

## THE EFFECT OF MILD ALKYLATION PRETREATMENT ON LIQUEFACTION REACTIVITY OF ARGONNE COALS

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### INTRODUCTION

Much of the recent research in direct coal liquefaction seeks to develop methods for dissolving coal at low reaction severity (perhaps defined as temperatures below 350 °C and pressures of 1000-1500 psig). Researchers at the Pittsburgh Energy Technology Center (1), the North Dakota Energy Research Center (2), Carbon Resources, Inc. (3), and the Colorado School of Mines (4) have investigated various methods for improving coal reactivity and liquid yields at mild reaction conditions. These studies showed that coal can be readily converted to THF soluble products via selective chemical attack rather than thermal bond scission, but that the rate and extent of coal dissolution at mild conditions is strongly dependent upon intrinsic coal reactivity. Thus the problem of optimizing low severity liquefaction performance becomes one of maximizing coal reactivity at these conditions.

The objective of this paper is to describe our efforts to improve intrinsic coal reactivity using mild acid-catalyzed alkylation as a pretreatment prior to liquefaction. The basis for this work derives from studies by Sternberg (5), Larsen (6), Sharma (7), and others where alkylation was utilized as a method for rendering coal soluble in THF or toluene to aid in structural analysis. Results from Sharma's work are particularly pertinent, since they demonstrate the ability to alkylate coal using alkyl alcohols rather than exotic and expensive chemical reagents such as tetrabutylammonium hydroxide, aluminum trichloride, methyl iodide, etc. Limited work has been reported which relates increased solvent solubility of alkylated coal to enhanced liquefaction reactivity. Schlosberg et al. (8) measured the reactivity of mildly alkylated Wyodak subbituminous and Illinois #6 bituminous coals in tetralin at 427 °C, 1500 psig hydrogen pressure and 130 minutes reaction time. A 10-21 wt% (MAF and alkyl group-free basis) increase in cyclohexane soluble conversion was noted for the alkylated coals.

### EXPERIMENTAL PROCEDURE

Pocahontas low volatile bituminous coal, Illinois 6 high volatile bituminous coal, Wyodak subbituminous coal, and Beulah-Zap lignite from the Argonne Premium Sample Bank were used as feed coals in these experiments. Ultimate analyzes for these coals are listed in Table I.

Table II summarizes the alkylation reaction conditions studied. Each experiment was performed at ambient conditions by suspending 5 g of coal in 40 cm<sup>3</sup> of alkyl alcohol and 0.1 cm<sup>3</sup> of concentrated H<sub>2</sub>SO<sub>4</sub> catalyst. After the prescribed reaction time, remaining alcohol was removed by roto-evaporation followed by vacuum drying (50 °C, 24 hrs.). Untreated coal samples were vacuum dried at the same conditions before liquefaction. Carbon analyses were performed on each alkylated coal sample using a Carlo-Erba model 1106 CHN analyzer

to measure the extent of alkylation as computed from the following formula:

$$\text{Extent of alkylation} = \frac{C_3 - C_1}{C_2 - C_3} \times 100$$

(g alkyl group/100 g MAF coal)

where:  $C_1$  = wt% carbon (MAF basis) in untreated coal  
 $C_2$  = wt% carbon in alkyl group  
 $C_3$  = wt% carbon (MAF basis) in alkylated coal

Liquefaction reactivity experiments were conducted in a 20 cm<sup>3</sup> tubing bomb reactor attached to an agitator and immersed in a fluidized sandbath. Table III lists reaction conditions used in these runs. A non-hydrogen donor vehicle (1-methylnaphthalene) and a hydrogen donor vehicle (9,10-dihydrophenanthrene) were used as solvents (2/1 solvent/coal ratio). Coal conversion was monitored using tetrahydrofuran (THF) extraction data corrected for the intrinsic THF solubility of untreated and alkylated coals.

Solubility measurements were conducted at ambient conditions and consisted of: 1) sonicating the liquid products from the tubing bomb reactor in excess THF, 2) centrifuging the mixture, and 3) decanting THF-soluble products and excess THF from the THF-insoluble residuum. This procedure was repeated at least two times or until no additional THF-insoluble products were recovered. The THF insolubles were vacuum-dried (100 °C, 24 hrs) to remove residual THF, weighed, and finally ashed. Coal conversion to THF soluble products was computed as follows:

$$\text{Coal conversion} = \frac{M_f - M_p}{M_f} \times 100$$

(wt% MAF basis)

where:  $M_f$  = mass of MAF THF-insoluble coal charged

$M_p$  = mass of MAF THF-insoluble products recovered  
 (corrected to satisfy the ash balance)

Photoacoustic Fourier Transform Infrared Spectroscopy (PAFTIR) was used to monitor functional group changes within the coal resulting from alkylation. The photoacoustic technique allows direct measurement of powdered solid state spectra without errors caused by low transmittance signals or variations in surface morphology. PAFTIR spectra generally measure solid properties to depths of about 40 angstroms.

## RESULTS AND DISCUSSION

### Alkylation Studies

Experiments were completed to study the effects of coal rank, alkyl group size, reaction time, and acid catalyst concentration on the extent of coal alkylation. Results from several of these runs are shown in Table IV. As mentioned earlier, all pretreatment studies were conducted at ambient temperature and pressure. The extent of alkylation increased with decreasing coal rank and roughly in proportion to each coal's oxygen content. As discussed later, this observation can be attributed to O-alkylation at phenolic and carboxylic sites in the coal. The extent of alkylation for Wyodak coal was less than 1.0 alkyl groups/100 carbon atoms using methanol or ethanol, but increased dramatically with n-propanol, n-butanol, or isobutanol. Other experiments using higher alcohols suggested that no

significant improvement in the extent of alkylation would be achieved over that obtained with n-propanol.

Approximately 50% of the ultimate extent of Wyodak coal alkylation was achieved in 30 minutes time, suggesting that highly reactive phenolic and carboxylic sites in the coal can be alkylated very quickly. The extent of alkylation increased with increased acid concentration below about 1.0 vol%. Higher acid concentrations had little effect on the extent of alkylation. Thus, it appears possible to mildly alkylate coal by varying the alkyl alcohol, reaction time, and acid concentration used.

#### Liquefaction Reactivity Studies

To study the effect of mild alkylation on liquefaction reactivity, samples of the four Argonne coals propylated for 3 hours with 1.0 vol% sulfuric acid catalyst were liquified in 1-methylnaphthalene solvent at low severity reaction conditions. Conversion results for these runs are summarized in Figure 1. Data for the corresponding untreated Argonne coals are included in this figure for ease of comparison. Propylation of each coal enhanced conversion to THF soluble products, although the effect increased dramatically with decreasing coal rank. A rough correlation was noted between the extent of propylation and improvement in liquefaction reactivity.

Figure 2 shows results from a series of low severity experiments using Wyodak coal which was alkylated with methanol, ethanol, n-propanol, n-butanol, and isobutanol (3 hrs, 1.0 vol% acid). These data suggest only a slight effect of alkyl group chain length on reactivity enhancement indicating that cheaper, commodity alcohols such as methanol may be used successfully as alkylating agent. This result indicates the potential for considering mild alkylation pretreatment on a larger process scale, although net methanol consumption must be better estimated before costs associated with alkylation pretreatment can be determined.

Finally, Figure 3 shows the effect of reaction temperature on the liquefaction reactivity of methylated (3 hrs, 1.0 vol% acid) and untreated Wyodak coals using DHP solvent. Clearly, mild alkylation pretreatment enhances reactivity over a range of conversion levels. This result is significant since it shows that mild alkylation may be a beneficial pretreatment even at conversion levels of commercial interest.

#### PAPTIR Studies

In an attempt to begin studying the reaction mechanisms governing our mild alkylation process, we analyzed each untreated and alkylated coal using Photoacoustic Fourier Transform Infrared Spectroscopy. Figure 4 shows the subtractive spectrum (alkylated coal spectrum minus untreated coal spectrum) for propylated Wyodak coal (3 hrs, 1.0 vol% acid). Several important features of this spectrum can be identified: 1) reduced O-H stretching in the 3200-3600  $\text{cm}^{-1}$  region, 2) increased aliphatic C-H stretching between 2800 and 3000  $\text{cm}^{-1}$ , 3) appearance of the C=O ester stretch near 1700  $\text{cm}^{-1}$ , 4) disappearance of the C=O carboxylate stretch near 1550  $\text{cm}^{-1}$ , and 5) appearance of C-O aliphatic and aromatic stretches near 1000  $\text{cm}^{-1}$ .

These observations are consistent with the dehydration and esterification reactions shown in Figure 5. Both reactions act to reduce hydrogen bonding within the coal structure which may have a direct positive impact on liquefaction reactivity. More indirectly,

these reactions lower the concentration of OH species in coal-derived products and hence, reduce the extent of retrogressive condensation via ether bridge formation. Reducing production of THF-insoluble condensation products increases the net THF-soluble coal conversion measured during the liquefaction experiment. What is unknown at this point is why such a small extent of reaction (perhaps less than 20% of the OH groups are typically alkylated) results in significant reactivity enhancement. None of the spectra collected have shown any significant evidence of C-alkylation.

#### SUMMARY AND CONCLUSIONS

Acid-catalyzed alkylation pretreatment of four Argonne coals using alkyl alcohols has been investigated as a method for improving liquefaction reactivity. The extent of alkylation increased with decreasing coal rank and, to some extent, increasing alkyl group size. Infrared spectroscopic studies of the treated and untreated coals indicated that alkylation occurred at phenolic and carboxylic sites within the coal, but no evidence of C-alkylation was noted. Mild alkylation pretreatment improved liquefaction reactivity for each coal studied over a range of reaction severity. The improvement in liquefaction reactivity correlated roughly with the extent of alkylation achieved.

#### ACKNOWLEDGEMENT

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Table I  
 ULTIMATE ANALYSIS OF FEED COALS

Wt% Dry Basis	Illinois #6	Pocahontas #3	Wyodak	Beulah-Zap
Carbon	65.7	86.7	68.4	65.9
Hydrogen	4.2	4.2	4.9	4.4
Nitrogen	1.2	1.3	1.0	1.0
Sulfur	4.8	0.7	0.6	0.8
Oxygen	8.6	2.3	16.3	18.2
Ash	15.5	4.8	8.8	9.7
Coal Rank	HVB	LVB	Subbit.	Lignite

Table II  
 ALKYLATION REACTION CONDITIONS STUDIED

Temperature: ambient (approx. 25 °C)  
 Pressure: ambient (approx. 0.85 atm)  
 Reaction Time: 0.5 - 24 hours  
 Alkylating Agent: methanol, ethanol, n-propanol, n-butanol, isobutanol  
 Catalyst: sulfuric acid (0.1 - 3.0 vol%)

Table III  
 LIQUEFACTION REACTION CONDITIONS STUDIED

Temperature: 315 °C, 350°C, 400°C  
 Pressure: 65 atm (initial, cold)  
 Reaction Time: 30 minutes  
 Feed gas: hydrogen  
 Solvents: 1-methylnaphthalene, 9,10-dihydrophenanthrene  
 Solvent/Coal weight ratio: 2/1

Table IV  
RESULTS OF AMBIENT ALKYLATION PRETREATMENT EXPERIMENTS

Coal*	Alcohol	Time (hrs.)	Acid Conc. (vol%)	Extent of Alkylation (groups/100 C atoms)
Ill.	n-propanol	3.0	1.0	1.2
Poc.	n-propanol	3.0	1.0	0.7
Wyo.	n-propanol	3.0	1.0	3.8
B-Z.	n-propanol	3.0	1.0	2.7
Wyo.	methanol	3.0	1.0	0.7
Wyo.	ethanol	3.0	1.0	0.6
Wyo.	n-butanol	3.0	1.0	3.9
Wyo.	isobutanol	3.0	1.0	3.7
Wyo.	n-propanol	0.5	1.0	2.5
Wyo.	n-propanol	1.0	1.0	2.9
Wyo.	n-propanol	6.0	1.0	4.3
Wyo.	n-propanol	24.0	1.0	4.6
Wyo.	n-propanol	3.0	0.1	0.6
Wyo.	n-propanol	3.0	0.5	1.0
Wyo.	n-propanol	3.0	2.0	3.6
Wyo.	n-propanol	3.0	3.0	4.0

\* Ill. = Illinois #6  
Poc. = Pocahontas #3

Wyo. = Wyodak  
B-Z = Beulah-Zap

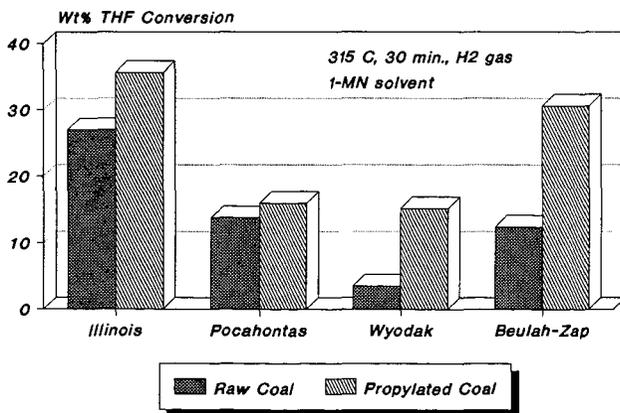


Figure 1. Effect of Propylation on Argonne Coal Liquefaction Reactivity at Low Severity Conditions

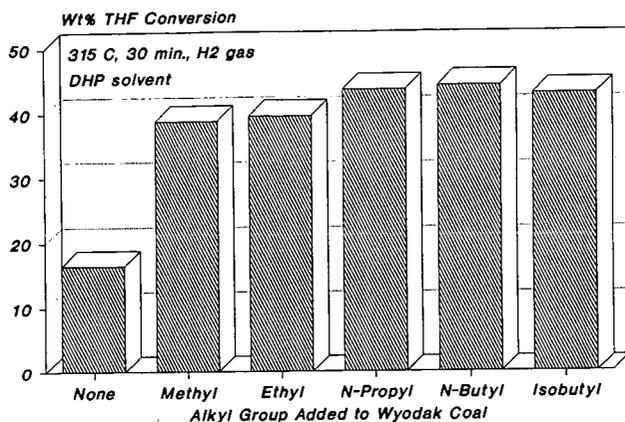


Figure 2. Effect of Alkyl Group Addition on Low Severity Wyodak Coal Liquefaction Reactivity

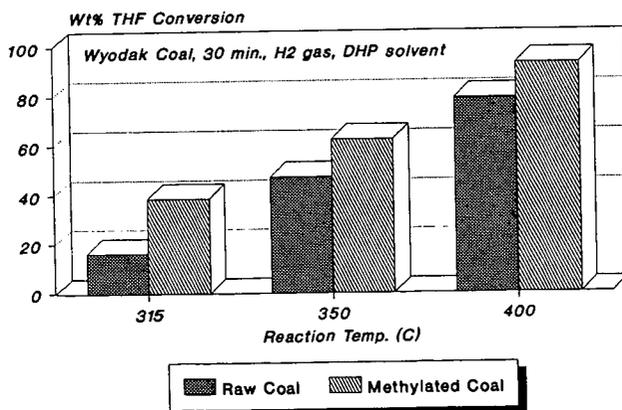


Figure 3. Effect of Reaction Temperature on Liquefaction Reactivity of Methylated and Untreated Wyodak Coal

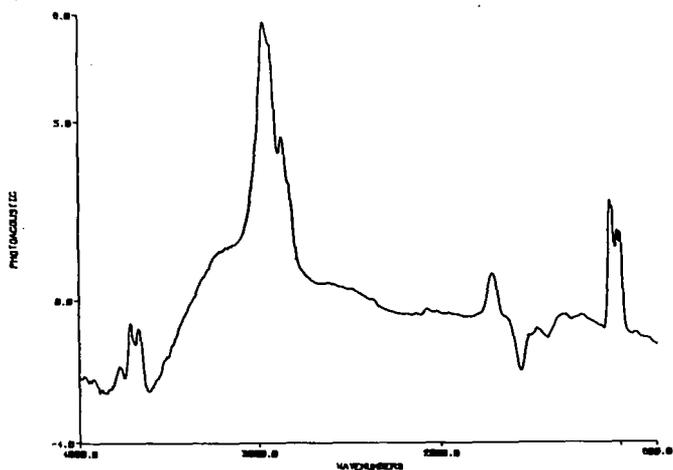


Figure 4. Subtractive Spectrum of Propylated Wyodak Coal Collected Using Photoacoustic Fourier Transform Infrared Spectroscopy

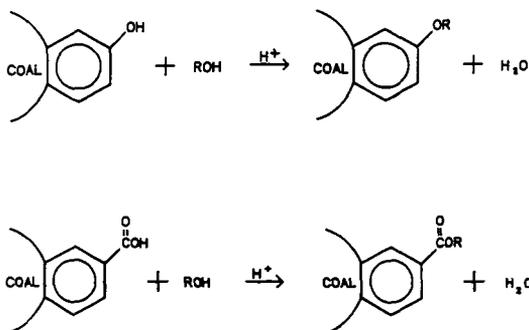


Figure 5. Phenolic Dehydration and Carboxylic Acid Esterification Reactions Occurring During Mild Alkylation Pretreatment