

DOE/PC/88812--T11

**PROCESS AND ANALYTICAL STUDIES OF ENHANCED LOW SEVERITY CO-PROCESSING USING SELECTIVE COAL PRETREATMENT**

DOE/PC/88812--T11

DE92 005269

DEC 30 1991

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**Quarterly Technical Progress Report for the Period**  
**September - November, 1989**

**DOE Contract No. DE-AC22-88PC88812**

**MASTER**

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## ABSTRACT

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This report describes progress on research during the fifth quarter of this contract dealing with applications of coal pretreatment techniques in coal hydroliquefaction by co-processing. The objectives of the project are to investigate various coal pretreatment techniques and to determine the effect of these pretreatment procedures on the reactivity of the coal. Reactivity enhancement will be evaluated under both direct hydroliquefaction and co-processing conditions. Coal conversion utilizing low rank coals and low severity conditions (reaction temperatures generally less than 350 °C) are the primary focus of the liquefaction experiments, as it is expected that the effect of pretreatment conditions and the attendant reactivity enhancement will be greatest for these coals and at these conditions.

Research during the past quarter focused on the experimental evaluation of the effect of oxygen alkylation as a pretreatment method for coal reactivity enhancement. An O-alkylation procedure developed by Liotta of Exxon was modified by variation of reaction time and subsequently used to generate samples of a Wyodak subbituminous coal (Argonne Premium Coal Sample Bank) that had been alkylated at two levels (6 and 12 methyl groups per 100 carbon atoms). Subsequent liquefaction of these samples at both low and high severity conditions under both direct hydrogenation (DHP vehicle) and co-processing (hydrotreated Cold Lake

atmospheric resid vehicle) modes of operation indicated that very substantial (as much as 200%) increases in conversion to THF solubles could be obtained at low severity conditions. A conversion of nearly 70% (DAF) was obtained at 350 oC, 30 minutes reaction time in DHP for one coal which had been alkylated to an extent of 12 methyl groups per 100 carbon atoms.

An investigation of the effect of hydrotreating on the resid vehicle was carried out by running comparative co-processing experiments using both the as-received resid and a sample of the hydrotreated resid in parallel microautoclave reactors. Results of these experiments indicated that hydrotreating of the resid had a negligible effect on its performance as a co-processing vehicle with respect to conversion of coal to THF solubles.

## TECHNICAL DISCUSSION

### LIQUEFACTION AND CO-PROCESSING EXPERIMENTS

The overall objectives of this program are to investigate mild chemical pretreatment techniques that will lead to increased coal reactivity and conversion and/or improved distillate yield from coal hydroliquefaction and coal/oil co-processing. The experimental portion of the program is being carried out in both tubing-bomb microautoclave (volumes of c.a. 20-cc) and 300cc stirred autoclave reactors. Screening of pretreatment and reaction conditions is done in the smaller reactors, while larger quantities of material are processed in the 300cc system when needed for detailed analytical workup.

The experimental program is being carried out in two phases. The first phase deals with evaluation of a variety of pretreatment techniques which are designed to attack specific chemical functionalities in the parent coal. The goal of this phase of the program is to develop a reactivity enhancement procedure that will permit coal to be "dissolved" in a stage one co-processing (or direct hydroliquefaction) reactor at mild conditions and in the absence of a catalyst. The second phase of the program will deal with an evaluation of the reactivity of the residuum plus coal-derived material from the low-severity stage one dissolver. Our basic tenant is that this material should, since it was derived at low severity conditions, contain less refractory materials and thus be more amenable to

upgrading in the second stage catalytic reactor. This increased reactivity should, in turn, be evidenced by an increase in distillate yield, operation at lower severity (for stage two), and reduced coke make on the catalyst.

#### 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. (1), and later modified by Ettinger and co-workers (2). 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 cm<sup>3</sup>) 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. The resid used was a sample of Cold Lake atmospheric tower bottoms that had been moderately hydrotreated (400 °C, 2 hours, NiMo/Alumina catalyst) in a batch stirred autoclave reactor (Autoclave Engineers 300 cm<sup>3</sup> magnedrive II system). The hydrotreated resid was used

without further fractionation following hydrogenation. 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 (CH<sub>3</sub>) 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.

A question has been raised recently concerning the effect of hydrotreating on the resid being utilized as the process solvent in our co-processing runs. As stated above, a sample of Canadian Cold Lake atmospheric resid has been hydrotreated under moderate severity conditions, and this material is used without further fractionation as the vehicle when data in the co-processing mode of liquefaction is desired. An examination of the effect of hydrotreating on the resid was made by running a set of parallel

liquefaction experiments at 350 °C, 30 minutes reaction time in the tubing bomb microautoclave. For this run sequence, one reactor utilized hydrotreated resid and the other a straight-run material. Samples of both alkylated and parent Wyodak subbituminous coal were included in this comparison. Conversion of coal to THF solubles at these conditions for both process solvents are shown below:

COAL CONVERSION (%THF, DAF)		
<u>RESID</u>	<u>RAW COAL</u>	<u>ALKYLATED COAL</u>
Straight-Run	13.44	38.03
Hydrotreated	15.03	36.16

Within the accuracy of the measurement, these numbers are essentially identical hence we conclude that the effect of hydrotreating on the solvent with respect to coal conversion to THF solubles is negligible.

#### CONCLUSIONS

Mild O-alkylation has been shown to be a beneficial pre-treatment method for Wyodak subbituminous coal which contains a substantial amount of organic oxygen. Similar results have been reported by other researchers (3), 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.

#### PLANS FOR THE COMING MONTHS

Research during the coming months will focus on completion of the run matrix for alkylation pretreatment. Literature work is now underway on solvent swelling, in order to identify a promising system to use in order to identify the effect of this procedure on coal reactivity under low-severity liquefaction and co-processing conditions. Initial two-stage runs (thermal{low severity}/catalytic) will be carried out during the next quarter as well.

#### REFERENCES CITED

1. Liotta, R.; Rose, K; Hippo, E. J. Org. Chem. 1981, 46, 277
2. Etinger, M.; Nardin, R.; Mahasay, S.R.; Stock, L.M. J. Org. Chem. 1986, 51, 2840
3. McMillen, D.F.; Serio, M.; Solomon, P. Proc. PETC Direct Liquefaction Contractor's Conf., October, 1989

TABLE 1  
ANALYSES OF RAW AND ALKYLATED COALS

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

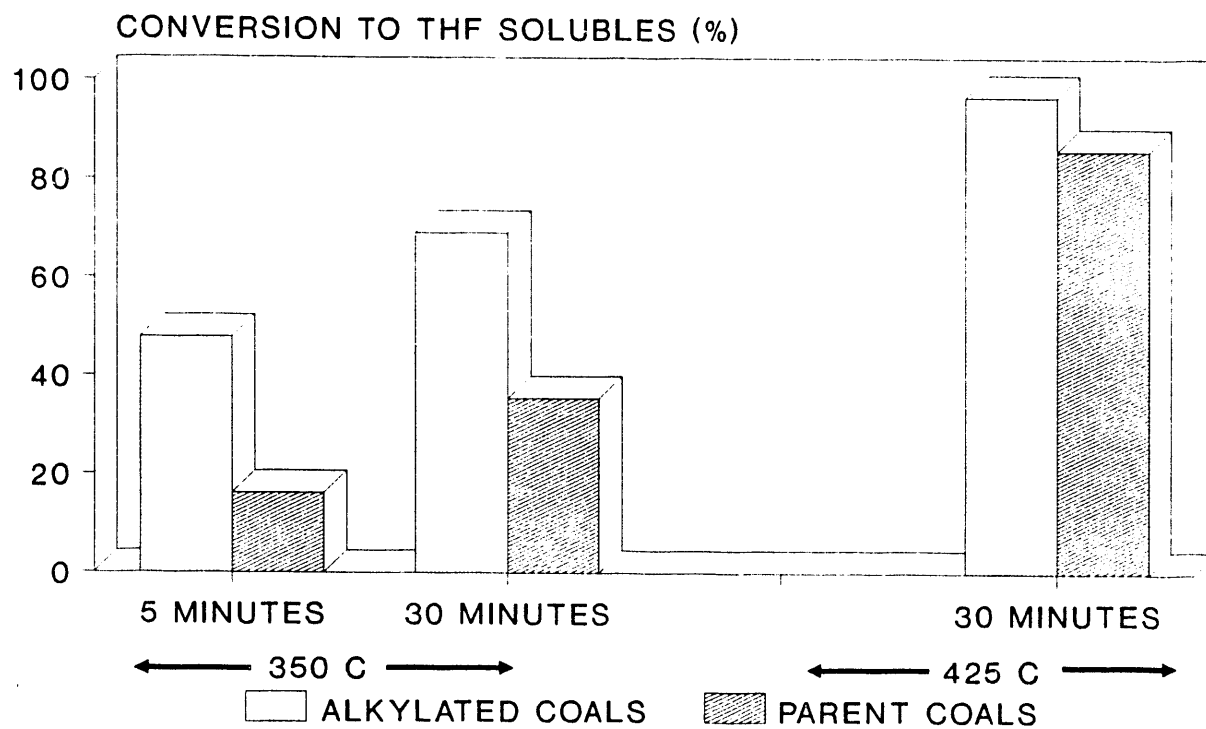
1. Extent of alkylation in units of number of alkyl (CH<sub>3</sub>) groups added per 100 carbon atoms

2. Analytical data provided by Argonne National Laboratories

3. Analyses performed by Huffman Laboratories, Golden, CO

FIGURE 1

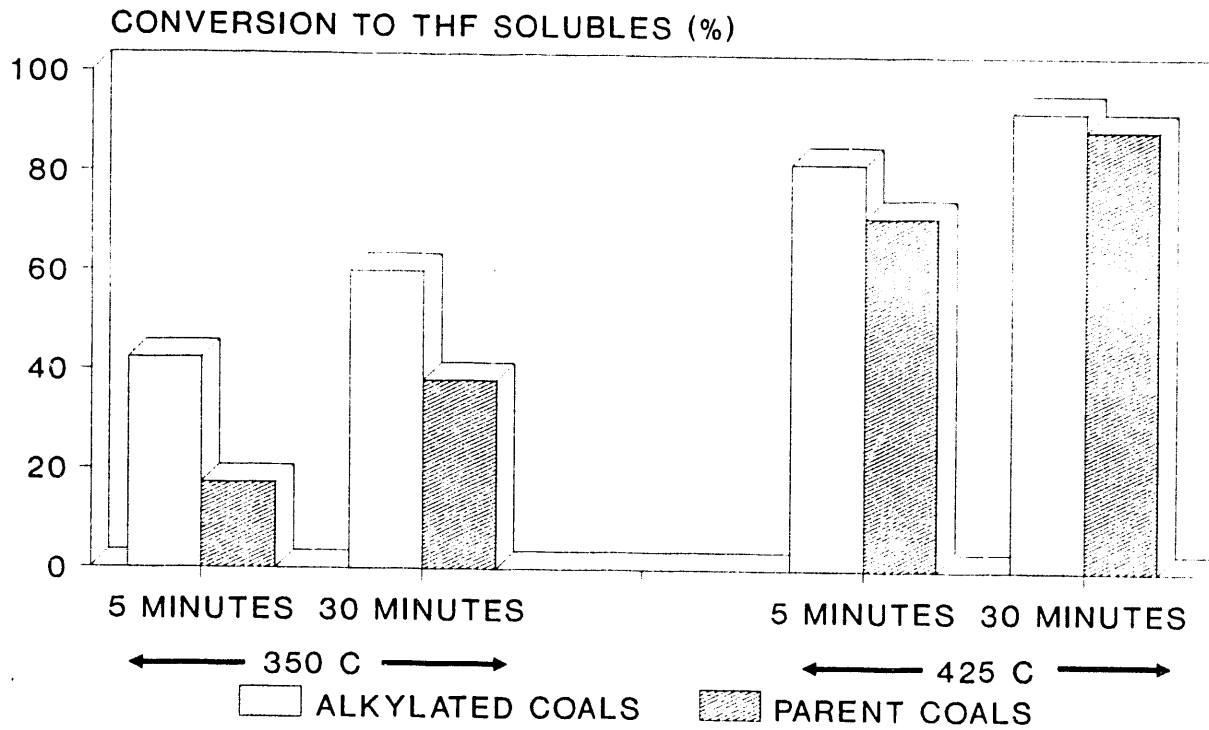
## REACTIVITY COMPARISONS IN DHP



EXTENT OF ALKYLATION = 12 GR/100 C ATOMS

FIGURE 2

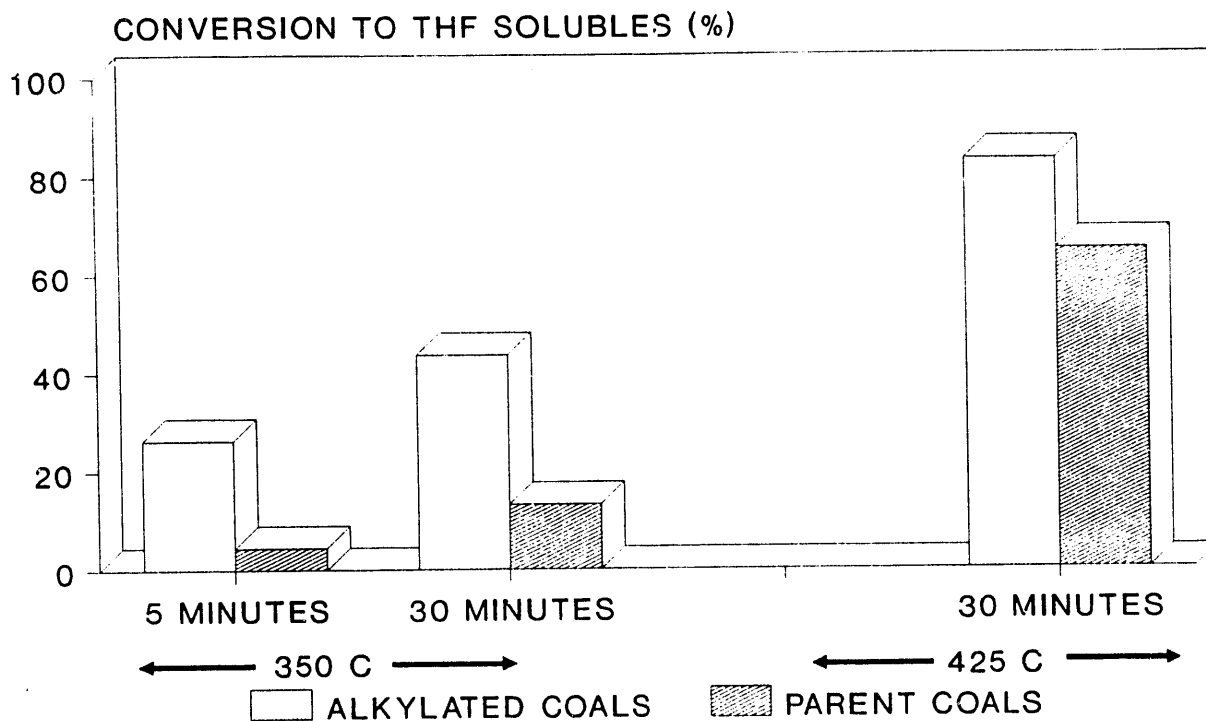
## REACTIVITY COMPARISONS IN DHP



EXTENT OF ALKYLATION = 6 GR/100 C ATOMS

FIGURE 3

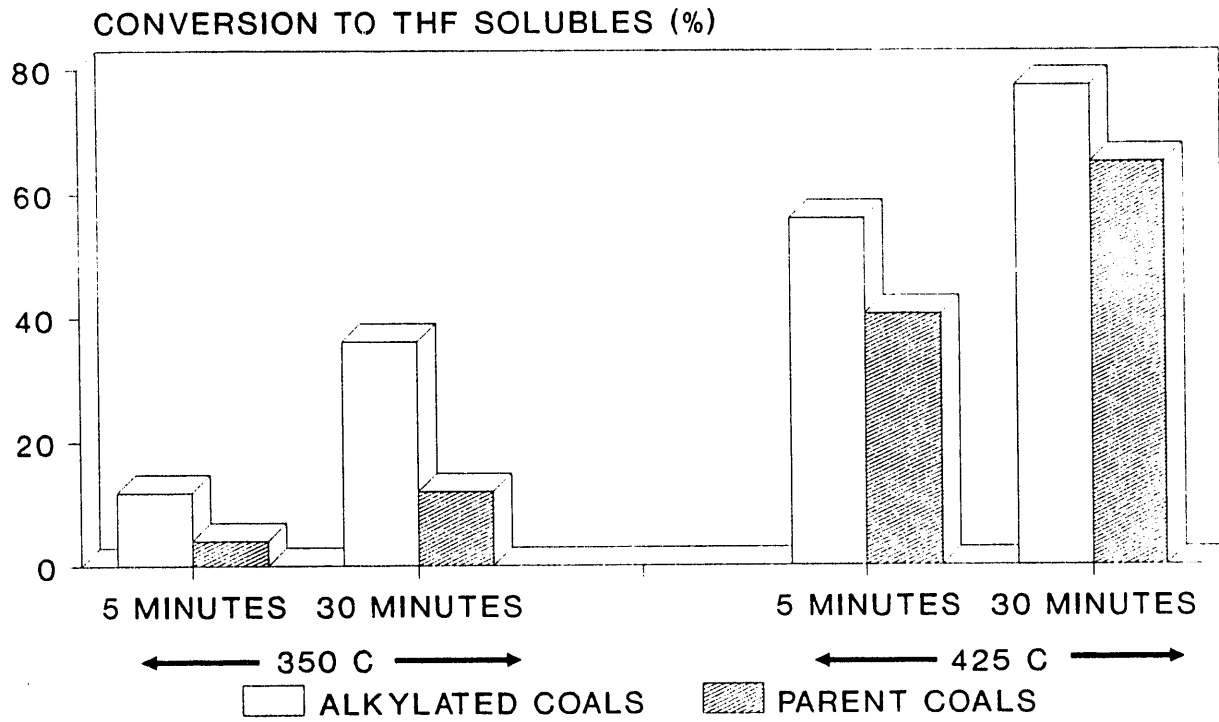
## REACTIVITY COMPARISONS IN RESID



EXTENT OF ALKYLATION = 12 GR/100 C ATOMS

FIGURE 4

## REACTIVITY COMPARISONS IN RESID



EXTENT OF ALKYLATION = 6 GR/100 C ATOMS

FIGURE 5

EFFECT OF ALKYLATION ON CONVERSION  
DIRECT HYDROGENATION CONDITIONS

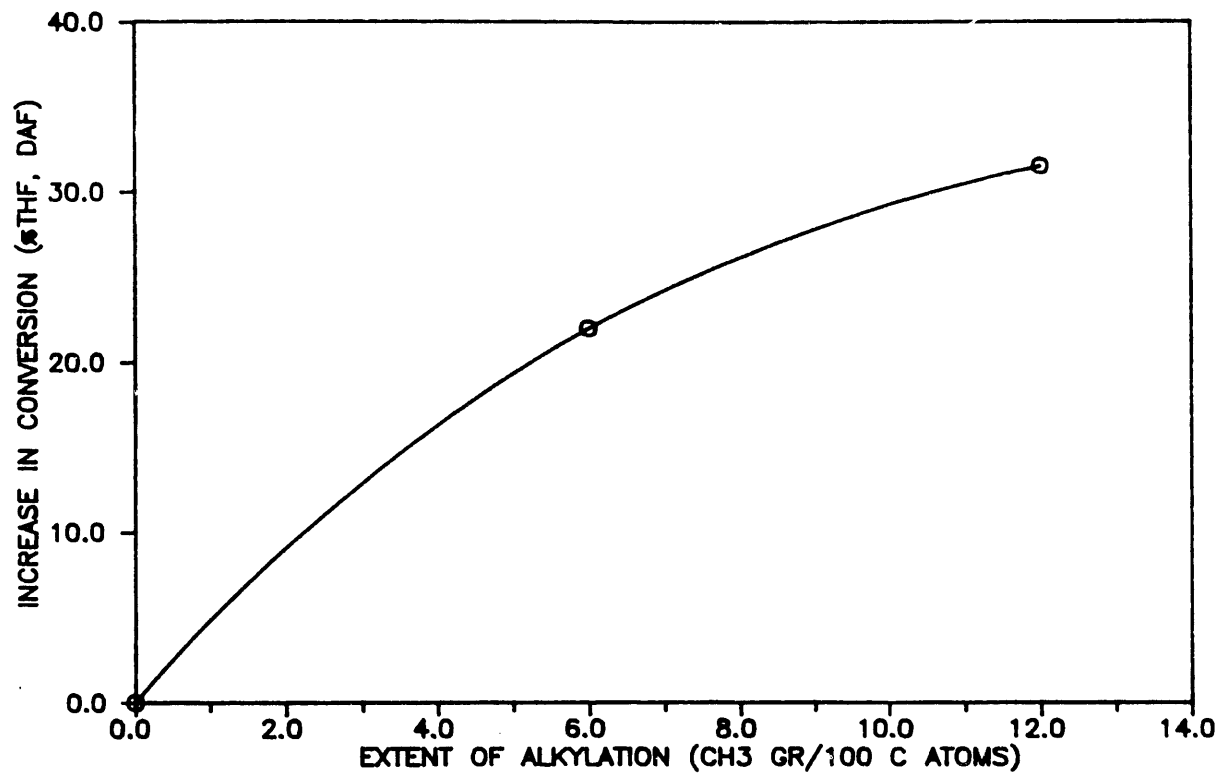
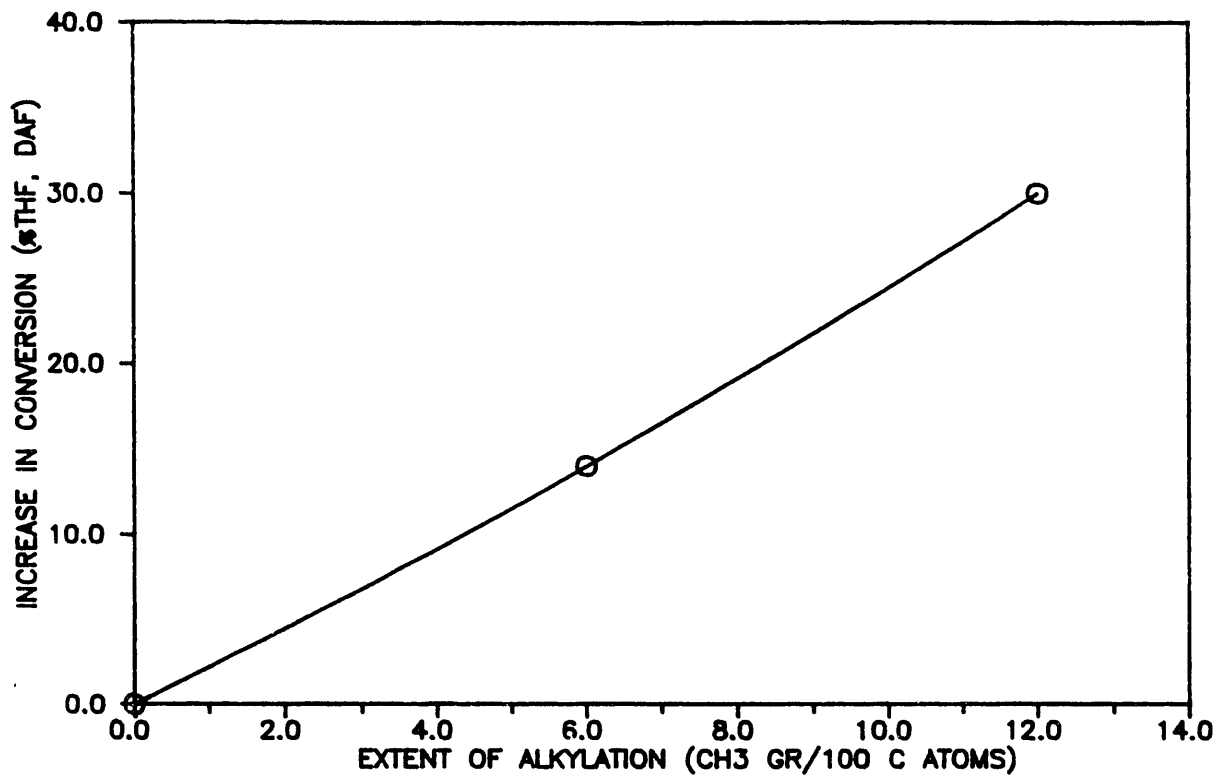


FIGURE 6

EFFECT OF ALKYLATION ON CONVERSION  
CO-PROCESSING CONDITIONS





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