

ENHANCED LOW SEVERITY COAL LIQUEFACTION USING SELECTIVE CALCIUM REMOVAL

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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 relatively 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. Analysis of treated Wyodak and Illinois #6 coal samples indicates that no organic phase alteration such as alkylation occurs during pretreatment, but that over 90 wt% of the calcium is removed from each coal. Calcium is thought to catalyze retrogressive reactions during coal pyrolysis, and thus calcium removal prior to low severity liquefaction minimizes the production of THF-insoluble products.

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.

However, as shown schematically in Figure 1, lowering the liquefaction severity reduces coal conversion and liquid product yields unless the intrinsic coal reactivity can be sufficiently enhanced using some method of physical or chemical pretreatment. The main challenge to developing a viable low severity liquefaction process scheme involves finding an efficient and inexpensive means of coal pretreatment which will provide high levels of conversion and liquid product yields at low reaction severity. 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.

Numerous chemical treatments including reductive and non-reductive alkylation (5,6), acylation (7), partial oxidation (8), alkali hydrolysis (9), and solvent swelling (10) have been used to disrupt the coal's organic structure and increase solvent solubility. Limited work has been reported in which the liquefaction reactivity of alkylated coals has been studied. Schlosberg et al. (11) 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.

More recently, the effect of chemical pretreatment on the inorganic constituents of coal via a vis liquefaction reactivity has been studied. Mochida (12) reported that hydrochloric acid can be used to destroy cationic bridges present in low rank coals, thereby reducing coordination between oxygen-containing functional groups and allowing better contacting between coal and solvent during the initial stages of dissolution. Joseph (13) reported that removal of sodium, potassium, and calcium from low rank coals enhances liquefaction reactivity. He attributes this effect to inhibited hydrogen transfer in the presence of these cations.

The objective of this paper is to present experimental results from a study in which mild chemical pretreatment using methanol and hydrochloric acid was used as a method to improve intrinsic coal reactivity at low liquefaction reaction conditions. Possible explanations for the observed reactivity enhancement will also be discussed.

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 (14). Coal samples were stored under argon in sealed ampules prior to pretreatment and liquefaction experiments.

Coal was pretreated by suspending 5 g of undried coal in 40 cm³ of methanol and 0.6 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 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 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. Portions of each untreated coal and pretreated coal were subjected to elemental analysis and ash analysis, as well as ¹H CRAMPS and ¹³C CP/MAS NMR, FTIR, Mossbauer, and XRD spectroscopy.

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. Dihydrophenanthrene (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 on a moisture and ash-free basis, correcting for the intrinsic solubility of the feed coal.

RESULTS AND DISCUSSION

Effect of pretreatment on low severity liquefaction reactivity. Reactivity data for the untreated and treated Argonne coals are shown in Figure 2. Each of these data points represents the average of 2-3 reactor experiments; conversion differences of 2.1 wt% or greater (maf basis) represent statistically significant differences in liquefaction reactivity at the 95% confidence level. 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 other investigators (15).

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 were obvious, although the reactivity of pretreated low rank coals (Wyodak and Beulah-Zap) increased much more than reactivity of the six bituminous coals.

Although vapor phase methanol/HCl mixtures have been shown to partially alkylate bituminous coals (16), NMR and FTIR measurements indicated no alkylation occurred during our pretreatment experiments. This result was confirmed by replacing methanol with hexane or acetone (two solvents which cannot participate in acid catalyzed alkylation chemistry) during pretreatment; the reactivity of coals pretreated with hexane/HCl and acetone/HCl was also enhanced.

In an attempt to separate the effects of methanol and HCl on reactivity enhancement, a series of experiments was completed in which samples of Wyodak subbituminous coal and Illinois #6 bituminous coal were pretreated using methanol only (no HCl addition) and HCl only (1.5 wt% HCl in distilled water, no methanol addition). Results of low severity liquefaction experiments using these treated coals are summarized in Figure 3. As expected, no reactivity enhancement occurred when coal samples were pretreated with only methanol. However, coal samples treated with HCl/water exhibited significant reactivity improvement, although less than observed using methanol/HCl. Blank pretreatment using only distilled water did not affect the low severity reactivity of either coal. Thus, we can conclude that, while the presence of a small concentration of HCl is essential for successful pretreatment, the addition of methanol or other organic solvent such as hexane or acetone improves pretreatment effectiveness. Mochida (12) attributes this effect to improved wettability of the coal surface by the organic solvent and thus better contacting between coal and acid.

Effect of pretreatment on coal composition. To begin elucidating the cause of the reactivity enhancement shown in Figure 2, we used several analytical techniques to study changes in the organic and inorganic phases of Wyodak and Illinois #6 coals during pretreatment. NMR and FTIR analyses indicated no measurable organic phase alterations with one exception. The Wyodak FTIR spectra indicated formation of carboxylic function groups during pretreatment, probably as a result of divalent (Ca,Mg) cationic bridge destruction (12,13). Mossbauer spectroscopy results demonstrated that pyrite was largely unaffected by treatment with methanol and HCl, eliminating the possibility that $FeCl_3$, a known coal dissolution catalyst, was being formed in the treated coal.

X-ray diffraction measurements were conducted on the low temperature ash (LTA) from untreated and treated Wyodak and Illinois #6 coals. These results indicated that over 90 wt% of the calcium was leached from each coal during pretreatment. In these spectra, calcium was observed only as $CaCO_3$ with no CaO or $CaSO_4$ present. This observation agrees with a report by Miller and Givens (17) that organically-bound calcium will convert to $CaCO_3$ rather than CaO during low temperature ashing. Elemental analyses of treated coal samples confirmed the extent of calcium loss during pretreatment, and also showed that a lesser amount of magnesium was also extracted.

Effect of calcium content on low severity liquefaction reactivity. To study further the effect of calcium content on liquefaction reactivity, Wyodak and Illinois #6 coal samples with varying calcium contents were prepared by varying the amount of acid used during pretreatment. Other pretreatment conditions were the same as described earlier. Results of low severity liquefaction runs using these samples are shown in Figure 4. The reactivity of both coals was enhanced as calcium was removed; once again, the effect was more pronounced for Wyodak coal, particularly at a calcium content of less than about 0.2 wt%.

Several low severity liquefaction experiments were completed in which calcium as CaCO_3 was added back to the reactor prior to liquefaction. In each experiment, the amount of calcium added was equivalent to the amount extracted during pretreatment. Results of these experiments are summarized in Figure 5. As these data show, the beneficial effect of MeOH/HCl pretreatment was almost completely negated by adding CaCO_3 to the liquefaction reaction system. A similar effect was observed when CaO was added during low severity liquefaction of pretreated Wyodak and Illinois #6 coals.

The mechanistic role of calcium during low severity coal dissolution is not completely understood. Mochida (12) attributed accelerated rates of low rank coal dissolution to the destruction of calcium dicarboxylate structures and therefore, less coordination of oxygen-containing function groups. Joseph (13) speculated that calcium and other exchangeable alkaline and alkaline earth cations impeded hydrogen transfer during coal dissolution; removal of these cations would improve the rate of hydrogen transfer to coal free radicals as they form, and thus improve the extent of coal conversion. Joseph also cited the propensity of calcium dicarboxylate structures to undergo cross-linking reactions during the initial stages of coal dissolution.

We hypothesize that, in addition to the effects cited above, the presence of calcium can directly catalyze retrogressive reactions involving coal-derived free radical species during low severity liquefaction. Numerous studies have cited the role of calcium (as CaCO_3 or CaO) in increasing char yields and reducing tar yields during coal pyrolysis; the char yield enhancement has been attributed to catalysis of metaphast recombination prior to devolatilization (18) and catalysis of repolymerization and secondary cracking reactions (19). We are presently conducting a series of model compound studies to help elucidate the mechanistic effects of calcium during low severity liquefaction.

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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

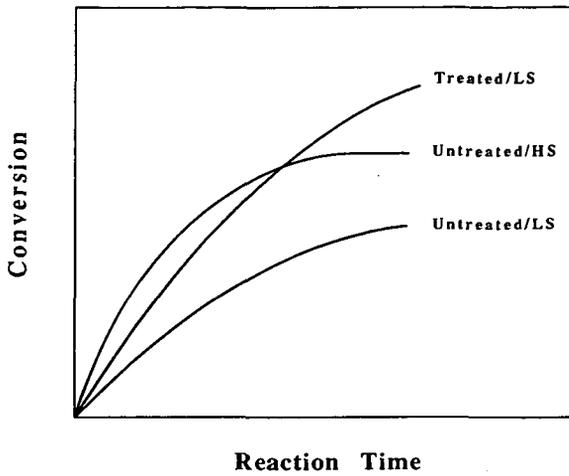


Figure 1 - Schematic Representation of Reactivity Enhancement Using Coal Pretreatment (LS = low reaction severity, HS = high reaction severity)

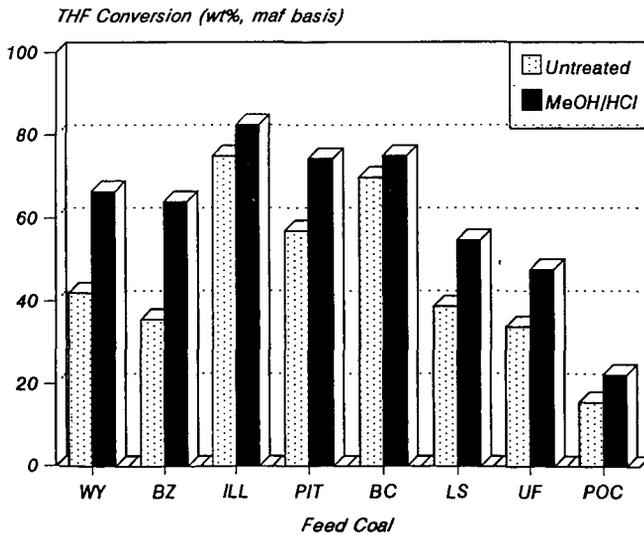


Figure 2 - Effect of Pretreatment with MeOH/HCl on Low Severity Liquefaction Reactivity of Argonne Coals

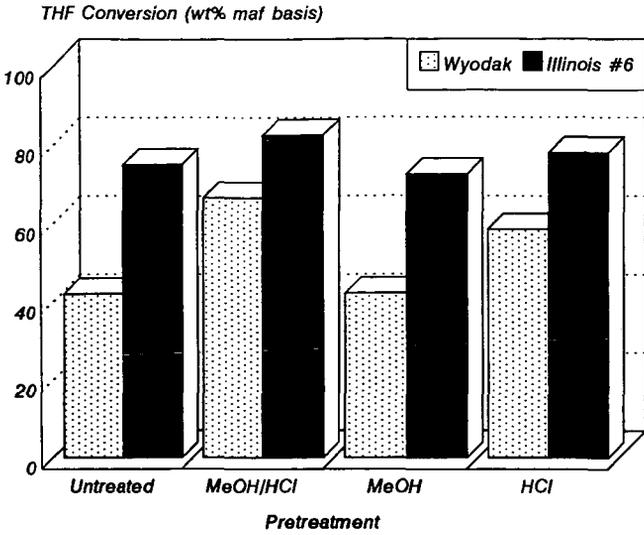


Figure 3 - Effect of Pretreatment with MeOH/HCl, MeOH, or HCl on Low Severity Liquefaction Reactivity of Wyodak and Illinois #6 Coals

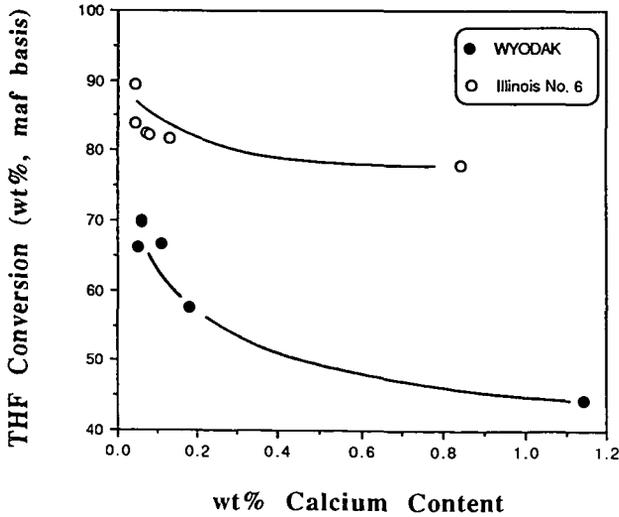


Figure 4 - Effect of Calcium Content on Low Severity Liquefaction Reactivity of Wyodak and Illinois #6 Coals

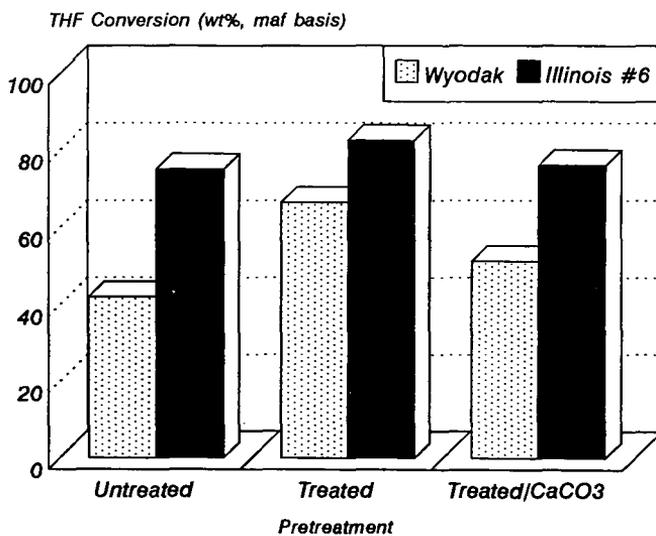


Figure 5 - Effect of Calcium Carbonate Addition on Low Severity Liquefaction Reactivity of Wyodak and Illinois #6 Coals