rocheleau (all of HNEI) for

their interest in this work. We also thank Professor Jefferson W. Tester (MIT), Dr. Johan Penninger (Twente University), Dr. Wilbur Hurst and Dr. Henning Ochel (NIST) for useful discussions, Dr. Mohammed A. Bayati (Barnebey and Sutcliffe Corp.) for supplying us the activated carbons used in this work, and three anonymous reviewers for their constructive comments.

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Received for review November 6, 1995

Accepted May 22, 1996*

IE950672B