

**EFFECT OF PRE-TREATMENT TECHNIQUES ON LOW SEVERITY COAL
LIQUEFACTION AND CO-PROCESSING**

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ABSTRACT

Liquefaction reactivities of a Wyodak subbituminous coal from the Argonne Premium Coal Sample bank have been measured for both raw and alkylated coals under a variety of reaction conditions. Coals have been alkylated to two different levels using a selective (O-alkylation) procedure, and liquefied at both low and high severity conditions in a pure hydrogen donor vehicle (DHP) and petroleum resid. Results show alkylation to be a powerful pretreatment technique for reactivity enhancement.

INTRODUCTION

Recent research efforts in direct coal hydroliquefaction have centered on development of methods for achieving high conversions and product yields at low reaction severity. Conducting the primary (first-stage) liquefaction step at low temperature has potential implications in terms of the inherent reactivity of the coal-derived materials for second-stage catalytic upgrading, in that these moieties should be less refractory than if produced under more conventional (e.g. high temperature) conditions. Further, the processing and economic advantages attendant to carrying out coal conversion at low temperatures/pressure/residence time combinations are clear.

One method for achieving this goal of high yield at reduced reaction severity is by employing a pretreatment step for the coal used in the liquefaction step. Researchers at the Pittsburgh Energy Technology Center (1), Stanford Research Institute (2), North Dakota Energy Research Center (3), University of Chicago (4), and Colorado School of Mines (5), have all recently reported on various methods for improving coal reactivity at mild reaction conditions. This paper describes our most recent efforts to improve intrinsic coal reactivity using alkylation as a pretreatment step prior to liquefaction. This work derives principally from the published studies of Schlosberg et al. (6), who investigated the liquefaction reactivity of two O-alkylated coals at high severity conditions (427 °C, 130 minute reaction time). These investigators found a 10-21% increase in cyclohexane soluble conversion for the alkylated coals.

EXPERIMENTAL

A Wyodak subbituminous coal from the Argonne Premium Coal Sample Bank was used as the starting material in all cases. The coal was alkylated following procedures first developed

by Liotta et al. (7), and later modified by Ettinger and co-workers (8). The alkylation reaction time was varied from the original Liotta recipe in order to achieve different levels of alkylation. The alkylated coal samples were dried under high vacuum (c.a. 10 microns) at approximately 90 °C, and analyzed by photoacoustic FTIR in order to verify that alkylation had occurred. Extent of alkylation was determined by elemental analysis of the dried samples (Huffman Laboratories, Golden, CO). Liquefaction experiments were carried out in tubing-bomb microautoclave reactors (volume of c.a. 20 cm³) under four sets of reaction conditions which were intended to simulate both low and high severity liquefaction under direct hydrogenation (DHP vehicle) and co-processing (petroleum resid vehicle) modes of operation. Low severity liquefaction and co-processing reactions were conducted at 350 °C, 5 and 30 minutes reaction time while high severity reactions were conducted at 425 °C, 5 and 30 minute reaction times. All reactions were carried out under a hydrogen blanket with an initial (cold) pressure of 7 MPa. Coal conversion was monitored by THF solubility.

RESULTS

Samples of the Wyodak subbituminous coal were alkylated to differing degrees by variation of alkylation time. Analyses of the raw and alkylated coals are presented in Table 1. As shown, an alkylation reaction period of 12 hours resulted in addition of 6 alkyl (CH₃) groups per 100 carbon atoms, while reaction for 24 hours gave 12 groups added per 100 carbon atoms. Results for liquefaction of these samples under both low and high severity conditions and in both direct hydrogenation and co-processing modes of conversion are presented in Figures 1 - 4. As shown, substantial improvements are present in liquefaction yields (THF solubility, DAF), with the greatest enhancement at low severity reaction conditions. At 350 °C, liquefaction enhancements range from 150% to 200% (based on raw coal conversion), with a nearly 70% conversion to THF solubles obtained for the most highly alkylated sample under direct liquefaction conditions at 30 minutes reaction time in DHP. Similar results are evident in the co-processing mode of operation, where conversions at low severity are, in some cases, three times higher than the parent coal.

Reaction at higher severity conditions reduces but does not eliminate the beneficial effect of the O-alkylation pretreatment. In general, the effect on conversion is in the range of 10 to 30%, with the largest increase noted for samples reacted in resid (co-processing mode). Very substantial conversions are obtained under co-processing conditions, as evidenced by a THF conversion of 83% for the most highly alkylated sample at 425 °C, 30 minutes reaction time.

The effect of extent of alkylation on reactivity at low severity is shown in Figures 5 (DHP vehicle) and 6 (resid), where conversion increase is plotted as a function of extent of alkylation. As shown, the effect of alkylation on reactivity is not linear, with the largest increase occurring between 0 and 6 groups added under direct hydrogenation liquefaction conditions.

CONCLUSIONS

Mild O-alkylation has been shown to be a beneficial pretreatment method for Wyodak subbituminous coal which contains a substantial amount of organic oxygen. Similar results have been reported by other researchers (9), who have also shown that the effect of O-alkylation is much lower when a low oxygen bituminous coal is pretreated in the same fashion. These data serve to reinforce the hypothesis that organic oxygen sites in coal function as initiators for regressive reactions during the initial stages of coal liquefaction. These regressive reactions may be of most significance during the heat-up period (in the pre-heater of a liquefaction reactor) where the hydrogen activity (in terms of radical quenching) of the system is relatively low. Selective alkylation may serve to passivate the oxygen sites, thus suppressing the cross-linking that takes place during initial stages of coal thermolysis.

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TABLE 1
ANALYSES OF RAW AND ALKYLATED COALS

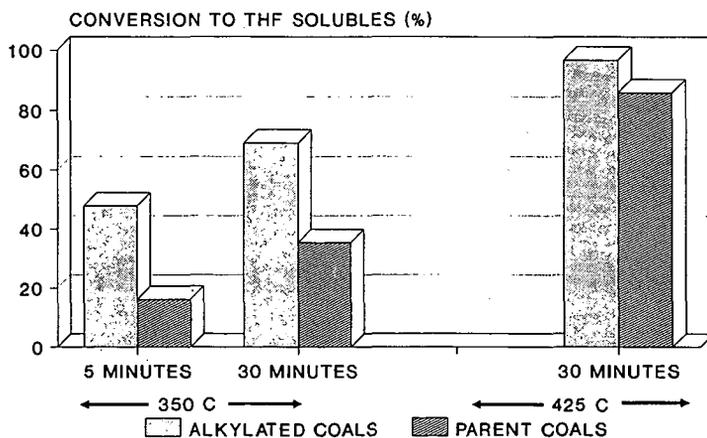
SAMPLE	DRY BASIS		ASH	E ¹
	C	H		
Wyodak (raw) ²	68.43	4.88	8.77	0.00
LW-7 ³	68.80	6.44	7.00	12.86
LW-8 ³	69.60	5.76	6.56	6.02

1. Extent of alkylation in units of number of alkyl (CH₃) groups added per 100 carbon atoms

2. Analytical data provided by Argonne National Laboratories

3. Analyses performed by Huffman Laboratories, Golden, CO

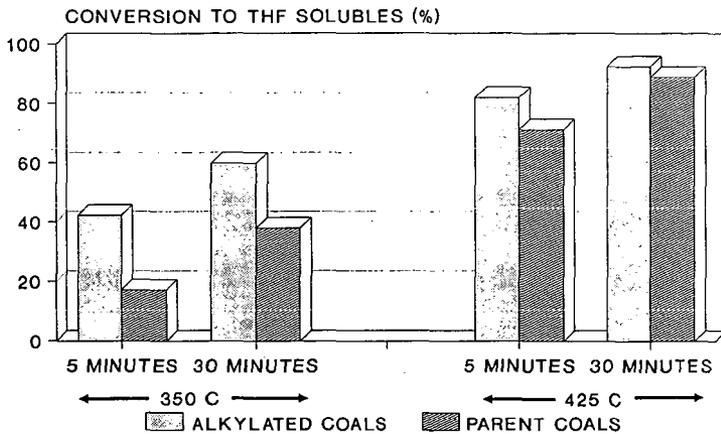
REACTIVITY COMPARISONS IN DHP



EXTENT OF ALKYLATION = 12 GR/100 C ATOMS

FIGURE 1

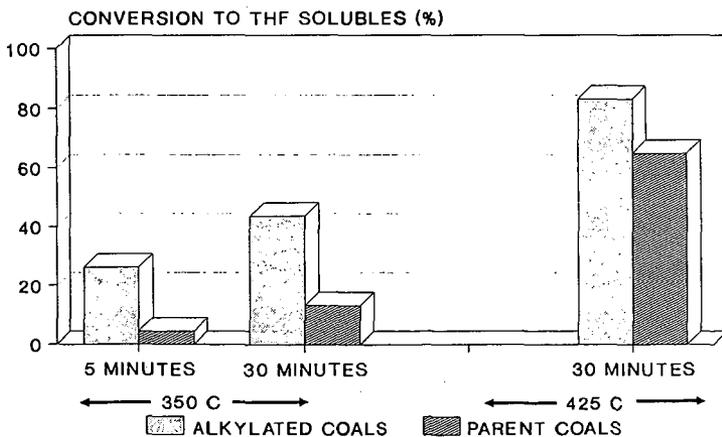
REACTIVITY COMPARISONS IN DHP



EXTENT OF ALKYLATION = 6 GR/100 C ATOMS

FIGURE 2

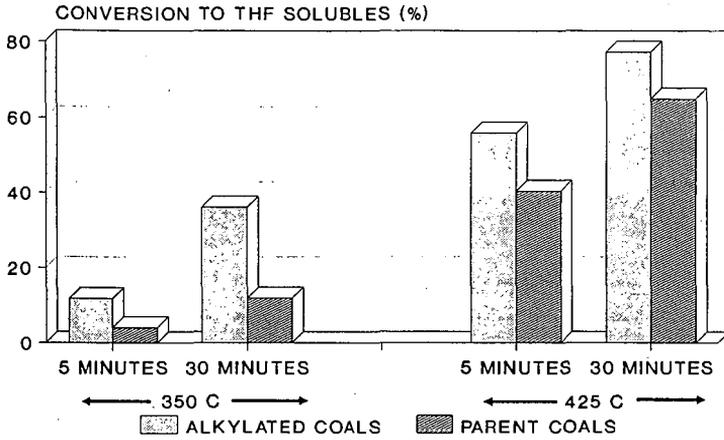
REACTIVITY COMPARISONS IN RESID



EXTENT OF ALKYLATION = 12 GR/100 C ATOMS

FIGURE 3

REACTIVITY COMPARISONS IN RESID



EXTENT OF ALKYLATION = 6 GR/100 C ATOMS

FIGURE 4

EFFECT OF ALKYLATION ON CONVERSION
 DIRECT HYDROGENATION CONDITIONS

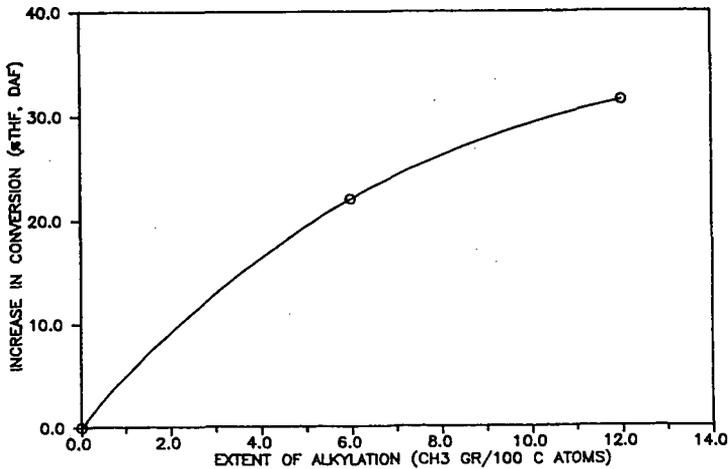


FIGURE 5

EFFECT OF ALKYLATION ON CONVERSION
CO-PROCESSING CONDITIONS

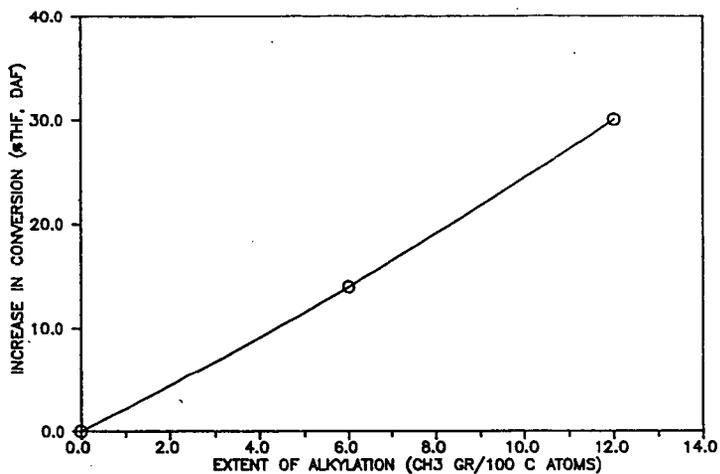


FIGURE 6