

MILD PRETREATMENT METHODS FOR IMPROVING THE LOW SEVERITY REACTIVITY OF ARGONNE PREMIUM COALS

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ABSTRACT

This paper describes results from an on-going coal pretreatment study with the goal of developing simple, inexpensive treatment options to enhance low severity coal dissolution reactivity. Data are presented for two pretreatment methods: 1) ambient treatment with methanol and hydrochloric acid, and 2) aqueous carbonic acid treatment. We have found that ambient pretreatment of eight Argonne coals using methanol and a trace amount of hydrochloric acid improves THF-soluble conversions by 24.5 wt% (maf basis) for Wyodak subbituminous coal and 28.4 wt% for Beulah-Zap lignite with an average increase of 14.9 wt% for liquefaction of the eight coals at 623 K (350°C) reaction temperature and 30 min. reaction time. Pretreatment with methanol and HCl separately indicated that both reagents were necessary to achieve maximum liquefaction improvement. The extent of calcium removal correlated well with reactivity enhancement in these experiments. This effect is attributed to the role of calcium as a catalyst for retrogressive reactions during the initial stages of dissolution. Preliminary treatment results using CO₂/H₂O suggest that the reactivity of bituminous coals such as Illinois #6 can be significantly enhanced with this method but that less improvement is seen for low rank coals such as Wyodak or Beulah-Zap.

INTRODUCTION

Much of the recent research in direct coal liquefaction seeks to develop methods for dissolving coal at lower reaction severity [often defined as temperatures below 623 K (350°C) and pressures in the range of 6.9-10.3 MPa (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 reaction severity reduces coal conversion reaction rates and liquid product yields unless the intrinsic coal reactivity can be sufficiently enhanced using some method of physical or chemical pretreatment prior to dissolution. Possible methods for reactivity enhancement include: 1) dispersed homogeneous or heterogeneous catalysts, 2) promoters such as basic nitrogen compounds, 3) physical pretreatment of the coal structure, or 4) chemical pretreatment of the coal's inorganic and organic fractions. Generally these methods all improve low severity coal liquefaction reactivity, but for various reasons (use of exotic, expensive, and sometimes hazardous chemical feedstocks; long pretreatment times; and the potential for incorporating undesirable chemical constituents into the coal), none have been seriously considered as a process step in coal liquefaction. The objective of the research described in this paper has been to develop simple, inexpensive coal pretreatment methods using readily available commodity chemicals to enhance low severity liquefaction reactivity of lignites, subbituminous, and bituminous coals.

In the past, chemical treatments including reductive and non-reductive alkylation (1,2), acylation (3), partial oxidation (4), alkali hydrolysis (5), and solvent swelling (6) have been used to disrupt the coal's organic structure, increase solubility in selected solvents, and improve liquefaction reactivity. Selected coal demineralization has also been studied as a method for enhancing liquefaction reactivity. Mochida (7) 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 (8) used ion exchange techniques to remove various cations from Wyodak subbituminous coal and North Dakota lignite. He found that removal of calcium, magnesium, sodium, and potassium from each low rank coal improved high severity [673 K (400°C), 3.5 MPa (500 psig) H₂, 60 min.] liquefaction conversion and product quality. This result was attributed to inhibited hydrogen transfer in the presence of alkaline and alkaline earth cations. Serio (9) also found that ion-exchanged and demineralized low rank coals were more reactive at high reaction severity. He attributed his results to reduced cross-linking of the treated coals during the initial stages of dissolution.

The objective of this paper is to present experimental results from a study in which two pretreatment methods were used to improve intrinsic coal reactivity at low severity liquefaction 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 analysis (10) and calcium content (11) data for each coal are listed in Table I. Additional chemical and physical properties of the Argonne coals have been reported (12).

Two methods of coal pretreatment were used in this study. The first method employed a liquid phase technique we developed based on the gas phase alkylation chemistry reported by Sharma (13). Coal was pretreated by suspending 5 g of undried coal in 40 cm³ of methanol and 0.2 cm³ (0.5 vol%) of concentrated hydrochloric acid in a 100 cm³ round bottom flask and continuously stirring the coal/methanol slurry on a magnetic stirring plate for the desired pretreatment time (usually 3 hrs.). The flask was connected to a cooling water condenser to reduce solvent losses by evaporation. Treated coal samples were washed with 500 cm³ aliquots of methanol and centrifuged to remove excess acid and soluble mineral species.

The second pretreatment method was based on a CO₂/H₂O treatment technique reported by Hayashi, et al. (14). Five gram samples of coal were pre-dried at 50°C in vacuum [1.3-2.6 Pa (10-20 millitorr)] for 1 hour and then placed in a 300 cm³ autoclave reactor. Distilled water (100 g) was added to the reactor which was then sealed, flushed with CO₂, and finally pressurized with CO₂ to 600 KPa (87 psig) pressure at ambient temperature. The coal/water slurry was agitated at 1000 rpm for the desired treatment time (usually 2 hours). At the end of each pretreatment run, the reactor was depressurized and the moist coal sample recovered from the slurry by centrifugation. Each sample was washed with 500 cm³ aliquots of distilled water to remove any water-soluble species present in the treated coal.

Coal samples from each pretreatment method were vacuum dried at 298 K (25°C) under 1.3-2.6 Pa (10-20 millitorr) pressure for 24 hrs. Untreated coal samples were vacuum dried at the same conditions prior to use. After drying, all treated and untreated coal samples were stored at room temperature in a vacuum desiccator at 13.3 Pa (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 NMR, ¹³C CP/MAS NMR, FTIR, Mossbauer, and XRD spectroscopy.

Liquefaction experiments were conducted in a 20 cm³ tubing bomb reactor system attached to an agitator and immersed in a fluidized sandbath. Low severity liquefaction conditions were set at 350°C reaction temperature, 6.9 MPa (1000 psig) initial cold hydrogen pressure, and 30 minutes reaction time. Dihydrophenanthrene (DHP) was used as hydrogen donor solvent (2/1 solvent/coal wt. ratio) in these runs. Coal conversion was monitored 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 20 min., 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-soluble products were recovered. Remaining THF-insolubles were dried at 373 K (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 each feed coal sample. Thus reported changes in coal conversion levels can be attributed solely to inherent differences in low severity coal liquefaction reactivity and not to changes in intrinsic solubility.

RESULTS AND DISCUSSION

Several sets of experiments were completed to evaluate the effectiveness of our pretreatment method in enhancing low severity liquefaction reactivity. In each set of runs, individual reactor experiments were duplicated and in some cases triplicated. Results shown in this paper represent average values of replicated runs; conversion differences of 2.1 wt% or greater (maf basis) represent statistically significant differences in liquefaction reactivity at the 95% confidence level.

Baseline low severity liquefaction reactivity data for the untreated Argonne coals are summarized in Figures 2 and 3. At the conditions studied, three of the high volatile bituminous coals [Illinois #6 (75.0 wt%), Blind Canyon (69.9 wt%), and Pittsburgh #8 (57.0 wt%)] gave the highest THF conversions. Wyodak subbituminous coal was the next most reactive coal (42.0 wt%), while Pocahontas low volatile bituminous coal was the least reactive sample studied (15.6 wt%). These reactivity data follow the generally accepted trends reported for thermal conversion of the Argonne coals (15).

Pretreatment with methanol and 1.5 vol% HCl for three hours at ambient conditions using the procedure described earlier enhanced low severity liquefaction reactivity for all eight Argonne coals. The absolute increase ranged from 24.5 wt% for Wyodak coal and 28.4 wt% for Beulah-Zap lignite to 5.2 wt% for Blind Canyon coal, and averaged 14.9 wt% for the eight coals. No simple trends in reactivity improvement with chemical or physical properties of the coals were obvious, although reactivity of the pretreated low rank coals (Wyodak and Beulah-Zap) increased much more than reactivity of the six bituminous coals.

Although Sharma (13) showed that vapor phase methanol/HCl mixtures would partially alkylate bituminous coals, elemental analyses of the treated coals indicated that little methylation (fewer than 0.1 methyl groups/100 C atoms) had occurred during liquid phase methanol/HCl pretreatment; no evidence of methylation was observed from NMR and FTIR measurements on untreated and treated coal samples. This result was confirmed by replacing methanol with hexane during coal pretreatment; reactivity of hexane/HCl pretreated coals was also enhanced. Since hexane cannot participate in the proposed alkylation chemistry, other effects must also contribute to the observed reactivity enhancement. Several pretreatment experiments were conducted using acetone in place of methanol or hexane and similar reactivity results were obtained. Throughout this portion of the study, we found no obvious trends relating reactivity enhancement, pretreatment solvent properties, and coal properties. Our general conclusion is that any simple organic solvent may be used to conduct the liquid phase pretreatment step.

The effect of CO₂/H₂O pretreatment on low severity liquefaction of the Argonne coals is also shown in Figures 2 and 3. With the exception of Blind Canyon coal, CO₂/H₂O pretreatment significantly enhanced low severity reactivity of each Argonne coal. Interestingly, the extent of enhancement for the two low rank coals (Wyodak and Beulah-Zap) was significantly lower than the enhancement observed using MeOH/HCl pretreatment. Conversely, CO₂/H₂O pretreatment of each bituminous coal except Blind Canyon and Lewiston-Stockton provided greater reactivity enhancement than MeOH/HCl pretreatment.

At this point, we can only speculate on the contrast in reactivity behavior between the two pretreatment methods. We have previously reported (16) that reactivity enhancement using MeOH/HCl pretreatment can be correlated with the extent of calcium removal and that HCl destroys calcium dicarboxylate bridging structures. We also presented model compound evidence (16) that calcium can directly catalyze retrogressive reactions involving coal-derived free radical intermediates during the initial stages of coal dissolution. Thus, it appears that given the reactivity enhancement data shown in Figures 2 and 3, we can tentatively conclude that CO₂/H₂O pretreatment more efficiently removes calcium from coals such as Illinois #6 in which calcium exists predominately as part of a discrete mineral phase, while MeOH/HCl pretreatment more efficiently removes calcium from dicarboxylate bridging structures which predominately occur in low rank coals. Further analyses of pretreated coals and additional model compound experiments are currently underway to help elucidate pretreatment effects on low severity coal liquefaction reactivity.

ACKNOWLEDGMENT

We wish to acknowledge financial support from the U.S. Department of Energy under Contract Nos. DE-AC22-88PC88812 and DE-FG22-90PC90289. Jenefer R. Olds performed the intrinsic solubility analyses for untreated and treated coal samples.

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Table I
Analysis of Feed Coals

Ultimate Analysis (wt% maf coal)	Wyodak	Beulah-Zap	Ill. #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
Calcium content (wt% maf coal)	1.20	1.54	0.96	0.21
Coal Rank	Subbit.	Lignite	HVB	HVB
Symbol	WY	ND	IL	PITT

Table I (cont.)
Analysis of Feed Coals

Ultimate Analysis (wt% maf coal)	Blind Canyon	Lewiston- Stockton	Upper Freeport	Pocahantas
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
Calcium content (wt% maf coal)	0.41	0.06	0.45	0.45
Coal Rank	HVB	HVB	MVB	LVB
Symbol	UT	WV	UF	POC

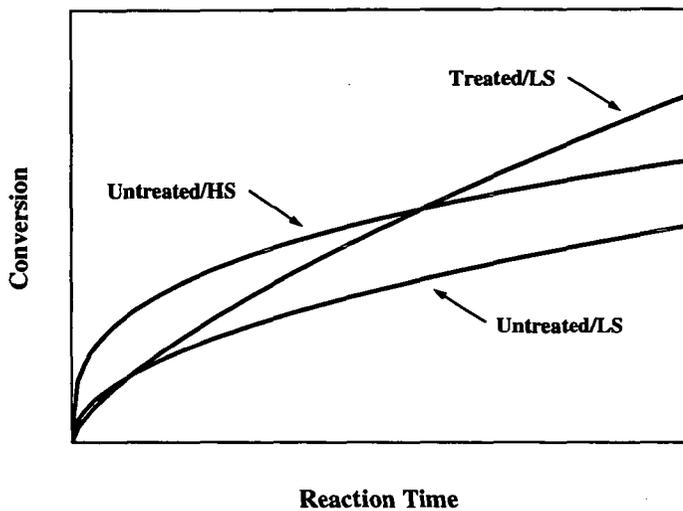


Figure 1 - Schematic Representation of Reactivity Enhancement Using Coal Pretreatment (LS = low reaction severity, HS = high reaction severity)

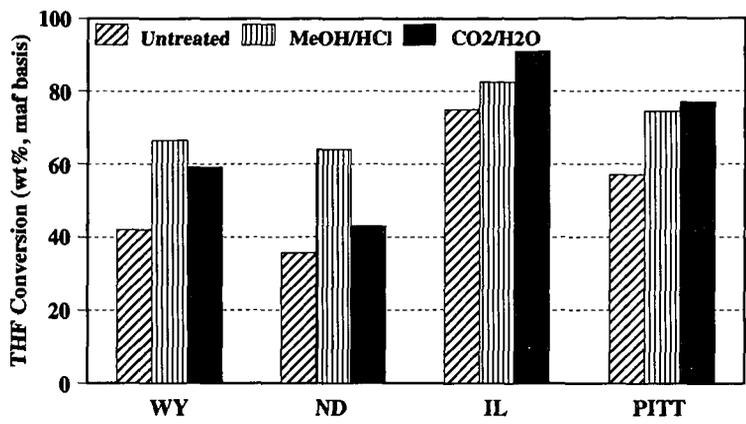


Figure 2 - Effect of Pretreatment with Methanol/Hydrochloric acid and Carbon Dioxide/Water on Low Severity Liquefaction Reactivity of Argonne Coals

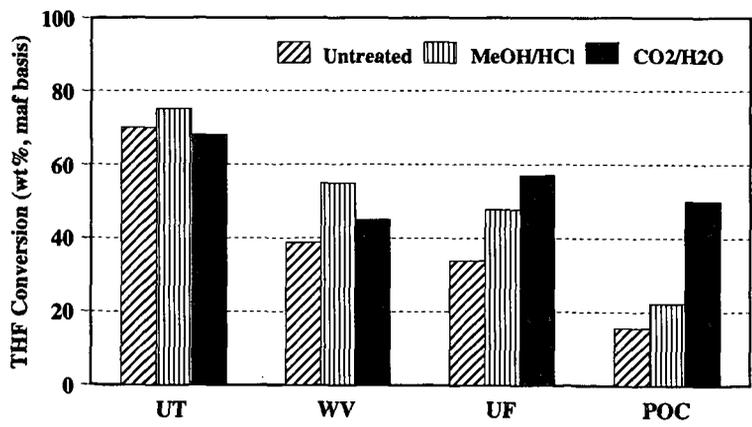


Figure 3 - Effect of Pretreatment with Methanol/Hydrochloric acid and Carbon Dioxide/Water on Low Severity Liquefaction Reactivity of Argonne Coals