

COPROCESSING OF CELLULOSIC WASTE AND COAL

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Introduction

Paper and other cellulosic wastes constitute more than half of landfill volumes. These materials could be a significant energy source¹; it is the object of this work to find ways of converting these huge volumes of waste to liquid transportation fuels.

It is well known, of course, that coal can be converted to liquid fuels. There are a number of ways of achieving this. A major route from coal to liquid fuels is by direct liquefaction in the presence of hydrogen or hydrogen donor solvents. Experiments have also demonstrated that cellulosic materials and biomass can be converted to oil in the same way^{2,3}. However, there has been little or no work on the coprocessing of coal and these wastes. We call this route A.

Another way to converting coal to liquids is via the so-called COSTEAM process which involves the treatment of coal with carbon monoxide or synthesis gas ($\text{CO} + \text{H}_2$) in the presence of water and an alkali compound as catalyst^{4,5,6}. Again, it has been demonstrated that cellulosic wastes can be converted to liquids in the same manner^{7,8}. However, as far as we know, there has been no work on coprocessing coals with these wastes via the COSTEAM process, which works particularly well with low rank coals such as lignite and subbituminous coals. Most of our coprocessing experiments are being carried out with cellulosic wastes and these coals. We call this route B.

Experimental

Route A (hydrogen and/or hydrogen donor solvents with a molybdenum catalyst)

Wyodak subbituminous coal, obtained from the Argonne Coal Sample Bank, and ordinary copy paper (6.7% moisture and 7.2% ash) were used in this study. Three grams (either coal, paper or a mixture of both), slurried with 12 g of tetralin and 5000 ppm of $\text{Mo}(\text{CO})_6$ plus 10,000 ppm of sulfur, were charged in a horizontally shaken 45cc microautoclave with an initial hydrogen pressure of 1000 psig. The reactions were carried out at two different temperatures (325°C and 400°C) for one hour with reaction pressures of about 1800 psig and 2300 psig, respectively.

The nonvolatile products were recovered with THF and then filtered through a cellulose thimble. The filtered materials (THF insolubles) were then extracted with boiling THF. The conversion to THF-solubles was calculated from THF insolubles on an maf basis. THF was removed by rotary evaporation and the product was fractionated into pentane-solubles (oil) and pentane-insolubles (asphaltenes). Since, in the case of H_2 -tetralin runs, pentane-solubles include the tetralin, some of which reacted during the reaction and some was lost during the product analysis, only asphaltenes were accurately measured. As a result, the oil and gas fraction was calculated by subtracting the recovered asphaltenes from the total converted. Gases were collected and analyzed by a GC equipped with a Porapak Q column and a 5A molecular sieve

column using a carrier gas with the composition of 8.5% H₂ and 91.5% He.

Route B (CO and H₂O with an alkali catalyst)

Severe mass transfer limitations were experienced in a microautoclave for CO-H₂O runs so that reactions in CO-H₂O environments were carried out in a 300cc autoclave. A total of 8 g of reactants mixed with 24 g of water and 1.02 g of Na₂CO₃ were used with 580 psig (cold) of CO. The reactor was heated to 400°C in about 50 minutes and was held for one hour while stirring at 1400 rpm. Due to the significant amount of water, pressures up to 4200 psig were registered. The reactor was then cooled to below 200°C in 10 minutes. Figure 1 shows a typical history of the temperature and pressure during a run in a CO-H₂O environment.

The same product analysis procedure was employed in Route B runs, except that oil fractions and gas fractions could be measured because the pentane solubles were free of tetralin. The oils were directly calculated from pentane solubles and the gas fraction by subtracting the oils from the oil and gas fraction which was determined from the asphaltene content.

Results and Discussion

Route A (H₂-tetralin system)

Table 1 lists the results at 400°C using a molybdenum catalyst with added sulfur. As expected, conversion of the paper is almost complete. It has been reported that only 90% of a caustic type of lignin was converted under similar conditions with no added catalyst⁹. The conversion of paper yielded only about 10% of high molecular weight asphaltenes with a large yield of oil and gas. Wyodak coal is also converted in high yield but with significant amounts of asphaltenes. Since conversions and yields of oil and gas are very high for paper, the conversion and yield of coal in the coprocessing runs were calculated with the assumption that addition of coal has no influence on paper conversion. As shown in Table 1, the conversion of coal was increased to 91.7% when the 33 wt% of paper was coprocessed, up from 86% of conversion when coal was reacted alone. However, the yield of oil and gas remained unchanged. Addition of paper evidently increased the conversion of coal. Increase in the amount of paper to 50 wt% in the coprocessing does not seem to increase this effect.

It has been proposed that the thermal depolymerization of lignin forms phenoxy radicals, which then cause scission of carbon-carbon bonds in coal⁹. Cellulose in paper can also form phenoxy radicals which may assist the liquefaction of coal in our coprocessing runs. It has also been hypothesized that, at temperatures as high as 400°C, phenoxy radicals polymerize or recombine so that their enhancing effect is minimal⁹. This may help explain the finding that the same oil and gas yield of coal was obtained in the coprocessing as that of coal alone.

Reactions were carried out at a lower temperature (325°C) and the results are listed in Table 2. Even at the lower temperature, paper gave high conversion (88.9%) and high oil and gas yields (77.2%). However, there was a decrease in conversion of coal when the reaction temperature was decreased to 325°C. Both the coal conversion and the yield of oil and gas from the coprocessing run are almost same as those from coal alone at 325°C, suggesting that the effect of paper is small at 325°C. This result is surprising since a synergistic effect of lignin during lignin-coal coprocessing is reported to be the most pronounced in this temperature range⁹.

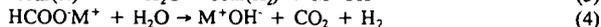
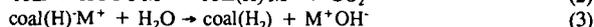
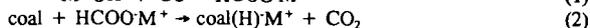
Route B (CO-H₂O system)

The results of runs in CO-H₂O environments with Na₂CO₃ catalysts at 400°C are summarized in Table 3. The paper conversion was almost as high as that in the H₂-tetralin case. However, the product contains more high molecular weight asphaltenes. The same trend is observed for the coal only run in COSTEAM. As stated earlier, there were severe mass transfer limitations in a microautoclave when reactions were carried out in a CO-H₂O environment. For example, the conversion of coal in a microautoclave at 400°C was about 32% in a CO-H₂O environment while that in a 300cc autoclave with stirring was 84%.

It should also be pointed out that the amount of oil (pentane solubles) can be quantitatively measured in CO-H₂O runs since no hydrogen-donor solvent was used. As can be seen in Table 3, most of the product from paper is gas, suggesting the reaction conditions are so severe that most of the liquid product formed light gaseous materials.

Addition of paper to coal provided only a slight increase in coal conversion (~1%). However, the coprocessing of paper with coal decreased the amount of asphaltenes to half of that produced from coal alone and almost doubled the amount of oils from coal. With the CO-H₂O route, the coprocessing of paper and coal yielded higher quality products. It is also possible that coal may, to a certain extent, prevent liquid formed from paper from reacting further to form gases.

It has been proposed that the pathway for conversion in the CO-H₂O system utilizing an alkali catalysts includes a formate intermediate^{4,5}.



Both the formate ion and water supply hydrogen to coal radicals, while reactions (1) and (4) complete the water-gas shift reaction to generate gaseous hydrogen. Table 4 shows the results of gas analyses for the runs listed in Table 3. As can be seen, about 78% of the CO is converted by the water-gas shift reaction to form hydrogen and CO₂ with a small amount of light hydrocarbons.

Since our experiments were carried out in a batch mode, the system pressures at room temperature after reaction were higher than the initial pressure of pure CO (580 psig) due to the water-gas shift reaction (water is condensed at room temperature). From the gas composition data with the final pressure at room temperature, the total conversion of CO can be calculated and is listed in Table 4. The total conversion of CO includes conversion to supply H₂ to coal and a water-gas shift reaction conversion. The difference between the total moles of CO converted and the moles of hydrogen produced gives the moles of hydrogen consumed by the reactants (coal and paper). The moles of consumed hydrogen thus calculated are also listed in Table 4. As can be seen, the total conversions of CO are all about 78%, regardless of the type of reactants. However, more hydrogen is consumed for coal conversion than for paper conversion. An intermediate amount of hydrogen is consumed by the mixture of coal and paper. According to the reaction pathway proposed, one mole of CO₂ should be produced for every mole of CO converted. However, the amount of CO₂ produced is less than the amount of CO converted. Even when the water-gas shift reaction was carried out in the absence of the reactants, the amount of CO₂ produced was smaller than H₂, suggesting that a significant amount of CO₂ is

dissolved in the aqueous phase. In the paper runs, larger amounts of CO₂ were produced than from coal runs, suggesting that a large portion of gas produced from paper is CO₂.

Summary

Based on an exploratory study of coprocessing of paper and subbituminous Wyodak coal, the following conclusions were drawn. A possible desirable effect of paper in coprocessing was observed in both the H₂/tetralin/Mo system and the CO/H₂O/alkali system at 400°C. More specifically, the conversion of coal was increased due to the addition of paper in the H₂/tetralin/Mo system, but the quality of the product seems to be unchanged. However, very little increase in coal conversion was observed when coprocessing in the CO/H₂O/alkali system, while the product quality of coal was significantly improved (more oil and less asphaltenes). No effect of paper was observed at 325°C in the H₂/tetralin/Mo system.

Acknowledgements

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Literature Cited

1. Anderson, L. L. and D. A. Tillman, "Fuels from Waste," p 10, Academic Press, New York, 1977.
2. Mill, I. J. and S. K. Fellows, *Fuel*, **64**, 1246 (1985).
3. Stray, G., P. J. Cassidy, W.R. Jackson, F. P. Larkins, and J. F. Sutton, *Fuel*, **65**, 1524 (1986).
4. Appell, H. and I. Wender, Div. Fuel Chem. Preprints, Amer. Chem. Soc. **12(3)**, 220 (1968).
5. Ross, D. S. and J. E. Blessing, *Fuel*, **57**, 379 (1978).
6. Fu, Y. C. and E. G. Illig, *Ind. Eng. Chem. Process Des. Dev.*, **15**, 392 (1976).
7. Appell, A. P., I. Wender, and R. D. Miller, U.S. Bur. Mines, Tech. Prog. Rep. 25, May 1970.
8. Schuchardt, U. and F. A. P. Matos, *Fuel*, **61**, 106 (1982).
9. Coughlin, R. W. and P. Altieri, *Fuel*, **65**, 95 (1986).

Table 1. Liquefaction in the H₂/tetralin/Mo system at 400°C for 1 hour.

Reactant	Conversion (%)	Asphaltenes (%)	Oil and Gas (%)
paper	98.6	10.2	88.4
coal	86.0	39.9	46.1
coal (50%) + paper (50%)	91.7 ^a	44.0 ^a	47.7 ^a
coal (67%) + paper (33%)	91.7 ^a	46.0 ^a	45.7 ^a

a: conversion and yield with respect to coal.

Table 2. Liquefaction results in H₂/tetralin/Mo system at 325°C.

Reactant	Conversion (%)	Asphaltenes (%)	Oil and Gas (%)
paper	88.9	11.7	77.2
coal	35.9	21.6	14.3
coal (67%) + paper (33%)	37.7 ^a	25.3 ^a	12.4 ^a

a: conversion and yield with respect to coal.

Table 3. Liquefaction results in the CO/H₂O/Na₂CO₃ system at 400°C for 1 hour.

Reactant	Conversion	Asphaltenes	Oil and Gas	Oil	Gas
paper	96.6	15.2	81.4	7.0	74.4
coal	84.2	42.8	41.4	15.1	26.4
coal(50%) + paper(50%)	85.3 ^a	22.9 ^a	62.4 ^a	38.1 ^a	24.3 ^a

a: conversion and yield with respect to coal.

Table 4. Gas compositions after 1 hour of run in CO/H₂O/Na₂CO₃ system at 400°C (initial pressure of CO=580 psig).

reactant	final pressure (psig)	CO	H ₂	CO ₂	CH ₄	C ₂ -C ₆	CO conversion (%)	H ₂ consumption (mole)
paper	950	14.2	37.8	47.1	0.9	0.1	77.1	0.078
coal	863	14.9	37.5	46.3	1.4	0.3	78.0	0.113
coal + paper	913	13.5	38.2	47.0	1.3	0.3	78.5	0.090

Figure 1. Typical heating and cooling for coal conversion (Route B).

