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STEAM PRETREATMENT FOR COAL LIQUEFACTION

Fourth Quarterly Report

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ABSTRACT

Steam pretreatment is the reaction of coal with steam at temperatures well below those usually used for solubilization. The objective of the proposed work is to test the application of steam pretreatment to coal liquefaction.

A 300 ml stirred autoclave for liquefaction tests is being installed.

Pretreatment and extraction tests were made with Blind Canyon coal alone, mixed with Illinois No. 6 coal, impregnated with iron, and impregnated with iron and sulfided using phenyl disulfide. Measurements show an increase in volatiles yield and a decrease in extraction yield with catalyst addition. These results are not yet definitive, because both yields may be artificially decreased by insoluble residue from phenyl disulfide.

About one gram of purified α-naphthylmethyl phenyl ether was prepared and an additional 0.8 gram were synthesized.

Steam pretreatment of the model compound α-benzylnaphthyl ether was repeated with a Pyrex liner for the reactor tube. No differences have yet appeared as a result of using this liner (compared to bare stainless steel), evidence against any catalytic wall effect.

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INTRODUCTION

This is the fourth quarterly report of a two year program on the application of steam pretreatment to the direct liquefaction of coal. Steam pretreatment is the reaction of coal with steam at temperatures well below those usually used for solubilization.

Steam pretreatment has been shown to be effective in coal pyrolysis. For steam pyrolysis, it has more than doubled the liquid yield, reduced the molecular weight of pyrolysis liquid by 31%, and increased yields in mild extraction. Studies of pretreated Illinois No. 6 coal indicate that steam reacts with the ether linkages in coal, replacing them with hydroxyl groups. The result is a partially depolymerized coal. The oxygen content of this pretreated coal is 27% that of the feed.

These results suggest that steam pretreatment prior to solubilization will be beneficial to the coal liquefaction process. It is the objective of this work to test this application. Direct liquefaction of steam pretreated coals will be carried out in a stirred autoclave and the results compared with those from the liquefaction of raw coal.

It is also an objective of this work to develop an improved understanding of the chemistry of steam pretreatment. For this purpose, model compounds will be reacted with steam under the same conditions as used for coal pretreatment and their products analyzed to determine reaction pathways.

CONSTRUCTION OF LIQUEFACTION TEST APPARATUS

Installation of the 300 ml stirred autoclave to be used in direct liquefaction tests was continued this quarter. Safety valves and additional fittings for coal injection have been ordered and received. An apparatus for Soxhlet extraction of liquid products has been prepared. Assembly for conventional slow heating operation will be completed next quarter and testing will begin.

PRETREATMENT STUDIES

Blind Canyon Coal

Pretreatment tests of Blind Canyon coal, Penn State Sample Bank DECS-6, were continued this quarter. The sample was used as received with a particle size of -20 mesh. Moisture content changes with time when this coal is exposed to the air. Consequently, rather than using an average of previously measured values, the moisture content determined before each run is used in calculating yields.

Several pretreatment tests were made to determine volatiles loss (Table 1). Coal was pretreated at 357C using a continuous flow of steam. The extraction yield for this run (FBE3) is given in Table 1 based on daf raw coal charged, volatiles not included. Previously reported yields from raw and pretreated coal (Third Quarterly Report, 1 April to 30 June 1991) at different temperatures are also given in Table 1 for comparison. At a pretreatment temperature of 357C, the extraction yield is lower than for raw coal. Evidently, the temperature range for even the slight improvement observed in earlier runs has been exceeded.

Table 1
Steam Pretreatment of Blind Canyon Coal

Run No.	Temperature (C)	Pressure (psi)	Extraction Yield (%)	Volatiles Loss (%)
RBE 1	raw	-	13.08	-
RBE 2	raw	-	13.79	-
FBE 2	335	750	14.74	3.58
FBE 1	340	750	15.62	4.35
FBE 3	357	750	12.50	4.43
VB 4	320	750	-	6.78

The next run was aimed at testing for catalytic components present in Illinois No.6 coal but not in Blind Canyon coal. A mixture of the two coals was prepared containing 20% of Illinois No.6 coal with 80% Blind Canyon coal. This mixture was pretreated in steam at 340C and 750 psia. Experimental extraction yields and volatiles

losses are given in Table 2 where they are compared with values calculated by linear interpolation from the component coals. No significant catalytic effect is apparent.

Table 2.
Pretreatment of Mixture Containing
20% Illinois No.6 and 80% Blind Canyon Coals

Run No.	Temperature (C)	Pressure (psi)	Extraction Yield (%)	Volatiles Loss (%)
calc.	raw	-	13.68	-
FM 1	340	750	18.19	3.62
calc.	340	750	17.50	5.15

These tests, however, do not rule out the possibility that the catalytic components must initially be highly dispersed. The next runs were, accordingly, conducted with Blind Canyon coal impregnated with iron. The sample, prepared at PETC, contained 2500 ppm iron (as FeOOH). The moisture content of this sample was determined to be 1.79%. Pretreatment was carried out at 340C and 750 psia. Volatiles yield during pretreatment and extraction yield following pretreatment were determined based on the daf raw coal charge. The results are given in Table 3 (run FBE 4) compared with the previously reported extraction yields from raw and steam pretreated coal. Apparently, use of iron gives only a slight change in product quality (increasing volatiles yield and decreasing extraction yield) without improvement in total yield.

In the next two runs (FBE 5 and 7), the effect of sulfur was tested. Blind Canyon coal impregnated with iron was sulfided (using phenyl disulfide) before steam pretreatment. The sample impregnated with iron (2500 ppm Fe as FeOOH) was mixed with phenyl disulfide. Two different ratios of phenyl disulfide to coal were used. The reactor was loaded with a mixture coal and phenyl disulfide under an inert atmosphere, sealed, and submerged in a 200 C fluidized bed for 40 minutes. The reactor was then removed from the bed while the bed was heated to 340 C in preparation for the steam pretreatment step. Pretreatment of the sample was carried out for 15 min at 340 C and 750 psia. The results are given in Table 3.

Taken at face value, these results show that the added catalysts increase volatiles yield while decreasing extraction yield. A possible defect of these experiments is that the yields of volatiles and extractables are separately determined by weighing the solid residue in each case. If phenyl disulfide itself leaves a solid residue or combines with the coal structure, these yields are artificially decreased. Both volatiles and extraction yields would then be higher than reported. Since decreasing the phenyl disulfide to coal weight ratio from 1 to 0.1 decreases the volatiles yield, it can be concluded that, in this environment, sulfur promotes the production of volatiles. On the other hand,

the simultaneous increase in extraction yield could be taken to indicate that these are masked by residue from phenyl disulfide. In the next quarter, a test will be conducted to see if these trends continue to an even lower ratio of phenyl disulfide to coal.

Table 3.
Steam Pretreatment of Blind Canyon Coal
at 340C and 750 psia.

Run No.	Coal Sample	Extraction Yield (%)	Volatiles Yield (%)	Total Yield (%)
RBE 1	raw	13.08	-	13.08
FBE 1	steam pretreated no catalyst	15.62	4.35	19.97
FBE 4	steam pretreated with Fe	14.18	6.00	20.18
FBE 5	steam pretreated with Fe + S disulfide/coal=1*	4.78	10.53	15.31
FBE 7	steam pretreated with Fe + S disulfide/coal=0.1*	8.57	8.80	17.37

* weight ratio of phenyl disulfide to coal.

MODEL COMPOUND STUDIES

Model Compound Purification

Purification of the first batch of α-naphthylmethyl phenyl ether was completed using a combination of trituration, recrystallization (at -70C) and flash column chromatography on basic alumina. To avoid rearrangement, it was necessary to work under conditions of very low acidity.

Crude α-naphthylmethyl phenyl ether was first triturated in ethanol to remove unreacted 1-(chloromethyl) naphthalene. This contaminant was also crystallized before the trituration procedure to minimize the amount of product lost during the trituration steps. Crude product was dissolved in a solution of hexane/ether/ethanol (5/2/2 volume ratio) for recrystallization. Four hours at -70C was adequate for recrystallization. Repeated flash column chromatography on basic Alumina using a solution of ether/hexane (2/10 volume ratio) allowed purification to be completed while

avoiding the previously encountered facile acid catalyzed rearrangements of the α-naphthylmethyl phenyl ether.

Solvents for ^1H NMR ($CDCL_3$) were passed through a basic Alumina pad to remove traces of acid (Figure 1).

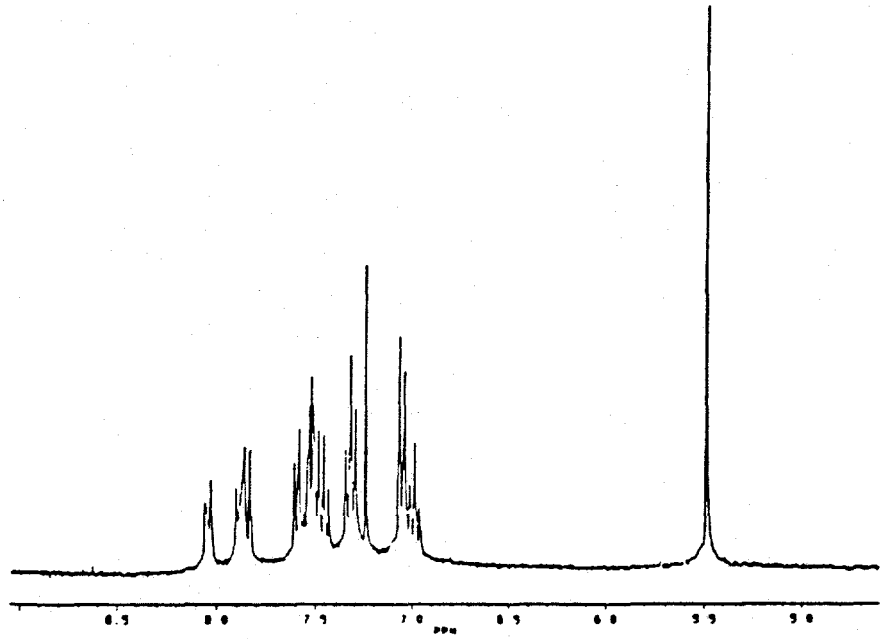

Figure 1. ^1H NMR of α-naphthylmethyl phenyl ether.

The first batch of α-naphthylmethyl phenyl ether yielded about one gram of purified material. An additional 0.8 gram were synthesized and is being purified.

Steam Pretreatment of Model Compounds

The steam pretreatment of α-benzylnaphthyl ether at 320 C and 750 psi was repeated (run MK1-2). In this case, a Pyrex insert was used to shield the reactants from the stainless steel reactor wall. One tenth of a gram of the compound was placed in a glass tube, inserted into the reactor, and sealed under an inert atmosphere. Pretreatment was carried out as described in previous reports.

After pretreatment, the gas phase present in the reactor tube was vented directly into the mass spectrometer for analysis. The liquid was analyzed by GC-MS. This spectrum proved to be identical to that previously obtained without using a glass liner in the reactor tube. Hence, no catalytic effects from the reactor wall are indicated. Preparative GC of the liquid is in progress so that unambiguous identification of the major components by NMR will be possible.

WORK PLANNED FOR NEXT QUARTER

Assembly of the autoclave system for conventional slow heating operation will be completed next quarter and testing will begin. An additional pretreatment test of Blind Canyon coal impregnated with iron and sulfur will be carried out at lower sulfur loading. Pretreatment of model compounds an product identification will be continued. Purification of the second batch of model compound α-naphthylmethyl phenyl ether will be completed.

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