

HYDROGEN PRODUCTION FROM HIGH MOISTURE CONTENT BIOMASS IN SUPERCRITICAL WATER

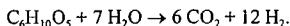
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INTRODUCTION

The goal of this work is to define conditions which enable the steam reforming of biomass (represented below as cellulose $C_6H_{10}O_5$) to produce hydrogen:



Earlier work has shown that when biomass is heated quickly in water above its critical pressure, no char is formed. Instead, the biomass decomposes into simple organic molecules dissolved in the water, which further decompose to hydrogen, carbon dioxide, and some methane when exposed to a carbon catalyst at temperatures above 600 °C. In this paper we detail the conditions which evoke the biomass steam reforming chemistry, and we offer insight into the influence of the reactor's wall on the product distribution.

APPARATUS AND EXPERIMENTAL PROCEDURES

The two flow reactors (see Figures 1 and 2) used in this work are 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 to temperatures as high as 800 °C. 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. In fact, in some experiments the temperature setpoint of the furnace was below the lowest temperature measured along the reactor wall. 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, in reactor #1 the reactant temperature is measured by a fixed, internal, annulus thermocouple which is located 5.08 cm upstream of the furnace (see Figure 1). 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.

The feeder consists of a cylinder, a movable piston, and two end-caps (High Pressure Equipment). The cylinder is first filled with the feedstock, then the piston is placed on top of the feed, and the two end-caps are 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 about 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 sawdust 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.

RESULTS

In earlier work we reported the ease of gasification of glycerol in supercritical water. Table 1 confirms the earlier result. In it we see that the hydrogen content of the gas increases from 38% to 51% after 3.45 hr, while the methane content decreases from 20% to 11%. During this time the total gas yield increased from 1.18 to 1.6 L/g and all the carbon in the feedstock was converted to gas. The increasing gas yield is due to the consumption of water and methane by the steam reforming reaction. Evidently this reaction is catalyzed by the reactor's wall and/or the carbon catalyst, which become more active (i.e. "seasoned") as time passes. When the gas yield reached a steady state, the feed was switched and sawdust paste was fed to the reactor for 4

hours. After this, glycerol was again fed to the reactor. Table 1 shows that the sawdust paste causes the reactor's wall and/or the carbon catalyst to lose some activity towards the steam reforming reaction.

The waste product generated by the commercial production of biodiesel fuel contains glycerol and methanol. We prepared a mixture of these two alcohols with a composition identical to that of the industrial waste. The gas produced from this mixture (see Table 2) is very rich in hydrogen, and the yield (2.05 L/g) is high. The water leaving the reactor was clean with a pH of 4-5. Evidently, this waste product is a perfect feedstock for hydrogen production.

As mentioned earlier, we prepare a sawdust paste by mixing wood sawdust into a starch gel, and this paste is easily fed to our reactors. Large quantities of wood sawdust are available at \$30 per dry ton, and the quoted price of corn starch in bulk is \$0.12 per pound. Using these values, the price of a 10 wt % sawdust, 3.65 wt % starch paste is \$0.043 per pound. Similarly, the price of a 20 wt % sawdust, 3.65 wt % starch paste is \$0.031 per pound. For comparison, the price of low sulfur coal is about \$0.025 per pound.

Sawdust paste gasification results from three consecutive runs (no intervening experiments) on different days are displayed in Table 3. In all 3 cases, the reactor plugged after 2 to 3 hours on stream. Although the measured temperatures were similar on 3 and 10 July, the gas yield increased from 1.61 to 2.18 L/g, and the hydrogen content of the gas increased from 43 to 57%. Because fresh carbon catalyst was employed with each experiment, we assumed that the increase in gas yield was due to a seasoning effect of the high temperature in the entrance region on the reactor's wall. To see if the seasoned wall would provide a high gas yield at lower temperatures, we employed a lower entrance temperature in the next experiment (21 July). Remarkably, the results were effectively identical to those of the first experiment. This result, and others indicate that high temperatures are requisite to achieve high gas yields with high hydrogen concentrations from wood sawdust.

CONCLUSIONS

1. A semi-solid gel can be made from 4 wt % (or less) corn starch in water. Wood sawdust and other particulate biomass can be mixed into this gel and suspended therein, forming a thick paste. This paste is easily delivered to a supercritical flow reactor by a cement pump.
2. Above the critical pressure of water, wood sawdust can be steam reformed over a carbon catalyst to a gas composed 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 TOC value, a neutral pH, and no color. This water can be recycled to the reactor.
3. The wall affects the gasification chemistry. Products from wood sawdust paste gasification decrease the activity of the wall towards hydrogen production by improving methane yields. These wall effects are strongly temperature dependent. High entrance temperatures strongly favor the methane steam reforming reaction and result in the production of a hydrogen rich gas.

ACKNOWLEDGMENTS

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Table 1. Gas composition from glycerol gasification in supercritical water at 28 MPa with coconut shell activated carbon catalyst using reactor #2 (exp. date: 2/19/98).

Feedstock	18.72 wt% glycerol in water				
Reactor peak temp / Catalyst bed temp	560°C/ 665°C				
Flow rate (g/min)	2.0				
Time on stream (hr)	Before paste ¹				After paste ²
	1.32	2.08	2.55	3.45	5.48
Product	Mole fraction				
H ₂	0.38	0.46	0.51	0.51	0.48
CO	0.02	0.03	0.03	0.03	0.03
CO ₂	0.35	0.33	0.31	0.32	0.32
CH ₄	0.20	0.13	0.12	0.11	0.16
C ₂ H ₆	0.05	0.04	0.04	0.03	0.01
Total gas yield (L gas / g of organics)	1.18	1.40	1.49	1.60	1.60
(g gas / g of organics)	1.01	1.11	1.13	1.18	1.17
C efficiency	0.96	1.00	1.00	1.01	1.01
Global mass balance	0.99	1.01	1.01	1.02	1.02

1. Poplar wood sawdust/corn starch paste was fed to the reactor for 4 hours after the gas generation from glycerol reached a steady state.
2. Glycerol was fed to the reactor again after the reactor plugged with the sawdust/corn starch paste.

Table 2. Gas composition from gasification of glycerol/methanol mixture in supercritical water at 28 MPa with coconut shell activated carbon catalyst using reactor #2 (exp. date: 3/13/98).

Feedstocks	Simulated biodiesel waste product			
Reactor peak temp / Catalyst bed temp	730°C/ 720°C			
Flow rate (g/min)	2.0			
Time on stream (hr)	0.42	0.73	1.25	1.68
Product	Mole fraction			
H ₂	0.64	0.64	0.65	0.64
CO	0.05	0.05	0.05	0.05
CO ₂	0.21	0.21	0.21	0.21
CH ₄	0.10	0.10	0.10	0.10
Total gas yield (L gas / g of organics)	2.05	2.05	2.05	2.05
(g gas / g of organics)	1.25	1.22	1.24	1.20
C efficiency	1.05	1.03	1.04	1.01
H efficiency	1.43	1.41	1.44	1.38
O efficiency	1.36	1.32	1.35	1.31
H balance	1.04	1.03	1.04	1.03
O balance	0.99	0.98	0.99	0.98
Global mass balance	0.98	0.97	0.98	0.97

Table 3. Gas composition from poplar wood sawdust / corn starch gasification in supercritical water at 28 MPa with coconut shell activated carbon catalyst on different dates using reactor #1.

Experiment date	7/3/97	7/10/97	7/21/97
Feedstocks (dry basis)	10.72 wt% sawdust/ 4.01 wt% corn starch	11.17 wt% sawdust/ 4.19 wt% corn starch	11.1 wt% sawdust/ 4.15 wt% corn starch
Reactor peak temp / Catalyst bed temp	790°C/ 685°C	790°C/ 700°C	732°C/ 690°C
Flow rate (g/min)	2.0		
Time on stream (hr)	1.62	1.52	1.42
Product	Mole fraction		
H ₂	0.43	0.57	0.45
CO	0.03	0.04	0.03
CO ₂	0.38	0.33	0.38
CH ₄	0.17	0.06	0.15
C ₂ H ₆	0.001	0.001	0.0
Total gas yield (L gas / g of organics)	1.61	2.18	1.57
(g gas/ g of organics)	1.37	1.65	1.48
C efficiency	0.96	1.01	1.01
Global mass balance	1.01	1.00	0.99

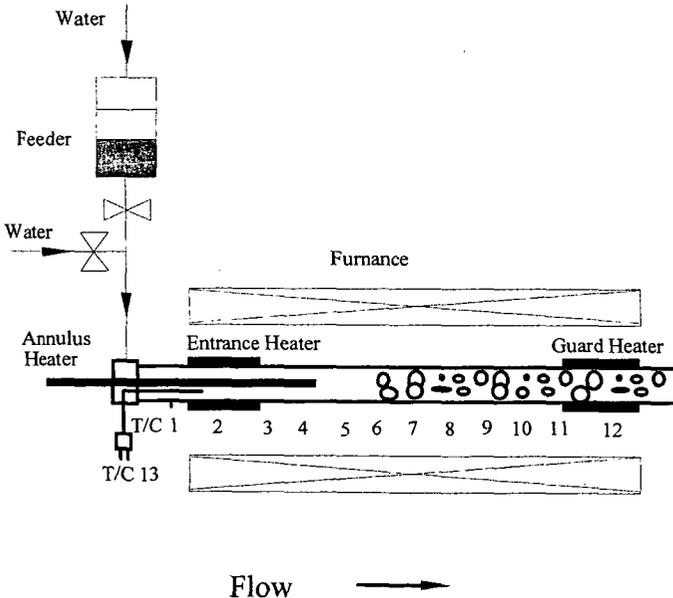


Figure 1. Reactor #1.

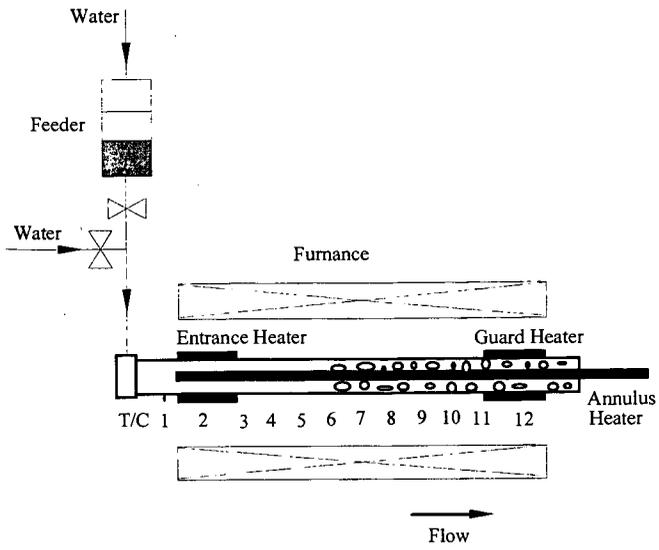


Figure 2. Reactor #2.