

INFLUENCE OF THE WATER-GAS-SHIFT REACTION ON LOW TEMPERATURE PRETREATMENT OF SUBBITUMINOUS COAL

Soon Chuan Lim, J. Brian Laihart and Edwin N. Givens
University of Kentucky, Center for Applied Energy Research,
3572 Iron Works Pike, Lexington, Kentucky 40511-8433

Keywords: Coal, carbon monoxide, water, alkali promoters

Abstract

In previous studies, we showed that subbituminous coals treated with CO and water in the presence of a base (NaOH, Na₂CO₃) at mild temperatures (300 °C) produced an improved liquefaction feed material. In this reaction coal undergoes significant structural modification as observed by the increased THF and pyridine solubility, lower oxygen content and higher atomic H/C ratio relative to the raw coal. In this paper, we discuss the impact of the water-gas-shift (WGS) reaction on the coal reaction. Strong correlations were found over a wide range of reaction conditions between THF solubility of the pretreated coal and both CO conversion and amount of hydrogen consumed. The effect of various sodium and ammonium salts on the reaction is discussed.

Introduction

Fischer and Schrader,¹ pioneered the liquefaction of coal with CO and water. Appell and Wender² in the late 60's revived interest in this approach as an alternative method for directly producing hydrogen in the liquefaction reactor. This led to the CoSteam process for liquefying low rank coals. Since then, the application of CO and water for liquefying various materials and the effect of added catalysts on these reactions have been widely studied.³ The addition of a strong base to this system significantly improves the conversion of coal to liquid products.⁴ In recent years, CO and water has been used to treat coal to enhancing its conversion during liquefaction and improve the product mix.^{5,6} This treatment results in chemically and structurally modifying the coal to produce an improved feed material.

The chemistry of the WGS reaction and the intermediates involved in the reaction are complex. Various mechanisms and intermediates have been proposed for coal conversion using CO and water.^{7,8} Recently, Horvath et al.⁹ provided evidence for the formation of formate ion at liquefaction temperature when they reacted coal with CO and water at 400 °C in a specially fitted ¹³C NMR spectrometer. At significantly lower temperatures (200 °C and below), King et al.¹⁰ showed that CO reacts rapidly with KOH to quantitatively form potassium formate. They showed that the production of hydrogen from the WGS reaction at these temperatures is catalyzed by the addition of a catalyst precursor such as Mo(CO)₆. In the absence of a suitable catalyst, the formate ion is relatively stable up to 300 °C.¹¹ Above 300 °C formate decomposes mainly to CO₂ and H₂ and partially undergoes dehydration to form CO. From the literature,^{2,4,7} it is evident that the success of liquefaction with CO and water has been attributed to the intervention of the formate ion. In this paper we present results to show the effect of the WGS reaction on the reaction of coal with CO and water at rather mild temperatures at or below 320°C.

Experimental

Coals - Wyodak coal from the Black Thunder (BT) mine in Wright, Wyoming, was ground to -200 mesh, riffled and stored in tightly sealed containers. Ultimate analyses was as follows: carbon, 73.9%; hydrogen, 5.2%; nitrogen, 1.3%; sulfur, 0.6%; oxygen, 19.0%O (by difference). Ash content on a dry basis was 6.12 wt%. All results are expressed as weight percent, moisture and ash-free coal (maf).

Reaction Conditions - Experiments were conducted in a 25 ml micro-reactor by adding, per gram of maf coal, up to 3 g of water and 0.06 to 1.0 mmol of promoter salt (NaOH, Na₂CO₃, NaCl, NH₄NO₃). The reactor was pressurized with CO (300-800 psig) and heated to 250 to 320°C a fluidized sandbath. The reactor was agitated at a rate of 400 cycles/min for periods between 30 min to two hours, and then rapidly quenched to room temperature. Gaseous products were collected and analyzed by gas chromatography. Solid and liquid products were recovered from the reactor using distilled water, filtered, and dried. Water-insoluble materials were separated by extracting with THF in a Soxhlet thimble for 18 hours and drying overnight at 80 °C at 16 kPa. The THF solubles were concentrated by removing excess THF. A 50:1 excess volume of pentane was added and the pentane insoluble material was filtered and dried. Only a very small amount of pentane soluble material was recovered which represented only a small proportion of the overall products, particularly when high CO pressures

were used.⁵ In coal reactions with a promoter and in the absence of CO or at low CO pressures (400 psig and below), soluble humic acids were recovered from the aqueous phase by precipitating the colloidal material with HCl (pH 1-2) followed by centrifugation and drying. The acidified aqueous layer was further extracted with ether. Total mass recovery, on a maf basis, was typically 90% or better at or below 300 °C and between 80-85% at 320°C. THF solubility of the solid products after pretreatment is defined as the proportion of material soluble in THF plus any humic acids, if present.

Results and Discussion

Water-Gas-Shift Reaction. Total CO_x recoveries from coal treatment runs with CO were typically greater than 98% and included unreacted CO, gaseous and dissolved CO₂, and formate ion present in the aqueous phase. For those reactions to which NaOH was added, the concentration of dissolved formate, which was based upon the equivalents of Na present, accounted for 4% of the total CO feed. No correction was made when any of the other salts were used in these reactions. Dissolved CO₂ in the aqueous phase, calculated at ambient temperature following Henry's law, accounted for only 1% of the total CO feed. CO conversions increased with temperature, with the maximum conversion of 34% being observed at 350 °C, which was equivalent to conversion of 7.5 mmol of CO per gram maf coal feed.

For a 20% conversion of CO, the theoretical amount of hydrogen produced from that portion of the CO that was converted to CO₂ via the WGS reaction was equivalent to 4.5 mmol/g maf coal. Addition of a promoter increases CO conversion significantly, but these values are low relative to the thermodynamic equilibrium value. Recovery efficiencies of H₂ were quantitative when coal was absent but decreased sharply in the presence of coal. The missing H₂ presumably was incorporated into the treated product and is reported as H₂ consumption in mg H₂/g maf coal.

Conversions of CO in aqueous solutions containing up to 2 mmol NaOH per 45 mmol CO were determined over a temperature range from 250 to 350 °C for a one hour reaction period (see Table 1). In the absence of NaOH, only 1% of the CO is converted. In the presence of NaOH, conversions increased steadily with temperature. Doubling the reaction time from one hour to 2 hours increased conversion by about 25% at 300 °C. However, under no circumstances were CO conversions equal to those that were reported previously for similar reaction conditions (~80%) attained in this study.⁸

In the presence of coal at 300 °C, 10% CO was converted in 1 hour (see Table 2). This level of conversion was significantly greater than the 1% observed in the absence of coal. When both NaOH and coal were present, 20% of the CO was converted which equalled that observed in aqueous NaOH in the absence of coal. The increase observed with coal, but in the absence of base, suggests that the cationic component in the coal may be acting as a weak promoter. This increase is still much less than observed with added NaOH, since coal added to caustic solution gave no additional CO conversion. The data indicate that reaction time is a strong dependent variable for converting CO. Conversion progressively increased over a period from 30 to 90 min from 12 to 23%, as shown in Table 3. Other salts also promote the WGS reaction. CO conversions in the presence of coal at 300 °C with added sodium carbonate, bicarbonate and chloride were 17, 21 and 16%, respectively. Since CO conversion occurs equally well in the presence of sodium chloride, obviously a basic system is not necessary for initiating CO conversion. Ammonium nitrate appears not to be a significant promoter for CO conversion, possibly because it decomposes at approximately 250 °C.

Coal Reaction. Treating Wyodak coal in CO/NaOH/water at 300 °C results in a 8 to 13 wt% decrease in the amount of solid material, as shown in Table 3. In the absence of CO or at lower CO pressures, a small amount of humic acids are also found in addition to a trace of ether soluble material. Only trace quantities of hydrocarbon gases are produced during the treatment. The major part of the decrease in weight is due to elimination of water and carbon oxides. The sizable increase in THF solubility of the treated material both in THF and pyridine indicates that significant modification has occurred to the coal structure. The solubility behavior of this THF material indicates it is almost completely pentane insoluble. Although the presence of NaOH is not necessary for achieving a reasonably high THF solubility in the water-insoluble product, there is improvement when it is present. However, the absence of CO has a much more dramatic affect on the reaction. The solubility in THF of the water-insoluble material obtained from hydrothermally treating the coal at 320°C in the absence of CO was only 11%. The water-insoluble material from the hydrothermal treatment in the presence of added NaOH at 320 °C was 9% soluble in THF. In the case of the NaOH

treatment 4 wt% humic acids and 1 wt% ether solubles were formed.

The amount of hydrogen that could not be accounted for in the material balances from these various CO treatments is presumably consumed by the water-insoluble product. The amount increased with increasing reaction time as well as temperature. For reaction periods from 30 to 90 min, the level of hydrogen incorporation in the product ranged from approximately 0.4 wt% up to 0.7 wt%, which is consistent with increases reported previously.⁶

Other salts also promote the conversion of CO, as well as produces a water-insoluble material having increased THF solubilities, as shown in Table 2. The THF solubilities of the water-insoluble materials from the sodium carbonate, bicarbonate and chloride promoted reactions were similar in magnitude to the amount of THF soluble material obtained when using NaOH. Ammonium nitrate, however, gave a material that was only 10% soluble. It is not entirely clear why NH_4NO_3 should give a lower THF solubility, even though it decomposes above 200 °C (m.p. 172°C). The hydrothermal reaction with CO should still result in a sizable improvement in the THF solubility of the water-insoluble product.

At high CO pressures, the total amount of coal derived material that is soluble in THF is equal to the THF solubility of the water-insoluble product. In the absence of CO or at low CO pressures, however, the total amount of THF soluble material derived from the coal includes humic acids and ether soluble material. A plot of total THF solubles versus the amount of converted CO from both current, as well as previously reported results, is shown in Figure 1. In these runs, Wyodak coal was treated at different temperatures, at different CO pressures, with different amount of water, and with different salts at different salt concentrations. The plot indicates a strong correlation exists between these variables.

A plot of THF solubility versus H_2 consumption also shows a strong correlation with an apparent intercept that approaches the origin (Figure 2). This parallel between THF solubility and H_2 consumption and the close approach of the H_2 intercept to the origin indicates that addition of hydrogen during treatment of the coal must be highly efficient.

Conclusions. The presence of sodium hydroxide, carbonate, bicarbonate and chloride salts promotes the conversion of CO at temperatures between 250 and 350 °C. Coal also promotes CO conversion but to a lesser extent than the sodium salts. The addition of Wyodak coal to these systems results in a water-insoluble material that is significantly more soluble in THF. Correlations were found between both the level of CO conversion and H_2 consumption and the THF solubility of the water-insoluble product. The close approach of both of these correlations to the origin is an indication of the high H_2 utilization efficiency of this treatment reaction.

Acknowledgement

The financial support of the Commonwealth of Kentucky and the Department of Energy under contract number DOE AC22-91PC91040 is gratefully acknowledged.

References

1. Fischer, F.; Schrader, H. *Brennst. Chem.* 1921, 2, 257. *Chem. Abs.* 1921, 15, 3900.
2. Appell, H.R.; Wender, I. *Preprints - Am Chem. Soc. Div Fuel Chem.* 1968, 12, 3, 220.
3. Oelert, H.H.; Siekmann, R. *Fuel* 1976, 55, 39.
4. Cassidy, P.J.; Jackson, W.R.; Larkins, F.P.; Louey, M.B.; Sakurovs, R.J. *Fuel Process. Technol.* 1986, 14, 231.
5. Lim, S. C.; Rathbone, R. F.; Rubel, A. M.; Givens, E. N.; Derbyshire, F. J. *Energy and Fuels*, 1994, 8, 294
6. Vaughn, S.N.; Siskin, M.; Katritzky, A.; Brons, G.; Reynolds, N.; Culross, C.C.; Neskora, D.R., United States Patent No. 5,151,173; Sept. 29, 1992.
7. Schuchardt, U.; Sousa, M. F. B. *Fuel*, 1986, 65, 669.
8. Elliott, D. C.; Sealock, Jr., L. J. *Ind. Eng. Chem. Prod. Res. Dev.* 1983, 22, 426.
9. Horvath, I. T.; Siskin, M. *Energy Fuels* 1991, 5, 933.
10. King, Jr., A. D.; King, R.B.; Yang, D. B. *J. Am. Chem. Soc.* 1981, 103(10) 2699.
11. Elliott, D. C.; Hallen, R. T.; Sealock, Jr., L. J. *Ind. Eng. Chem. Prod. Res. Dev.* 1983, 22, 431.

Temperature, °C	350	320	320	300	300	300	250	250
CO press, psig	800	800	800	800	800	800	800	800
NaOH Conc, mmols/g maf coal	1	1	Nil	1	1	Nil	1	Nil
Reaction Time, min	60	60	60	120	60	60	60	60
CO _x recovery, mole%	102	100	100	91	96	97	97	98
CO Conv, mol%	34	27	1	19	15	1	5	1

Salt promoter	none	NaOH	Na ₂ CO ₃	NaHCO ₃	NaCl	NH ₄ NO ₃
Salt conc, mmol/g maf coal	-	1	0.5	1	1	1
CO _x recovery, mol%	97	100	99	101	97	99
CO Conv, mol%	10	20	17	21	16	13
CO Conv, mmol/g maf coal	2.0	4.0	3.4	4.0	3.0	2.2
Missing H ₂ , % theoretical	84	86	82	86	51	42
H ₂ Consumption, wt% maf coal	0.33	0.63	0.56	0.60	0.31	0.18
WI ^b Product, wt% maf coal	90	92	93	89	90	88
Solubility of WI in THF, wt%	22	28	32	24	24	10

a. 300 °C, 800 psig CO cold (approx. 20 mmol/g maf coal), 3 g water/g maf coal.
b. WI = water insoluble product

Reaction Time, min	30	60	90
CO _x recovery, mol%	98	100	100
CO Conv, mol%	12	20	23
CO Converted, mmol/g maf coal	2.4	4.0	4.0
Missing H ₂ , % theoretical	70	86	84
H ₂ Consumption, wt% maf coal	0.33	0.63	0.68
WI ^b Product, wt% maf coal	91	92	87
Solubility of WI in THF, wt%	20	28	26

a. 300 °C, 800 psig CO cold (approx. 20 mmol /g maf coal), 1 mmol NaOH/g maf coal, 3 g water/g maf coal
b. WI = water insoluble product

Table 4. Legend for Figures 1 and 2 ^a					
	Promoter Salt	mmol Salt/ g maf coal	CO Pressure, psig	Temp °C	Reaction Time, min
A	NaOH	0.06	300	250	60
B	NaOH	0.5	550	275	60
C	NaOH	0.06	800	250	60
D	NaOH	1.0	800	300	60
E	NaOH	1.0	800	300	30
F	NaOH	1.0	800	300	90
G	NaOH	1.0	800	320	60
H	Na ₂ CO ₃	0.5	800	300	60
I	NaHCO ₃	1.0	800	300	60
J	NaCl	1.0	800	300	60
K	NH ₄ NO ₃	1.0	800	300	60

a. Water added at 3 g/g maf coal.

Fig.1 The Effect of CO conversion on THF Solubility of Treated Coal

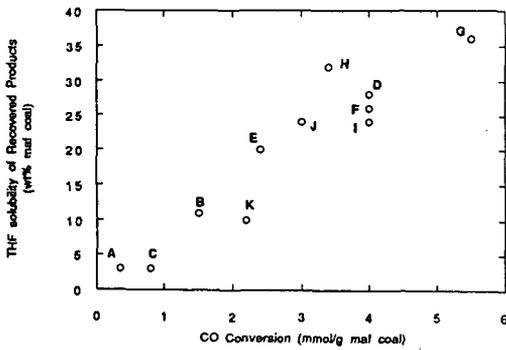


Fig.2 The Effect of Hydrogen Consumption on THF Solubility of Treated Coal

