Effect of Pressure on Low Temperature Gasification of Wet Cellulose into Methane Using Reduced Nickel Catalyst and Sodium Carbonate

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A water slurry of cellulose was directly gasified to methane using a reduced nickel catalyst and sodium carbonate at 400 °C under pressure (9-28 MPa) for 1 h. Methane yield depended on operating pressure and the highest yield was 190 mg per 1 g cellulose at around 15 MPa This value was 1.5 times that in the literature.

Biomass is a renewable resource. Many studies have been carried out on the thermochemical conversion of biomass into fluid fuels. Elliott et al.[1-3] of the Pacific Northwest Laboratory reported water slurry of biomass to be directly gasified to methane rich fuel gas using a reduced nickel catalyst and sodium carbonate at 350-450 °C under pressurized nitrogen. This gasification requires no drying of feed stock and consumes less energy; biomass usually has high moisture content and drying requires much energy to vaporize the moisture. In this gasification, reduced nickel is considered to catalyze methane production and sodium carbonate to promote the reaction as a co-catalyst. High pressure is required for methane production in terms of equilibrium. The reaction rate of gasification is slow and much catalyst is needed. Water is to be in steam or supercritical at around 400 °C according to operating pressure. The state of water will probably influence the reaction rate and mechanism, but there is no description regarding operating pressure and the state of water. This study was conducted to examine the effect of pressure on gasification to achieve a greater reaction rate (methane yield).

Cellulose, a major component of woody biomass, was used as the starting material. The cellulose sample was microcrystalline (E. Merck), and it was dried at 105 °C for 24 h prior to the study. The amounts of carbon, hydrogen, and oxygen of the cellulose, determined by an elemental analyzer (Perkin-Elmer, 2400 CHN), were 42.5, 7.4, and 50.1%, respectively. The reduced nickel catalyst (about 50 wt% of nickel content) was prepared by ordinary precipitation.[4,5] Sodium carbonate solution was added to a slurry of kieselguhr and nickel nitrate solution at 70 °C to obtain the precipitate. The precipitate was then dried at 105 °C for 12 h, crushed to 60-150 mesh, calcined at 350 °C for 4 h, and reduced with hydrogen at 350 °C for 4 h to finally obtain the reduced nickel catalyst.

The reaction was performed in a stainless steel (SUS-F316L) autoclave (100 cm^3) with a magnetic stirrer. Water, cellulose, the reduced nickel catalyst, and sodium carbonate were charged into the autoclave. Nitrogen was used to purge residual air. Further nitrogen was usually added to 0.8 MPa. The reaction was started by heating the autoclave with an electric furnace. It took about 1 h to raise the temperature to 400 °C. This temperature was maintained constant for 1 h. Pressure in the autoclave, monitored with a pressure transmitter, rose with temperature. During the reaction at 400 °C, pressure was kept constant. The operating pressure was defined as the pressure at 400 °C. Following completion of the reaction, the autoclave was cooled to room temperature with an electric fan.

The gas product was collected in a gas sampling bag. Its volume was measured with a gas meter (Shinagawa Seiki, W-NK-0.5Bf). The amounts of methane, ethane, ethylene, propane, and propylene were determined by a gas chromatograph (Shimadzu, GC-9A) equipped with a hydrogen flame ionization detector and a packed column (Squalane on Alumina). Hydrogen, nitrogen, carbon dioxide, and carbon monoxide were measured by a gas chromatograph (Shimadzu, GC-12A) with a thermal conductivity detector and a packed column (MS-5A or Porapak Q).

The results and reaction conditions are summarized in Table 1. Gas was obtained in the yields of 66 to 93 wt% to the cellulose, which is shown as total in Table 1. Oil, char-like residue and a water-soluble material also were produced as by-products in only small yields (less than 6 wt%, respectively). Therefore this paper has no special discussion about by-products. Run 1 was performed under the same conditions as in experiment by Elliott,[3] with essentially the same results. In Run 2, water loading was reduced to decrease operating pressure, with consequent increase in methane yield. Run 2 differed from Run 1 not only in operating pressure but partial pressure of water and moisture content as well the cellulose/water ratio. Runs 3 and 4 were conducted to determine the effects of these parameters on

Table 1. Operating Pressure, Gas Components, and the Ratio of Methane to Carbon Dioxide with Variation in Water Loading, Cellulose Loading, and Initial Nitrogen Pressure

Run[a]	Water / g	Cellulose / g	Initial Pressure / MPa	Operating Pressure[b] / MPa	Gas components / mg per 1 g cellulose							CH_4 / CO_2 / mol / mol
					CH_4	CO_2	H_2	CO	C_2H_6	C_3H_8	Total	
1	30	3.0	0.8	26.4	113	598	22	2	8	6	756	0.52
2	20	3.0	0.8	19.0	174	627	13	2	7	5	832	0.76
3	20	3.0	3.0	25.4	113	504	16	1	10	8	660	0.62
4	30	4.5	0.8	28.4	115	527	24	2	10	7	690	0.60
5	10	3.0	0.8	14.8	190	702	20	7	6	4	933	0.74
6	5	3.0	0.8	9.0	168	511	14	11	10	5	721	0.90
Ref. 3	300	30	0.8	No data	125	671	20	1	14	-	831	0.51

[a] Nickel catalyst loading was 0.5 g (0.75 g for Run 4) and sodium carbonate loading, 1.02 g (1.53 g for Run 4).
[b] Operating pressure means the pressure in the autoclave at 400 °C.

methane yield. In Run 3, the amounts of cellulose and water were the same as in Run 2, but nitrogen was added to 3 MPa to increase the operating pressure. Methane yield in Run 3 decreased, although the partial pressure of water and moisture content were the same as in Run 2. In Run 4, cellulose and water were 1.5 times as much as in Run 2 to increase operating pressure. Methane yield in Run 4 decreased, but moisture content was the same as in Run 2. Methane yields in Runs 1, 3 and 4 were essentially the same, as was also operating pressure. The partial pressure of water differed for Runs 1 and 3 and moisture content differed for Runs 1 and 4. Methane yield thus depends only on operating pressure, but not on the partial pressure of water or moisture content.

The effect of operating pressure was further examined to improve methane yield. In Runs 5 and 6, it was reduced with decrease in water loading. Methane yield was highest at 15 MPa (Run 5). Optimal operating pressure should thus be around 15 MPa. This highest value (190 mg per 1 g cellulose) was 1.5 times that reported by Elliott.[3]

The product gas consisted mainly of methane and carbon dioxide, as shown in Table 1. The molecular ratio of methane to carbon dioxide was calculated for assessment of selectivity. It increased in the order of Run 1 < Runs 3, 4 < Runs 2, 5 < Run 6 toward unity. From a comparison of the results of Runs 1 to 4, the ratio was shown to depend on operating pressure and moisture content (cellulose/water ratio), but not on the partial pressure of water. Lower operation pressure and moisture content are preferable for greater methane selectivity. The ratio approached unity and thus the following equation should be the stoichiometric reaction of cellulose and water to produce methane and carbon dioxide:

$$(C_6H_{10}O_5)_m + mH_2O \rightarrow 3mCH_4 + 3mCO_2$$

This equation indicates that water functions not only as a solvent but reactant as well. Water is consumed by the hydrolysis of cellulose and regenerated by the degradation of cellulose. Since hydrogen also was obtained as shown in Table 1, with the coproduction of oil and char-like residue, steam-carbon/hydrocarbon reaction ($C + H_2O \rightarrow CO + H_2$) and water-gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) may occur. Methane may thus be formed through the reaction of methanation ($CO + 3H_2 \rightarrow CH_4 + H_2O$).

Operating pressure in Runs 1, 3 and 4 was higher than the supercritical pressure (18 MPa) of water. In Runs 2, 5 and 6, it was less than the supercritical pressure. Water should thus be supercritical for Runs 1, 3 and 4 and in gaseous (steam) for Runs 2, 5 and 6. Although this gasification is possible in either the supercritical or gaseous phase, the reaction rate in the latter is considered to be higher than that in the former. The reaction like steam gasification and/or steam reforming should be possible in case of the gaseous phase.

Methane yield depended only on operating pressure, and not on the partial pressure of water or moisture content. It was highest at around 15 MPa; this being 1.5 times that indicated in the literature. The molecular ratio of methane to carbon dioxide depended on operating pressure and moisture content (cellulose/water ratio), but not on the partial pressure of water. It approached unity with decrease in these parameters. Water was either steam or supercritical, depending on the operating pressure. The reaction rate was probably higher in steam than in supercritical water.

References and Notes

1 D. C. Elliott, R. S. Butner, and L. J. Sealock, Jr., *Res. Thermochem. Biomass Convers.*, **1988**, 696.

2 D. C. Elliott, G. G. Neuenschwander, E. G. Baker, R. S. Butner, and L. J. Sealock, Jr., 25th Intersociety Energy Conversion Engineering Conference, Reno, Nevada, USA, August 1990, Proceedings.

3 L. J. Sealock, Jr. and D. C. Elliott, U. S. Patent 5019135 (1991); *Chem. Abstr.*, **115**, 94724g (1991).

4 "Syokubaikouza," No. 5, ed. by Catalyst Society of Japan, Koudansha, Tokyo (1985), p.57.

5 T. Shirazaki and N. Toudou, "Syokubaichosei," Koudansha, Tokyo (1974), p.79.