

PARAMETRIC EVALUATION OF LOW TEMPERATURE CO PRETREATMENT OF
SUBBITUMINOUS COAL

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Abstract

Thermal CO pretreatment of subbituminous coal in aqueous media at 250-300°C produces a water-insoluble product having a higher hydrogen content, lower oxygen content, increased solubility and higher volatility. Both the conversion and water-gas-shift (WGS) reactions are catalyzed by OH⁻, CO₃²⁻ and HCO₃⁻, although under some conditions significant WGS reaction is not accompanied by comparable modification to the coal structure. Turnover numbers in the NaOH-catalyzed WGS reaction in excess of 100 were observed. Thermal, optical and chemical characterization data on the modified coal is presented. Improved liquefaction conversion and oil yields of the pretreated material were observed relative to the corresponding untreated coal.

Introduction

Earlier work has shown that pretreating coal can impact on its performance in subsequent processing to provide higher yields and better product slates.¹ Pretreatment can contribute toward lowering the processing costs of converting coal to liquid fuels. The application of CO in conversion of coal in aqueous media was pioneered by Fischer and Schrader² and later revived by Appell and co-workers.³ They found that the CO/H₂O system is effective for converting low-rank coals to liquid products via the WGS reaction along with removal of heteroatoms (particularly oxygen).⁴

Previously, we reported that pretreating a subbituminous coal with CO in an aqueous media at 300°C produces a material which has a higher atomic H/C ratio, lower oxygen content, higher pyridine solubility and a liquefaction reactivity comparable to untreated coal.⁵ As an extension of the preceding study, the effect of temperature, NaOH concentration and CO pressure on pretreatment was evaluated and the effect of adding different salts (NaOH, Na₂CO₃, NaHCO₃) on the reaction was studied. In addition, the liquefaction of the pretreated coal was determined.

Experimental

Coals - Ultimate analyses of Clovis Point and Black Thunder Wyodak coals, that had been ground to -200 mesh, riffled and stored in tightly sealed containers, are given in Table 1.

Procedures - Microautoclave coal pretreatment and liquefaction experiments were performed in 25 ml reactors which, after loading and pressurizing, were submerged in a fluidized sand bath at reaction temperature and agitated vertically at a rate of 400 cycles per minute. After quenching, gaseous products were collected and analyzed. In coal pretreatment experiments solid and liquid products were scrapped and washed from the reactor with water and then filtered and air dried at 4°C. These products were separated into the THF insoluble, THF soluble/pentane insoluble (PA+A), and pentane soluble fractions. The difference between the weight of coal charged to the reactor and the sum of the THF insolubles plus PA+A is reported as oil+gas+water (OGW).

In the liquefaction experiments solid/liquid products were separated into THF insoluble, PA+A, and pentane soluble (oil+water) fractions. Conversions and product yields are reported on a moisture and ash free (maf) basis assuming complete recovery of ash in the THF insolubles. Further details of the experimental work-up procedure have been reported elsewhere.⁵ Larger scale coal pretreatments were performed in a 1-liter stirred autoclave by adding 80 ml. of water to the reactor which was sealed and pressurized with CO to 800 psig. The reactor was heated to $310 \pm 5^\circ \text{C}$ and a slurry containing 150 g dry coal in an additional 120 ml water, containing the required amount of NaOH or Na_2CO_3 , was injected into the hot reactor. After approximately 7-8 minutes, the temperature of the reactor had returned to the reaction temperature. After 1 hour the reactor was cooled and depressurized and the solid product was removed from the reactor and separated in the manner described above.

Analysis - Optical microscopic techniques are discussed elsewhere.⁵ Both as-received and CO-pretreated Black Thunder coal were analyzed simultaneously by thermogravimetry/differential thermal analysis/differential thermogravimetry (TG/DTA/DTG) on a Seiko TG/DTA 320. The conditions were: heating rate of $10^\circ\text{C}/\text{min}$ from ambient temperature to 120°C ; a 15 min hold at 120°C to remove surface moisture; a heating rate of $10^\circ\text{C}/\text{min}$ from 120°C to 600°C ; He sweep rate of 200 ml/min; and constant sample volume weighing approximately 20 mg.

Results and Discussion

CO Pretreatment - Experiments to define the effects of temperature, CO pressure, and NaOH concentration on conversion and product distribution were organized in a 2^3 factorial format as shown in Table 2. The experiments were organized around low and high levels for each of the independent variables, i.e., temperatures of 250°C and 300°C , starting CO pressures of 300 and 800 psig, and NaOH molar concentrations of 0.021 and 0.33. Results from these experiments show that the yield of THF soluble product is substantially higher at 300°C than at 250°C , irrespective of the initial CO pressure and NaOH concentration. From the magnitude of the THF conversions at 300°C , there appears to be an interactive effect of NaOH concentration and CO pressure. THF conversions for three of these four runs are in excess of 23 wt% while the other at 300 psig CO and 0.021M NaOH gave a somewhat lower THF conversion. The magnitude of the THF soluble products at 250°C is quite small but uniform and fail to show any definite trend in their distribution. The effectiveness of the CO-pretreatment at the lower NaOH concentrations is encouraging since it shows that the base concentration can be reduced.

The results observed earlier⁵ plus those reported here show that humic acids (HA) are observed only at 300°C and at CO pressures (cold) of 400 psig or less. Likewise, at 300 psig CO, HA is favored by increasing NaOH concentration. This agrees with previous studies which showed that the HA yield is dependent primarily on reaction temperature, pH and reaction time.⁶ HA appears to diminish as PA+A increases and its disappearance parallels an increase in the H/C ratio in the water insoluble product.

In most cases, especially at higher CO pressures, coal dissolution reports to the PA+A fraction rather than the OGW fraction. However, as our previous results on Clovis Point Wyodak coal showed, treatment at low CO pressures, such as in the presence of 200 psig CO or in the absence of CO, i.e., in N_2 , results in formation primarily of OGW

product.⁵ The resulting pretreated products have lower H/C ratios, i.e., 0.72 and 0.75 in the presence of 200 psig CO and in the absence of CO, respectively, relative to coal, which has a H/C ratio of 0.83. The H/C ratio for the 800 psig CO-pretreated product was 0.92. The products prepared at low CO pressures are significantly more intractable with pyridine compared to products prepared at 800 psig CO. The pyridine extract yields (wt. maf basis) were 4% for untreated coal, 6% for coal treated in the absence of CO (in N₂), 9% for coal treated with 200 psig CO, and 60% for coal treated with 800 psig CO. Optical microscopy showed that the coal treated at 800 psig CO pressure underwent significant modification relative to the original coal.

In general, temperature appears to have little impact on the extent of the WGS reaction. The maximum WGS conversion obtained in this series was 88%, which experimentally confirms that the reaction is not thermodynamically limited. However, CO conversion appears to plateau at approximately 50% in the higher temperature and pressure experiments. Extending the reaction period to two hours increased CO conversion by only 5%. Similar limitations on CO conversions have been reported in the reaction with NaOH to make sodium formate.⁷

Hydrogen that is generated by the WGS reaction and then apparently consumed in the reaction is higher at 800 psig CO (18-20 mg/g maf coal) than observed at 300 psig (ca. 10 mg/g maf coal). This disappearance or "consumption" of hydrogen that occurs at 250°C has not been correlated to either coal reconstruction or an increase in the H/C ratio in the product. We are investigating whether this hydrogen is being "stored" in one of the WGS reaction intermediates (e.g. Na formate, formic acid, etc.) as proposed by Elliott⁸ and others.⁹ Unquestionably, base catalyzes the disappearance of CO and formation of H₂ by the WGS reaction. The molar ratio of CO converted per mole of NaOH initially present in the experiments with 0.021M NaOH varies between 96 and 183:1, while for those experiments at 0.33M the ratio varies from 9 to 12:1. Although WGS conversions are higher at the lower pressures, turnover numbers increase at higher CO pressures.

Comparative conversions and product distributions from CO pretreatment in 0.33M solutions of NaOH, Na₂CO₃, and NaHCO₃ are shown in Table 3. Even though the pH of the starting NaHCO₃ (pH ~ 8.5) solution is significantly lower than that of the NaOH or Na₂CO₃ solutions (pH >13), they all catalyze the WGS reaction to a similar extent. Likewise, the relative THF solubilities as well as the optical microscopic properties of the water insoluble products are quite similar. Clearly, HCO₃⁻ is effective in promoting both the WGS reaction and the corresponding pretreatment of coal.

The volatilization of the water insoluble product is considerably higher than for the coal itself as shown by TGA (Figure 1a). In addition, the temperature of maximum volatilization decreases from 442°C for untreated coal to 432°C and 429°C for Na₂CO₃ and NaOH treated samples, respectively (Figure 1b). This suggests a reduced molecular weight distribution.

Liquefaction - CO-pretreated coals gave better THF conversion than untreated coal under mild liquefaction conditions (see Table 4). The increased conversion from both the NaOH and Na₂CO₃ catalyzed water insoluble products reported almost exclusively to the PA+A fraction. Catalyzed liquefaction in the presence of both NiMo/alumina (Shell 324)

and nanometer size iron oxide (Nanocat[®]) provided even sharper differentiation of the pretreated coal versus the untreated coal as shown in Table 5. The NiMo catalyst added at a level of 0.1 wt% Mo on dry coal increased oils+water conversion by 10 wt% and iron oxide added at a level of 1 wt% on dry coal increased conversion by 5 wt% and oils+water conversion by 7 wt%. All of the pretreated coal runs show a decrease in gases production and a lower H₂ consumption than for untreated coal. Presumably, the lower oxygen content in the pretreated coal would reduce the water portion of the oils+water fraction.

Conclusions

Temperature is the dominant independent variable in the CO-pretreatment of subbituminous coal with a significant interactive effect at 300°C between CO-pressure and NaOH concentration. NaOH concentrations as low as 0.021M were found to be effective in promoting both the WGS reaction and in pretreating the coal. NaHCO₃ was found not only to be effective in promoting the WGS reaction but also in giving water-insoluble product that is comparable to water-insoluble product from NaOH and Na₂CO₃ catalyzed CO-pretreatment. The volatility of the product increases versus untreated coal. In addition, the temperature decreases at which maximum volatilization occurs. Catalyzed liquefaction of CO-pretreated coal gives increased THF conversion and oil yield plus better H₂ utilization compared to untreated coal.

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	Clovis Point	Black Thunder
Composition, wt% maf		
Carbon	71.0	73.9
Hydrogen	4.9	5.2
Nitrogen	1.3	1.3
Sulfur	1.1	0.6
Oxygen, by difference	21.7	19.0
Ash, wt% dry coal	6.94	6.12
H/C Ratio	0.83	0.84

Condition ^b	LLL	HLL	LHL	HHL	LLH	HLH	LHH	HHH
Temp, °C	250	300	250	300	250	300	250	300
CO, psig ^c	300	300	800	800	300	300	800	800
NaOH, mol/l	0.02	0.02	0.02	0.02	0.33	0.33	0.33	0.33
THF Conv	5	16	6	23	7.4	26	9	32
PA+A	3	8	2	18	7.5	18	9	29
Humic Acids	-	1	-	-	-	4	-	-
O+G+W	2	7	4	5	-	4	-	3
WGS Shift ^d	58	56	36	41	n.a. ^e	88	45	45
H ₂ Consump, mg/g maf coal ^f	10	9	18	20	n.a.	6	20	20

a. 25 ml reactor; 1 hour reaction time; 2 grams dry coal; 20-22 wt% moisture; 3.25 g water/g maf coal; all conversions and yields based upon maf coal.

b. L = low, H = high; sequence: temperature, CO pressure, NaOH concentration.

c. CO pressure (cold).

d. $\text{WGS Conv}(\%) = \frac{[\text{CO}_{in}] - [\text{CO}_{out}]}{[\text{CO}_{in}]}$

e. n.a., not available

f. $\text{H}_2 \text{ Consump (mg/g maf coal)} = [\text{H}_2(\text{from WGS})] - [\text{H}_2(\text{final})]$

Catalyst	NaOH	Na ₂ CO ₃	NaHCO ₃
Coal ^b	BT	BT	CP
THF Conv.	32.0	37.2	36.0
Product Distribution, wt% maf coal			
PA+A	29.0	29.5	31.1
Oils+Gas+Water	3.0	5.7	4.9
WGS Reaction ^c	45	47	51
H ₂ Consump, g/g maf coal ^d	20	22	24
Pyridine Solubles ^e	60	56	n.a. ^f
a. Conditions: 800 psig CO with 5.5 ml of 0.33M Na salt solution, 300°C, 1 hr. b. BT is Black Thunder Wyodak coal; CP is Clovis Point Wyodak coal. c. $WGS\ Conv(\%) = ([CO_{in}] - [CO_{out}]) / [CO_{in}]$ d. $H_2\ Consump\ (mg/g\ maf\ coal) = [H_2(\text{from WGS})] - [H_2(\text{final})]$ e. Wt% of water-insoluble product. f. n.a. not available			

	Na ₂ CO ₃	NaOH	Untreated
THF Conversion	80.4	80.4	74.7
Product Distribution, wt% maf coal			
PA+A	53.4	50.6	43.9
Oil+water	24.3	30.0	26.1
Gases	2.7	2.0	4.7
H ₂ Consump, mg/g maf coal	17.8	18.6	21.4
Total H ₂ Consump, mg/g maf coal ^b	27.3	27.1	34.2
a. 400°C, 2 g dry coal/2 g tetralin, 1 hr, 800 psig H ₂ (cold), 25 ml reactor. b. Includes hydrogen from tetralin solvent.			

Table 5. Catalyzed Liquefaction of CO-Pretreated Coal ^a				
	Pretreated Coal ^b		Untreated Coal	
	Shell 324 ^c	Nanocat ^d	Shell 324 ^c	Nanocat ^d
Added Fe, wt% dry coal	-	1.0	-	1.0
Added Mo, wt% dry coal	0.1	-	0.1	-
THF Conv, wt% maf coal	84	86	83	81
Product Distribution, wt% maf coal				
PA+A	43	52	49	50
Oils+Water	39	32	29	25
Gases	2	2	5	6
Total H ₂ Consump, mg/g maf coal ^e	31	29	34	34

a. Liquefaction conditions: 400°C, 2 g dry coal/2 g tetralin, 1 hr, 800 psig H₂ (cold), 25 ml reactor.
b. Pretreated coal prepared in 1-liter autoclave with 0.19M Na₂CO₃ (3.7 wt% maf coal), 800 psig CO, 310±5°C.
c. NiMo/alumina (2.8 wt% Ni, 12.4 wt% Mo) ground to -100 mesh; dimethyldisulfide added to provide a S/added metal(s) (mol/mol) ratio of 2.
d. 63 wt% Fe.
e. Includes hydrogen from tetralin solvent.

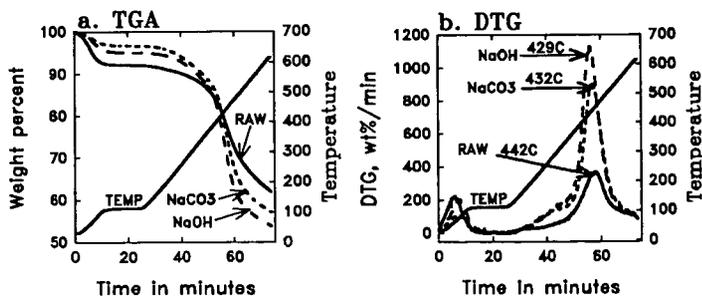


Figure 1a,b. Thermal analysis of CO-pretreated coals.