CHEMISTRY LETTERS, pp. 1199-1202, 1985.

DIRECT LIQUEFACTION OF WOOD BY ALKALI AND ALKALINE EARTH SALT IN AN AQUEOUS PHASE

Tomoko OGI,* Shin-ya YOKOYAMA, and Katsuya KOGUCHI
National Research Institute for Pollution and Resources,
16-3 Onogawa, Yatabe, Tsukuba, Ibaraki 305

Catalytic effects of various salts of alkali and alkaline earth metals were tested in the direct liquefaction of wood in an aqueous phase without a reducing agent like H_2 or CO. A marked effect of sodium, potassium and calcium salts was observed for the production of heavy oils in more than 50% yields.

Thermochemical conversion like pyrolysis, gasification and liquefaction of lignocellulosic materials into gaseous or liquid fuels has been receiving a recent attention as fossil hydrocarbon supplies are dwindling. Lignocellulosic materials like wood are composed of two chemically different components, that is, the carbohydrate based cellulose and hemicellulose, and aromatic based lignin. Since the heating values of these materials are low owing to a high content of oxygen, an efficient removal of oxygen must be needed to produce a fuel which is competitive with petroleum.

One such process (PERC Process) is that based on the research in late 1960s by Appell and co-workers1) at the Pittsburgh Energy Research Center of the U.S. Bureau of Mines. They demonstrated that solid organic materials, including urban refuse, agricultural wastes, wood and bovine manure, can be converted directly to a liquid resembling heavy fuel oil by reacting them with synthesis gas in the presence of a catalyst such as sodium carbonate. Since then, a great number of works have been reported on direct liquefaction of lignocellulosic materials with H_2 and/or CO in the presence of suitable catalysts.2-5) Recently, Schuchardt et al. have shown that sugar cane bagasse can be liquefied with sodium formate and water,6) and Nelson et al. reported the cellulose liquefaction in an aqueous phase under pressurized nitrogen atmosphere in the presence of sodium carbonate.7)

In the previous papers, the direct liquefaction of wood without reducing agents like H_2 and/or CO was investigated in the presence of K_2CO_3 and Ni_2CO_3,8) and further studies on the effects of pressure, reaction temperature, holding time and wood/catalyst/water ratio were reported.9) The present paper describes the catalytic effects of various alkali and alkaline earth salts on the yields and the properties of heavy oils.

The wood (Konara, *Quercus serrata Thunb.*), characterized in Table 1, was chipped and ground to 80 mesh. Prior to liquefaction, the wood powder was dried at 110 °C under reduced pressure for 24 h.

All experiments were carried out in an autoclave (100 ml). The wood powder

Table 1. Analysis of the Wood

Composition (wt%)			
Holocellulose	Lignin	Alcohol and benzene soluble extracts	Ash
77.89	21.27	2.08	0.38
Elemental analysis (wt%)			
C	H	O[a)]	N
46.65	5.83	47.31	0.21

a) The content of oxygen was determined by difference.

(5.0 g), catalyst (about 2.9 x 10^{-3} mol as alkali or alkaline earth metal) and water (30 ml) were added to the autoclave. After sealing it and flushing with argon, the autoclave was pressurized to a required argon pressure (2.0 MPa). The temperature was raised to 300 °C within 30 min while being stirred and the autoclave was cooled just after the temperature attained to 300 °C. The volume and composition of overhead gas were measured by a gas chromatograph equipped with a Unibeads C column. The autoclave was then opened and the reaction mixture was carefully removed. The heavy oil-like products which coated the autoclave wall were washed off with acetone and the reaction mixture was exhaustively extracted with the same solvent. After the filtration, the filtrate was evaporated from the extract using a rotary evaporator. The heavy oil obtained in this manner was dried under reduced pressure for 30 min at 35 °C. The elemental analysis of heavy oil was made outside the laboratory (Analysis Section of the Fuel Society of Japan) and the oxygen content was calculated by difference.

The yield of heavy oil and the carbon and hydrogen recovery (CHR), the carbon and hydrogen contents in the heavy oil to those in wood, were defined as:

$$\text{Heavy oil yield (\%)} = \frac{\text{Weight of heavy oil}}{\text{Weight of wood}} \times 100 \qquad (1)$$

$$\text{CHR (\%)} = \frac{\text{Weight of C and H in heavy oil}}{\text{Weight of C and H in wood}} \times 100 \qquad (2)$$

All calculations were on moisture and ash free basis.

Table 2 showed the effects of wood/catalyst/water ratio. In comparison with the run without the addition of a catalyst, the yield of heavy oil increased to a great extent by the addition of a catalyst. Two runs marked with asterisk gave the results for searching the reaction conditions leading to higher yield. From Table 2, it can be seen that the catalyst loading has little effect on the yield and CHR in the range of 2-20 wt% (on dry wood basis) under the same reaction conditions.

The results obtained with various catalysts were shown in Table 3. The marked effect of catalysts was also demonstrated. Among potassium and sodium salts, no significant difference was observed on the yield, CHR and the elemental composition of the product oils, excepting the case of NaCl. In the case of NaCl, the yield of heavy oil was quite low and its post-treatment was difficult to deal with due to heterogeneity of heavy oil. From Table 3, we see that alkali and alkaline earth salts except chloride give good catalytic effects on the direct liquefaction of wood.

Table 2. Effect of Wood/Catalyst/Water Ratio

Wood(g)/ Catalyst(g)/ Water(ml)	Heavy oil extracted				
	Yield(%)	CHR(%)	Elemental analysis (%)		
			C	H	O
5/ 0 /30	5.0	7.4	70.90	6.97	22.13
5/0.1/30	21.4	32.1	71.86	6.88	21.26
5/0.5/30	26.2	40.6	74.15	7.18	18.67
5/ 2 /30	24.6	38.8	74.87	7.75	17.38
5/0.2/30* a)	47.6	62.0	62.06	6.33	31.61
5/0.5/30* a)	43.8	58.7	63.85	6.43	29.72

a) K_2CO_3 was used as a catalyst. All runs except those marked with asterisk were performed at 2.0 MPa and 350 °C for 30 min. Runs marked with asterisk were performed at 2.0 MPa and 300 °C for 0 min.

Table 3. Effect of Catalyst

Catalyst	(g)	Heavy oil extracted				
		Yield(%)	CHR(%)	Elemental analysis (%)		
				C	H	O
None	-	22.2	31.4	67.39	6.94	25.67
$CaCO_3$	0.290	39.6	52.8	63.39	6.45	30.16
$Ca(OH)_2$	0.215	48.5	64.1	62.36	6.69	30.95
Na_2CO_3	0.154	50.8	71.1	66.54	6.92	26.54
NaOH	0.119	50.7	70.1	65.82	7.14	27.04
HCOONa	0.198	50.4	66.7	62.93	6.20	30.87
NaCl	0.169	15.9	21.7	64.29	7.03	28.68
K_2CO_3	0.200	47.6	62.0	62.06	6.33	31.61
KOH	0.161	51.0	70.0	64.90	7.34	27.76
HCOOK	0.244	52.1	70.7	64.26	7.07	28.67

Concerning the catalytic effect of alkali metal salts, there has been little description about roles that a catalyst plays in the liquefaction with some exceptions. Appell and co-workers proposed the mechanism for sodium carbonate-catalyzed conversion of carbohydrate to heavy oil in the presence of ambient CO.$^{10)}$

(i) Reaction of sodium carbonate and water with carbon monoxide to yield sodium formate:

$$Na_2CO_3 + 2CO + H_2O \longrightarrow 2HCOONa + CO_2$$

(ii) Dehydration of vicinal hydroxyl groups in a carbohydrate to an enol, followed by isomerization to ketone:

$$\text{-CH(OH)-CH(OH)-} \longrightarrow \text{-CH=C(OH)-} \longrightarrow \text{-CH}_2\text{-CO-}$$

(iii) Reduction of newly formed carbonyl group to the corresponding alcohol with formate ion and water:

$$HCOO^- + \text{-CH}_2\text{-CO-} \longrightarrow \text{-CH}_2\text{-CH(O}^-\text{)-} + CO_2$$

$$\text{-CH}_2\text{-CH(O}^-\text{)-} + H_2O \longrightarrow \text{-CH}_2\text{-CH(OH)-} + OH^-$$

(iv) The hydroxyl ion reacts with additional carbon monoxide to regenerate the formate ion:

$$OH^- + CO \longrightarrow HCOO^-$$

Actually, there exist many side reactions involving decomposition, condensation and cyclization, and the product is a complex mixture of oxygenated compounds. In the present experiment, CO, which was not initially charged, evolved during the reactions and the amounts of CO were almost equivalent mol to catalysts in both cases of Na_2CO_3 and K_2CO_3. Therefore, the reaction mentioned in (i) will proceed without an addition of CO. In the cases of sodium and potassium hydroxides, they can convert easily to their carbonates in the presence of CO_2 as demonstrated below:11)

$$2MOH + CO_2 = M_2CO_3 + H_2O \quad \text{(M=alkali metal)}$$

Since the analysis of gas phase after the liquefaction reveals that CO_2 evolved mainly (about 90 vol% of gas phase), the reaction mentioned above will probably occur under the reaction conditions. It is thus concluded that the formate, carbonate and hydroxide of sodium and potassium behave identically under the reaction conditions. With regard to calcium salts, much remains unknown though it is believed that they contribute the liquefaction through hydrolysis. It is to note that NaCl retards the liquefaction and it suggests that the brined wood is unacceptable for this type of liquefaction.

In summary, wood can be directly and efficiently liquefied in the presence of catalyst under inert gas instead of hydrogen and/or carbon monoxide. Among the catalysts tested, inexpensive alkali and alkaline earth salts such as NaOH, KOH, $Ca(OH)_2$, Na_2CO_3, and K_2CO_3 are sufficient for wood liquefaction. The yield of heavy oil attains to about 50% or more and the CHR exceeds 70%.

References

1) H. R. Appell, Y. C. Fu, S. Friedman, P. M. Yavorsky, and I. Wender, "Report of Investigation 7560," U. S. Bureau of Mines, Pittsburgh (1971).

2) D. G. B. Boocock, D. Mackay, M. Mcpherson, S. Nadeau, and R. Thurier, Can. J. Chem. Eng., 57, 98 (1979).

3) D. G. B. Boocock, D. Mackay, H. Franco, and P. Lee, Can. J. Chem. Eng., 58, 466 (1980).

4) T. E. Walton and W. W. Paudler, Fuel, 60, 650 (1981).

5) R. L. Eager, J. F. Mathews, and J. M. Pepper, Can. J. Chem. Eng., 60, 289 (1982).

6) U. Schuchardt and F. A. P. Matos, Fuel, 61, 106 (1982).

7) D. A. Nelson, P. M. Molton, J. A. Russell, and R. T. Hallen, Ind. Eng. Chem. Prod. Res. Dev., 23, 471 (1984).

8) S. Yokoyama, T. Ogi, K. Koguchi, and E. Nakamura, Liquid Fuels Technology, 2, 155 (1984).

9) T. Ogi, S. Yokoyama, and K. Koguchi, Sekiyu Gakkaishi, 28, 239 (1985).

10) H. R. Appell, "Fuels from waste," ed by L. Anderson and D. A. Tillman, Academic Press, New York (1977), Chap. VIII, pp. 121-140.

11) M. J. Veraa and A. T. Bell, Fuel, 57, 194 (1978).

(Received May 13, 1985)