

MILD COAL PRETREATMENT TO ENHANCE LIQUEFACTION REACTIVITY

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ABSTRACT

This paper reports results from an on-going process development study in which coal is converted to liquid products at relative mild reaction conditions. The process consists of three main steps: 1) mild pretreatment of the feed coal at ambient conditions using methanol (or other common organic solvent) and a trace amount of hydrochloric acid to enhance dissolution reactivity and dry the coal, 2) low severity thermal dissolution to obtain a very reactive coal-derived residual intermediate product amenable to upgrading, and 3) catalytic upgrading of the residual products to distillate liquids. We have found that mild pretreatment of Wyodak subbituminous coal using methanol/HCl can provide an improvement in THF conversion of greater than 30 wt% at 350° C reaction temperature. Possible explanations for the observed reactivity enhancement include mild alkylation at oxygen sites in the coal's organic phase, leaching of selected elements from the coal's mineral matter phase, or formation of chlorinated species such as $FeCl_3$, which are known to be active coal dissolution catalysts.

INTRODUCTION

Much of the recent research in direct coal liquefaction seeks to develop methods for dissolving coal at low reaction severity (defined as temperatures below 350° C and pressures of 1000-1500 psi). The incentives for developing a viable low severity liquefaction process are numerous; they include: 1) reduced hydrocarbon gas production resulting in reduced feed gas consumption and enhanced hydrogen utilization efficiency, 2) suppressed retrogression of primary coal dissolution products resulting in enhanced distillate and residuum product quality, 3) production of high boiling residuum which is less refractory and thus more amenable to catalytic upgrading in a conventional second-stage hydrocracker, 4) substitution of less expensive off-the-shelf vessels, piping, valves, pumps, etc. in place of expensive, custom-designed units, and 5) less severe slurry handling and materials of construction problems as a result of lower operating temperatures and pressures.

Researchers at several locations including the Pittsburgh Energy Technology Center (1), the University of North Dakota Energy and Environmental 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 tetrahydrofuran (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 conversion becomes one of maximizing coal reactivity at these conditions.

The objective of this paper is to present recent experimental data in which mild chemical pretreatment using methanol or other common organic solvent and hydrochloric acid is used as a method to improve intrinsic coal reactivity at low reaction severity. The original basis for this work derives from studies by Sternberg (5), Liotta (6), Sharma (7) and others where alkylation was used as a method for rendering coal soluble in THF or toluene to aid in structural analysis. Sharma's work demonstrated the ability to mildly alkylate coal using alkyl alcohols. Limited work has been reported in which the liquefaction reactivity of alkylated coals has been studied. Schlosberg et al. (8) measured the reactivity of alkylated Wyodak subbituminous and Illinois #6 bituminous coals in tetralin at 427° C, 1500 psi hydrogen pressure and 130 min. reaction time. A 10-21 wt% (maf and alkyl group-free basis) increase in cyclohexane conversion was noted for the alkylated coals.

EXPERIMENTAL PROCEDURE

The entire suite of eight coals from the Argonne Premium Coal Sample Bank was used as the source of feed coals for this study. Ultimate analyses for these coals are listed in Table I. Coal samples were stored under argon in sealed ampules prior to pretreatment and liquefaction experiments.

Pretreatment experiments were performed using a liquid phase technique we developed based on the gas phase alkylation chemistry reported by Sharma (Z). Coal was pretreated by suspending 5 g of undried coal in 40 cm³ of methanol and 0.1 cm³ of concentrated hydrochloric acid in a 100 cm³ round bottom flask and continuously stirring the coal/methanol slurry on a magnetic stirring plate for 3 hrs. The flask was connected to a cooling water condenser to reduce solvent losses by evaporation. Several experiments were completed in which dry nitrogen was used to blanket the coal/methanol slurry; elemental analyses of the treated coals showed no difference in the extent of oxidation when the system was purged with nitrogen and when it was vented to the atmosphere. Several blank experiments using hexane or acetone in place of methanol were also completed.

After pretreatment, most of the organic solvent was decanted off and the moist coal sample washed with three 50 cm³ aliquots of fresh solvent to remove residual acid. Any remaining solvent was recovered by roto-evaporation and vacuum drying (50° C, 10-20 millitorr pressure, 24 hrs.). Untreated coal samples were vacuum dried at the same conditions before liquefaction. After drying, all treated and untreated coal samples were stored at room temperature in a vacuum dessicator (0.1 torr) before analysis or liquefaction. Reactor runs were scheduled so that each coal sample was stored for less than 12 hours before use.

Liquefaction experiments were conducted in a 20 cm³ tubing bomb reactor attached to an agitator and immersed in a fluidized sandbath. Low severity reaction conditions were set at 350° C reaction temperature, 1000 psig initial cold hydrogen pressure, and 30 min. reaction time. Dihydro-phenanthrene (DHP) was used as hydrogen donor solvent (2/1 solvent/coal wt. ratio) in these runs. Coal conversion was measured using THF extraction data corrected for the intrinsic THF solubilities of treated and untreated coals. Solubility measurements were conducted at ambient conditions and consisted of three steps: 1) sonicating the liquid products from the tubing bomb reactor (or feed coal sample) in excess THF for 10 min., 2) centrifuging the mixture at 2000 rpm for 15 min., and 3) decanting THF-soluble products and excess THF from the THF-insoluble residuum. This procedure was repeated at least two times until no additional THF-soluble products were recovered. Remaining THF-insolubles were dried at 100° C for 24 hours to remove residual THF, weighed, and finally ashed. Coal conversion to THF-soluble products was computed as follows:

$$\text{Coal conversion (wt\% maf basis)} = \frac{M_f - M_p}{M_f} \times 100$$

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)

RESULTS AND DISCUSSION

Baseline reactivity data for the untreated and treated Argonne coals are shown in Figures 1 and 2. Each of these data points represents the average of 2-3 reactor experiments. The average standard deviation for the dataset shown is ± 1.8 wt%.

At the low severity reaction conditions studied, three of the high volatile bituminous coals [Illinois #6 (72.1 wt%), Blind Canyon (69.6 wt%), and Pittsburgh #8 (57.0 wt%)] gave the highest THF conversions. Wyodak subbituminous coal was the next most reactive coal (44.4 wt%), while Pocahontas low volatile bituminous coal was the least reactive sample studied (15.6 wt%). These

reactivity data follow the same trends reported for the Argonne coals by several other investigators.

Pretreatment with methanol and HCl using the procedure described earlier enhanced low severity liquefaction reactivity for all eight Argonne coals. The absolute increase ranged from only 5.5 wt% for Blind Canyon coal to 31.5 wt% for Wyodak coal, and averaged 18.0 wt% for the eight coals. No simple trends in reactivity improvement with chemical or physical properties of the coals are obvious, although the reactivity of pretreated low rank coals (Wyodak and Beulah-Zap) increased much more than reactivity of the six bituminous coals.

Interestingly, replacement of methanol with hexane during coal pretreatment also enhanced low severity liquefaction reactivity. Since hexane cannot participate in the alkylation chemistry proposed by Sharma (7), other effects must also be contributing to the observed reactivity enhancement. Some possibilities include: 1) leaching of calcium, magnesium, iron, and perhaps other species from the coal mineral matter, and 2) formation of chlorinated mineral species such as $FeCl_3$, which are known to be active coal dissolution catalysts (9,10). Other as yet unknown effects are certainly possible as well. Several additional sets of experiments and analyses are currently being conducted to begin elucidating the existence and importance of these effects.

Figure 3 compares the effect of our mild pretreatment method using methanol/HCl with low severity reactivity enhancement data for Wyodak coal samples alkylated using the Liotta (6) and Sternberg (5) alkylation techniques. As shown, our method provided a significant reactivity improvement even though the extent of alkylation was very low. These data also indicate that effects in addition to alkylation at oxygen and carbon sites in the organic coal structure are contributing to the observed improvements in coal liquefaction reactivity.

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Table I
Ultimate Analysis of Feed Coals

Wt% Dry Basis	Wyodak	Beulah-Zap	Illinois #6	Pittsburgh #8
Carbon	68.4	65.9	65.7	75.5
Hydrogen	4.9	4.4	4.2	4.8
Nitrogen	1.0	1.0	1.2	1.5
Sulfur	0.6	0.8	4.8	2.2
Oxygen	16.3	18.2	8.6	6.7
Ash	8.8	9.7	15.5	9.3
Coal Rank	Subbit.	Lignite	HVB	HVB
Symbol	Wy	BZ	Ill	Pit

Table I (cont.)
Ultimate Analysis of Feed Coals

Wt% Dry Basis	Blind Canyon	Lewiston-Stockton	Upper Freeport	Pocahontas
Carbon	76.9	66.2	74.2	86.7
Hydrogen	5.5	4.2	4.1	4.2
Nitrogen	1.5	1.3	1.4	1.3
Sulfur	0.6	0.7	2.3	0.7
Oxygen	10.8	7.8	4.8	2.3
Ash	4.7	19.8	13.2	4.8
Coal Rank	HVB	HVB	MVB	LVB
Symbol	BC	LS	UF	POC

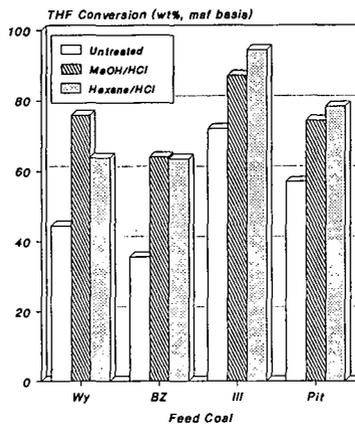


Figure 1. Effect of Pretreatment with MeOH/HCl and Hexane/HCl on Low Severity Liquefaction Reactivity of Argonne Coals

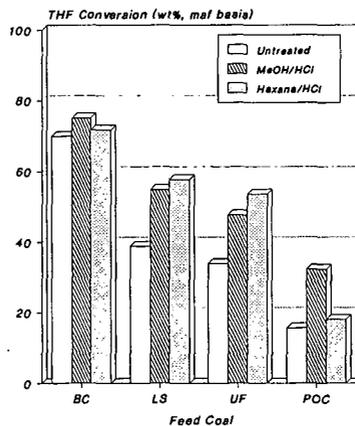


Figure 2. Effect of Pretreatment with MeOH/HCl and Hexane/HCl on Low Severity Liquefaction Reactivity of Argonne Coals

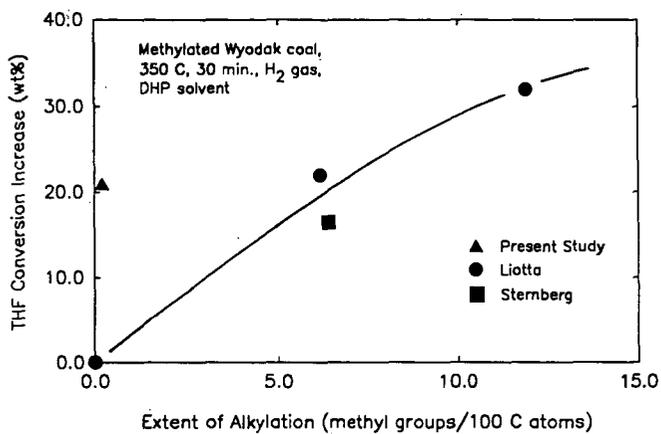


Figure 3. Liquefaction Reactivity Enhancement as a Function of Alkylation Extent for Three Pretreatment Methods