

CATALYTIC GASIFICATION OF WET BIOMASS IN SUPERCRITICAL WATER

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Keywords: Wet biomass, Catalytic gasification, Supercritical water

INTRODUCTION

Wet biomass (water hyacinth, banana trees, cattails, green algae, kelp, etc.) grows rapidly and abundantly around the world. As a biomass crop, aquatic species are particularly attractive because their cultivation does not compete with land-based agricultural activities designed to produce food for consumption or export. However, wet biomass is not regarded as a promising feed for conventional thermochemical conversion processes because the cost associated with drying it is too high. This research seeks to address this problem by employing water as the gasification medium. Prior work has shown that low concentrations of glucose (a model compound for whole biomass) can be completely gasified in supercritical water at 600°C and 34.5 MPa after a 30 s reaction time (Dehui et al., 1993). Higher concentrations of glucose (up to 22% by weight in water) resulted in incomplete conversion under these conditions. The gas contained hydrogen, carbon dioxide, carbon monoxide, methane, ethane, propane, and traces of other hydrocarbons. The carbon monoxide and hydrocarbons are easily converted to hydrogen by commercial technology available in most refineries. This prior work utilized capillary tube reactors with no catalyst. A larger reactor system was fabricated and the heterogeneous catalytic gasification of glucose and wet biomass slurry of higher concentration was studied to attain higher conversions.

EXPERIMENTAL

A schematic drawing of the reactor system is presented in Figure 1. The reactor was constructed of Inconel 625 tubing with a 0.375" OD and 0.187" ID. The temperature of the reactant flow was abruptly raised to a desired value using an entry heater/cooling water jacket combination. The reactor was maintained at isothermal conditions using a furnace and downstream heater/cooling water jacket combination. To improve the heat transfer from the heaters to the fluids inside the reactor, the heaters were coiled on stainless steel rods in direct contact with the Inconel reactor. Different amounts of solid catalyst could be packed inside the reactor, giving the desired weight hourly space velocity (WHSV), which is defined as the ratio of the mass flow rate of the reactant to the mass of a proprietary "catalyst X" used in the heated zone. The axial temperature profile along the reactor's functional length of approximately 0.48 m was measured with 15 fixed, type K thermocouples. Pressure in the reactor system was measured using a pressure transducer. A back pressure regulator reduced the working pressure from 34.5 MPa to atmospheric pressure. After passing through the back pressure regulator, the reactor effluent then passed through an in-house fabricated glass gas-liquid separator. The gas flow rate was measured using a wet test meter.

The aqueous solution of glucose was fed into the reactor by an HPLC pump. A balloon feeding system was employed to feed the wet biomass slurry. Wet biomass was first ground with a blender and then with a homogenizer. The heterogeneous biomass slurry filled the 500 ml high pressure/temperature vessel, which was equipped with a magnetic drive. A meteorological balloon was placed in the vessel together with the biomass slurry. Water was pumped into the balloon, and as the balloon expanded the biomass slurry was forced into the reactor.

The analysis of the gaseous products was accomplished on a gas chromatograph 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. The following gases were detected as the products of glucose gasification: H₂, CO, CO₂, CH₄, C₂H₄, C₂H₆, C₃H₆, and C₃H₈. Gas yields were calculated as the ratio of mole of detected gas to the mole of reactant. Carbon gasification efficiency was calculated as the ratio of carbon converted into gas.

Ten cubic centimeters of the liquid effluent from the experiments were dried in small beakers in an oven and the weight gain measured. A dark tar deposit remained on the bottom of the beaker after the drying for lower temperature or higher concentration. Tar yield was calculated as the ratio of the weight of tar to the weight of the reactant.

RESULTS AND DISCUSSIONS

1. Temperature effect

The effect of temperature on the gasification of glucose in the presence of catalyst X is shown in Table 1. Complete carbon conversion was observed at 600°C; however, as temperature dropped, carbon gasification efficiency decreased drastically. When the reaction temperature was

below 580°C, resulting in incomplete gasification conversion, the liquid effluent became yellowish and there was a thin layer of a dark brown, oil-like tar. Figure 2 illustrates the amount of tar present in the liquid sample as a function of reaction temperature. It is obvious that the tar yield in the liquid sample increases as temperature decreases. The tar yield at 600°C is significantly small.

2. Reactant concentration effect

When 0.2 M glucose was gasified without the solid catalyst X at about 30 s residence time in supercritical water at 600°C, 34.5 MPa, complete carbon conversion was observed. The liquid sample was clear. As the reactant glucose concentration increased, the carbon conversion decreased. With 0.8 M glucose reactant, the conversion dropped to 88%, and a dark brownish oil layer was present in the liquid sample.

The presence of solid catalyst X resulted in complete conversion of glucose feed with concentration as high as 1.2 M at a WHSV of 22.2 (g/h)/g (see Table 2). The liquid effluent was clear. Gas yields of H₂, CO, CH₄, and CO₂ increased significantly with the addition of catalyst X.

3. Pressure effect

When the pressure increased from 25.6 MPa to 34.5 MPa, the overall carbon gasification efficiency remained almost the same. However, as pressure increased, the yield of methane increased. This finding confirms the results of Elliott et al. (Elliott et al., 1993a, 1993b; Baker et al., 1989; Sealock et al., 1993).

4. Deactivation of catalyst

Deactivation of catalyst was observed in an 8-hour experiment using 1.2 M glucose as a reactant. As shown in Table 3, the carbon gasification efficiency decreased, while the solid residual and carbon content in the liquid sample increased with time.

The liquid samples were collected for total organic carbon (TOC) analysis. TOC yield was calculated as the weight ratio of carbon in the liquid effluent to that in the reactant. Because of the lower carbon gasification efficiency, more carbon remained in the liquid effluent at the later stage of the experiment, as indicated in Table 3. Notice that the tar yield (which is a measurement of the non-volatile residual in the liquid effluent) also increased with time.

5. Whole biomass gasification

Various whole biomass feeds, including water hyacinth, depithed bagasse liquid extract, sewage sludge, and paper sludge, were studied in the packed bed reactor. The gasification of the above feeds with catalyst X at 600°C, 34.5 MPa, resulted in a complete conversion to gas. The gas contained H₂, CO₂, CH₄, and trace amounts of high hydrocarbons. The amount of carbon monoxide in the gaseous product mixture was very small. Virtually no tar or char products were detected by the evaporation of the liquid effluent. The TOC analysis confirmed this result. Typical results are illustrated in Table 4, which presents data for the gasification of sewage sludge.

CONCLUSION

Glucose as high as 22% by weight in water can be completely gasified to a hydrogen-rich gas with catalyst X at a WHSV as high as 22.2 (g/h)/g in supercritical water at 600°C, 34.5 MPa. Complete conversions of low concentrations of whole biomass feeds, including water hyacinth, depithed bagasse liquid extract, and sewage sludge, have also been achieved.

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Table 1. Temperature effect on the gasification of glucose in supercritical water with catalyst X (1.0 M glucose reactant, WHSV = 13.5 (g/h)/g, 34.5 MPa)

Temperature	600°C	550°C	500°C
Gas yields			
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	0.01	0.01	0.02
C ₂ H ₆	0.25	0.10	0.07
C ₃ H ₆	0.01	0.03	0.04
C ₃ H ₈	0.11	0.05	0.04
Carbon gasification efficiency	0.98	0.54	0.51
Tar yield	0.1%	0.9%	1.3%

Table 2. Glucose reactant concentration effect on the gasification efficiency in supercritical water at 600°C, 34.5 MPa, with catalyst X. (Flow rate: 1.0 cm³/min)

	1.2 M glucose with 0.6 g catalyst (WHSV = 22.2 (g/h)/g)	0.8 M glucose with no catalyst (Res. time = 28 s)
Gas yield		
H ₂	2.24	0.70
CO	0.79	1.63
CO ₂	3.09	2.01
CH ₄	1.23	0.75
C ₂ H ₄	0.00	0.04
C ₂ H ₆	0.35	0.22
C ₃ H ₆	0.00	0.04
C ₃ H ₈	0.13	0.09
Carbon gasification efficiency	1.03	0.88
Tar yield	0.008%	Not available

Table 3. Stability of catalyst X in a continuous run of glucose gasification in supercritical water at 600°C, 34.5 MPa (1.2 M glucose, WHSV = 19.9 (g/h)/g, catalyst X 2.55 g)

Time on stream	0.7 h	1.77 h	3.92 h	5.2 h
Gas yield				
H ₂	3.83	3.85	1.97	1.53
CO	0.79	0.63	2.41	2.71
CO ₂	3.32	3.49	1.84	1.18
CH ₄	0.95	0.94	0.93	0.83
C ₂ H ₄	0.00	0.00	0.01	0.01
C ₂ H ₆	0.26	0.26	0.25	0.21
C ₃ H ₆	0.00	0.01	0.01	0.02
C ₃ H ₈	0.15	0.13	0.11	0.09
Carbon gasification efficiency	1.00	1.00	1.01	0.91
Tar yield	0.02%	0.03%	0.07%	0.16%
TOC yield	1.4%	2.5%	5.4%	5.8%

Table 4. Sewage sludge gasification in supercritical water at 600°C, 34.5 MPa, with catalyst X (28 g/dm³ sewage sludge with 2.96 g catalyst X, WHSV = 0.50 (g/h)/g)

Gas product	Yield ^a	Mole fraction ^b
H ₂	2.7%	33%
CO	3.5%	2.9%
CO ₂	66.2%	36%
CH ₄	16.3%	24%
C ₂ H ₄	0.05%	0.04%
C ₂ H ₆	7.7%	5.7%
C ₃ H ₆	0.3%	0.15%
C ₃ H ₈	1.7%	0.89%
total	98.4%	
Liquid yield ^c	0.99%	
TOC analysis	0.28 g-carbon / dm ³	
Mass balance ^d	99.4%	

a Gas yield = weight of gas / weight of reactant

b Mole fraction = mole of gas / total mole of gas in the effluent

c Liquid yield = weight of solid residue in liquid / gram of reactant

d Mass balance = total gas yield + liquid yield

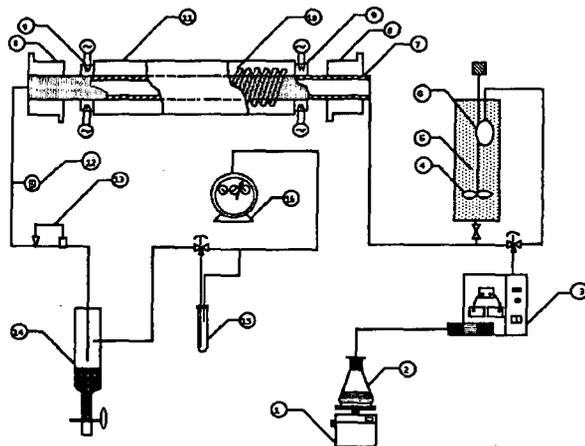


Fig. 1. Reactor system scheme. 1) Balance; 2) Flask with reactant; 3) HPLC pump; 4) Feeding vessel with agitator; 5) Wet-biomass slurry; 6) Balloon; 7) Inconel 625 tube; 8) Cooling jacket; 9) Heater; 10) Furnace; 11) Furnace shell; 12) Pressure transducer; 13) Back pressure regulator; 14) Gas sample output; 15) Liquid-gas separator; 16) Wet test meter

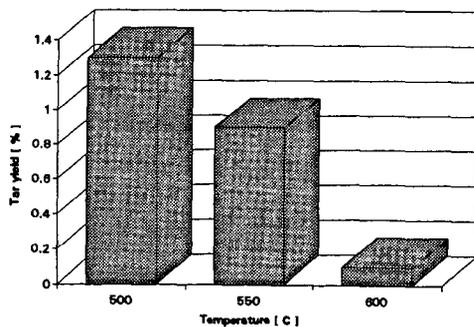


Fig. 2. Tar yield vs. reaction temperature (1.0M glucose reactant, WHSV = 13.5 (g/h)/g)