

LIQUEFACTION REACTIVITY ENHANCEMENT OF COAL BY MILD ALKYLATION TECHNIQUES

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ABSTRACT

Utilization of coal pretreatment techniques including mild alkylation and solvent swelling has been investigated to determine the effect of these procedures on the reactivity of coal. Alkylation recipes investigated have included both selective (O-methylation, Liotta) and non-selective (Sterlberg) techniques where the reaction conditions are adjusted to bring about a minimal alkylation extent. The degree of reactivity enhancement has been evaluated under both direct hydroliquefaction and coal/oil co-processing conditions, and at both low and high severity reaction conditions. Pretreatment and liquefaction experiments have been carried out using two coals, Illinois #6 hvB and Wyodak subbituminous from the Argonne Premium Coal Sample Bank. All experiments were conducted in tubing bomb microautoclave reactors utilizing DHP for the direct hydroliquefaction experiments and Cold Lake resid for co-processing runs. Coal conversion was determined based on THF solubility.

Results of these experiments have indicated that alkylation is a beneficial pretreatment step for enhancing the reactivity of coal. The effect is greatest at low severity reaction conditions (350 °C, 5 minutes), and for the low rank (high oxygen) coal which was selectively O-methylated. Oxygen alkylation was not effective for the high rank (Illinois #6 hvB) coal under all reaction conditions studied. Non selective methylation was found to be ineffective for reactivity enhancement of the low rank coal (Wyodak subbituminous), but effective in the case of high severity co-processing reaction conditions for the high

rank coal. Preliminary results on liquefaction of coals pre-swollen in acetone have shown that this procedure is also very effective in terms of promoting additional conversion, with a marked increase found in the yield of hexane solubles for the swollen coals.

Introduction and Background

Modern coal structure theories suggest that coal consists of a complex, loosely-bound polymeric structure containing numerous strong and weak cross-linkages, hydrogen bonds, guest molecules, and interactions among various functional groups (1). Numerous studies have shown that application of chemical reaction techniques such as alkylation can greatly increase the solubility of coal at ambient conditions in organic solvents such as toluene or tetrahydrofuran. These findings suggest that coal is a much less condensed and refractory material (and therefore inherently more reactive) than previously thought. Thus, the apparent low reactivity of many coals is, in fact, an artifact caused by excessive retrogression during the initial stages of conventional liquefaction. This hypothesis is especially true for low rank coals, where the high concentration of organic oxygen can lead to rapid condensation during the heating-up period.

Current coal liquefaction processing schemes incorporate staged reaction conditions and multiple reactor systems. As the name suggests, two-stage liquefaction utilizes two separate vessels, where coal solubilization takes place in the first reactor followed by catalytic upgrading of the coal-derived material in the second. Significant difficulties are encountered with catalyst deactivation due to coking in the stage-two reactor, primarily due to high concentrations of pre-asphaltenes present in the products of the stage-one processing step. These high molecular weight moieties are, in part, caused by the severity of the first-stage coal dissolution step which promotes regressive reactions and the production of species

which are ultimately more condensed and refractory (and hence less reactive) than the starting coal.

As an alternative to the use of high severity reaction conditions in the stage-one reactor, low severity liquefaction coupled with coal pretreatment for purposes of reactivity enhancement has been proposed. This combination would permit dissolution of coal under much milder reaction conditions thus minimizing the extent of retrogression, but would still maintain acceptable levels of coal conversion by employing chemical methods to enhance the inherent reactivity of coal. A variety of physical and chemical steps have been proposed as pretreatment techniques, including alkylation and solvent swelling.

The process of coal alkylation has long been utilized for purposes of rendering coal into a soluble state. The literature on coal alkylation is voluminous, and will only be briefly reviewed for purposes of this discussion. The reader is referred to Larsen and Kuemmerle (2) for a selective review of coal alkylation and to Stock (3) for a detailed review on reductive alkylation. Heredy and Neuworth (4) first recognized that coal could be chemically depolymerized and rendered soluble at ambient conditions by using it as an alkylating agent. Procedures for reductive alkylation of coal were first developed by Sternberg and his co-workers (5). While alkylation of coal following the procedures developed by Sternberg is relatively non-selective, methods for selective (oxygen) alkylation have been developed and published by Liotta et al. (6,7).

Extensive research has been carried out on solvent swelling of coal. The basic phenomenon revolves around the observation that, when contacted with a suitable solvent, coals will often absorb their own weight in solvent with a resulting volumetric expansion that can be as large as 100% (8, 9). The nature of this solvent/coal interaction is very solvent and coal specific, that is not all coals will swell and only certain solvents are effective. The primary

usefulness of solvent swelling to date has been as a tool in the study of coal structure, in that the behavior associated with this swelling phenomenon is characteristic of the behavior of polymeric materials such as macromolecular gels. While the exact nature of the chemical effect caused by swelling is not known, it is thought that weak linkages in the coal matrix such as hydrogen bonds and polar complexes are disrupted by the action of the solvent, creating more mobility for the coal matrix and freeing "guest molecules" which are occluded in the coal structure.

Applications of alkylation and solvent swelling for reactivity enhancement of coal have not been investigated extensively. Schlosberg et al. (10) reported that Friedel-Crafts alkylation was a beneficial pretreatment step for coals liquefied under high severity, direct hydroliquefaction reaction conditions. Rincon and Cruz (11) have reported on liquefaction of three coals that were pre-swollen in THF and hydroliquefied in four different solvents (tetralin, anthracene oil (AO), hydrogenated anthracene oil (PHO), and a mixture of AO and PHO) prior to hydrogenation. Their results indicated that significant enhancement in the conversion of coal to THF solubles had taken place, and that the extent of enhancement was related to the degree of swelling. Recently, Joseph (12) has reported on the liquefaction of several coals that had been pre-swollen in a variety of polar and non-polar solvents and subsequently liquefied in tetralin at 400 °C following removal of the swelling agent. Results from this study indicated a marked improvement in conversion of the pre-swollen coal to both THF and hexane solubles. Bockrath et al. reported on solvent swelling studies of liquefaction residues, and correlated the extent of swelling with the extent of conversion of coal to THF solubles upon liquefaction (13).

The objective of the research described below was to evaluate the effectiveness of two pretreatment methods (alkylation and swelling) in terms of their effect on the

reactivity of coal under both direct hydroliquefaction and co-processing reaction conditions.

Experimental

Two coals (Illinois #6 and Wyodak) from the Argonne Premium Coal Collection sample bank were employed for all alkylation and liquefaction experiments. Coals were alkylated according to the recipes described by Sternberg (xx) and Liotta (xx) following procedures in the literature. In order to obtain the desired low extents of alkylation, reaction times were varied from those prescribed. Determination of the extent of alkylation was computed by carbon and hydrogen balance based on the elemental analysis of the parent and alkylated coals.

Liquefaction of the alkylated and parent coals was carried out in rapidly heated tubing bomb microautoclave reactors of approximately 20 cm³ volume. The reactor system utilizes a manifold system so that two samples can be liquefied simultaneously; hence each run consisted of an alkylated sample with the parent coal run in parallel at the same conditions as a control. This system has been shown in previous studies to enable identification of reaction artifacts and facilitate the collection of high quality liquefaction data (14). A solvent (resid or DHP) to coal ratio of 2/1 (wt/wt) with an initial (cold) hydrogen pressure of 1000 psi was maintained for each run. Reactions in the direct hydrogenation mode were carried out using dihydrophenanthrene as the liquefaction vehicle, while co-processing runs were conducted with hydrotreated Cold Lake petroleum resid (atmospheric tower bottoms) as the vehicle. Hydrotreating conditions for the resid were 1 hour at 400 °C at an initial (cold) hydrogen pressure of 1000 psi with a NiMo/Alumina catalyst (Shell 324). Conversion was characterized by THF solubility for the experiments where alkylation was used as the pretreatment method, and THF and hexane solubility for the swelling experiments. Gas make was quantified by mass balance, and in limited runs the gas

composition was quantitatively speciated using a krypton tracer.

Results

Results for liquefaction and co-processing conversion of both Wyodak and Illinois #6 coals to THF solubles are shown in Figures 1-8. In each case, the results are first presented in terms of the absolute conversion to THF solubles, followed by a companion figure which shows the same data represented in terms of a percent increase over the base conversion (defined by the non-alkylated coal sample). In all cases, the conversions cited below have been corrected for the intrinsic THF solubility of the coals (parent and alkylated) - hence these data represent conservative estimates of the actual THF conversions that would be attained in a liquefaction process. This correction was made so that the effect of alkylation and swelling on the liquefaction reactivity of the coal could be determined in the absence of the increased solubility brought about by the pretreatment step alone. All runs presented in these figures are the average of at least two experiments. Where replicates of the same conditions did not agree to within $\pm 2\%$, the run was repeated until the desired level of reproducibility was achieved. A five factor (coal, solvent, temperature, time, pretreatment method) statistical analysis of the full data set indicated that the standard deviation of the conversion data was on the order of 4.3%. In all cases, data for conversion of coal for the co-processing runs at the lowest severity reaction conditions (5 min., 350 °C) are not presented due to adduction of the vehicle and the resulting apparent negative THF conversions.

Application of the Liotta recipe to the Wyodak coal resulted in an addition of 6 methyl groups per 100 carbon atoms. For the Illinois #6 coal the extent of alkylation (methylation) achieved was 3.7. In general, the data shown in Figures 1-4 indicate that use of an oxygen-selective

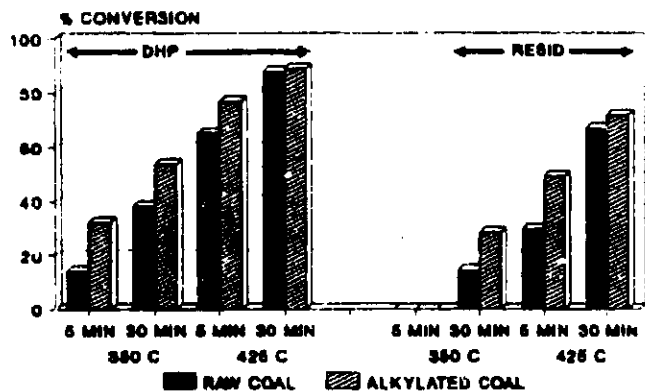
alkylation procedure for coal pretreatment is very beneficial for the low rank (Wyodak subbituminous) high organic oxygen coal, and not beneficial for the high rank (Illinois #6 hv bituminous) low organic oxygen coal. The percentage increase in THF conversion is greatest (120%) at lowest severity (350 °C, 5 minutes) in DHP, and at intermediate severity in resid (100 and 60% at 350 °C, 30 minutes and 425 °C 5 minutes respectively). Although the percentage change in conversion is relatively small at higher conversion levels, an increase of only 10% in overall coal conversion can have a profound influence on the overall economics of coal liquefaction (15). The effect of oxygen alkylation on the reactivity of Illinois #6 coal under direct hydroliquefaction reaction conditions is much smaller, with the percentage increase in conversion declining from approximately 20 to zero as severity increases. The effect of mild O-alkylation on the high rank coal is negative under co-processing reaction conditions, with the alkylated coals giving lower conversions than the parent coals regardless of the severity level.

Data on conversion to THF solubles for coals alkylated following the Sternberg recipe is shown in Figures 5-8. Trends in these results are less easily identified than was the case for the Liotta-alkylated coals. Many of the conversions for the alkylated coals are lower than those for the associated parent (non-alkylated) coals. This is especially true for reactions carried out under co-processing conditions (resid vehicle) for the low rank (Wyodak) coal samples. The effect of non-selective alkylation on the reactivity of the high rank (Illinois #6 bituminous) coal is minimal under direct hydroliquefaction reaction conditions, but appreciable under co-processing reaction conditions. A 50% increase in conversion relative to the base case for the non-alkylated coal is seen at the highest severity level studied in this program (425 °C, 30 minute reaction time).

Several possible explanations exist for the reactivity changes described above. Passivation of organic oxygen functionalities by selective O-alkylation may inhibit regressive reactions that are caused by these species. McMillen (16) and Moroni (17) have both described benefits that could derive from removal or minimization of the role of oxygen during direct coal liquefaction. This effect would be very significant during the early stages of liquefaction by preventing formation of refractory species with molecular weights larger than the parent coal.

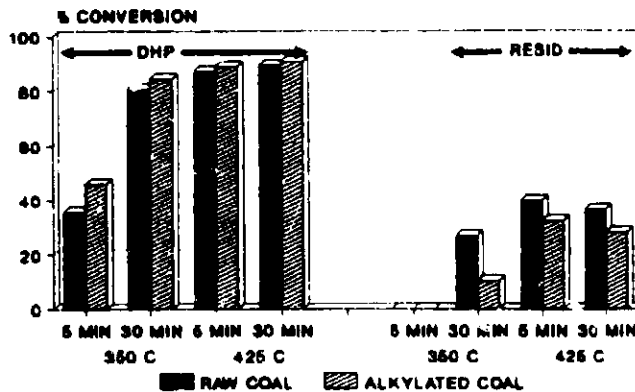
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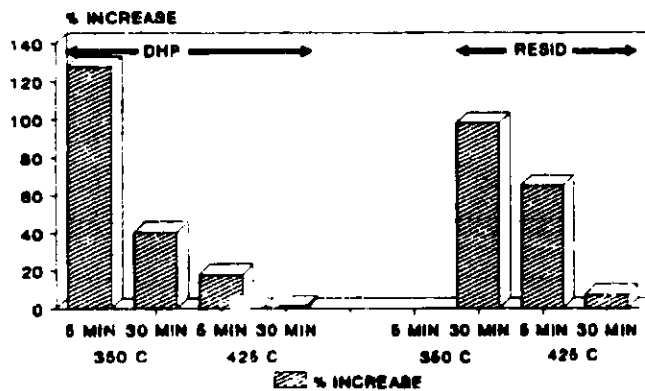
6 CH₃ GRPS/100 C ATOMS

Figure 1 Conversion data for liquefaction of mildly alkylated (Liotta procedure) Wyodak coal



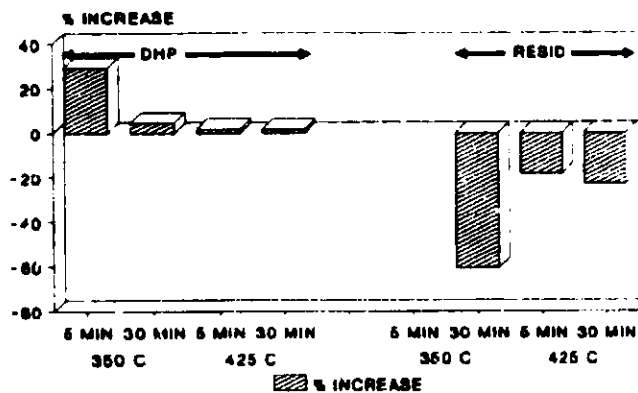
3.7 CH₃ GRPS/100 C ATOMS

Figure 3 Conversion data for liquefaction of mildly alkylated (Liotta procedure) Illinois no. 6 coal



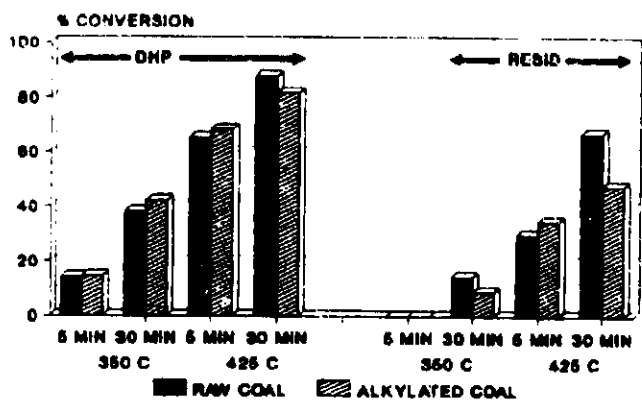
6 CH₃ GRPS/100 C ATOMS

Figure 2 Percentage reactivity change for mildly alkylated (Liotta procedure) Wyodak coal



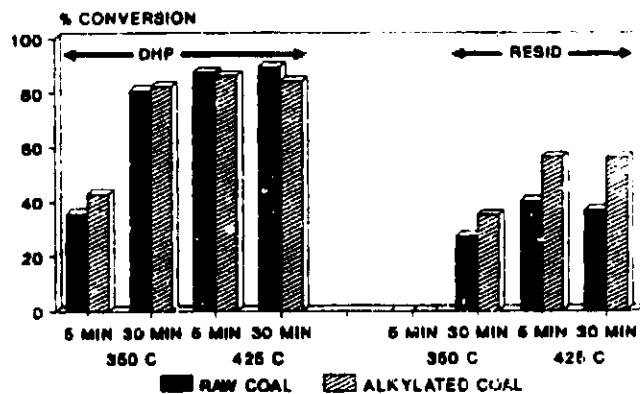
3.7 CH₃ GRPS/100 C ATOMS

Figure 4 Percentage reactivity change for mildly alkylated (Liotta procedure) Illinois no. 6 coal



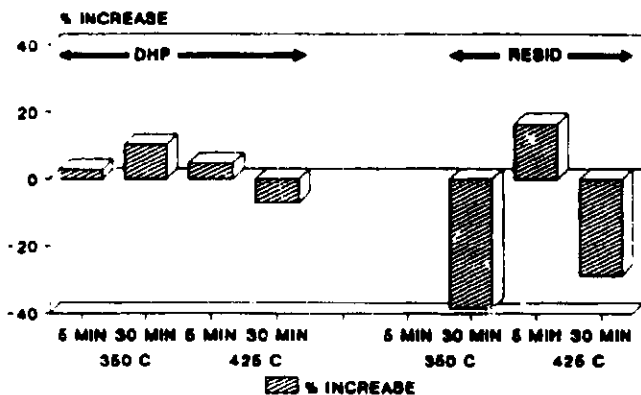
3.3 CH₃ GRPS/100 C ATOMS

Figure 5 Conversion data for liquefaction of mildly alkylated (Sternberg procedure) Wyodak coal



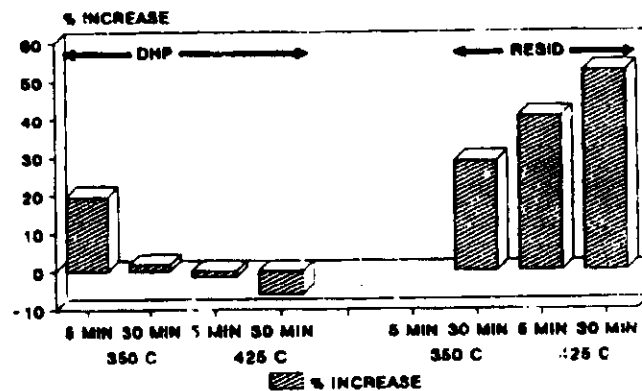
3.1 CH₃ GRPS/100 C ATOMS

Figure 7 Conversion data for liquefaction of mildly alkylated (Sternberg procedure) Illinois no. 6 coal



3.3 CH₃ GRPS/100 C ATOMS

Figure 6 Percentage reactivity change for mildly alkylated (Sternberg procedure) Wyodak coal



3.1 CH₃ GRPS/100 C ATOMS

Figure 8 Percentage reactivity change for mildly alkylated (Sternberg procedure) Illinois no. 6 coal