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REVIEW

STEAM PRETREATMENT FOR COAL LIQUEFACTION

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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.

Installation of the stirred autoclave for conventional slurry liquefaction (slow heating) was completed and preliminary testing carried out. Two liquefaction tests with untreated Illinois No. 6 coal gave satisfactory results.

An additional pretreatment test of Blind Canyon coal was conducted this quarter which confirms the tentative conclusions previously reached: volatiles yields are increased by the addition of sulfided iron catalyst; it is not possible to ascertain (by the procedure used) whether extraction yield decreases or remains constant.

Chromatographic separation and analysis of the products from treated α -benzyl naphthyl ether has been continued. A transformation of the product over several weeks has been noted. The ^1H nmr spectrum of this product obtained in a glass lined reactor is found to be different from that obtained previously in a stainless steel reactor.

The model compound α -naphthylmethyl phenyl ether has been steam pretreated and the analysis of its liquid product started. Three major components have been identified.

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INTRODUCTION

This is the fifth 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 stirred autoclave for conventional slurry liquefaction (slow heating) was completed. Preliminary testing was carried out.

The system was pressure tested with cold nitrogen and a dry run was made. No coal or solvent was used in these tests. The empty reactor was sealed, purged with nitrogen, and leak tested to 2000 psia. Minor leakage was corrected. The reactor was then pressurized to 885 psia. Using an electric furnace, the autoclave was heated in 45 min to 400 C and maintained at this temperature for 20 min. The operating pressure at this temperature was 1700 psi. Once satisfactory maintenance of pressure was verified, the reactor was allowed to return to room temperature.

With the completion of these preliminary tests, the autoclave was ready for coal liquefaction trials using conventional methods.

LIQUEFACTION TESTS

Two slurry liquefaction tests were carried out in the 300 ml stirred autoclave operating in the conventional slow heating mode using Illinois No. 6 coal (Penn State DECS-2, CFI No. 27, Sample A) with a particle size of -20 mesh.

Ten grams of coal, previously dried in a vacuum oven at 110 C for 16 hours, were mixed with 100 ml of tetralin in the reaction vessel. The reactor was sealed, pressurized with cold nitrogen and leak tested at 2000 psia. Minor leakage was corrected. The nitrogen was then replaced by hydrogen, flushing twice and then pressurizing to 500 psia. Using an electric furnace, the autoclave was heated to 400 C in 35 min and maintained at this temperature for 30 min. The operating pressure at 400 C was 1300 psi. To terminate the run, the heater was turned off and removed from the autoclave. When ambient temperature was reached, the reactor was vented and opened. The contents of the reaction vessel were transferred to a weighed cellulose Soxhlet thimble (double thickness) using hexane as the transfer solvent. The reaction products were extracted sequentially with hexane, toluene and THF. The thimble and its contents were dried to constant weight after 18 hours of extraction with each solvent. It should be noted that in this procedure, the first extraction is carried out with a mixture of hexane and tetralin as recovered from the reactor. This gives a higher yield than hexane alone.

From these weights, coal conversion was calculated on a daf basis. The product distribution is classified as follows: oils and gases (hexane soluble), asphaltenes (toluene soluble), preasphaltenes (THF soluble). According to Joseph (1991), the gas yield is less than 5%. The results are shown in Table 1 along with literature values for comparison.

Table 1

Liquefaction of Illinois No.6 Coal

Run No.	Total	Conversion (wt%)		Preasphaltenes
		Oils	Asphaltenes	
C1*	(68.6)	31.5	17.9	18.5
C2	68.6	31.1	14.2	23.3
Joseph, 1991	69	22	31	16

* In run C1 the coal sample was not previously dried. Some loss of material occurred during transfer of liquefaction products from the reaction vessel giving a high total yield of 86.2%. To correct for this, the values reported above have been normalized to the total yield of run C2.

The procedure and conditions are those used by Joseph (1991). While the total yields are identical, our yields of oils and preasphaltenes are higher but asphaltenes are lower. This may be caused by differences in the two samples of Illinois No. 6 coal employed.

The preliminary operating tests of the autoclave have been completed. While modifications to the extraction procedure may be explored in the future, the above results are considered satisfactory for the present. Modification of the reaction system for coal slurry injection and rapid heating will be carried out next quarter.

PRETREATMENT STUDIES

Blind Canyon Coal

An additional pretreatment test of Blind Canyon coal was conducted this quarter (run No. FBE8). The sample of coal impregnated with iron (2500 ppm Fe as FeOOH) was again used, but the weight ratio of phenyl disulfide to coal was further reduced to 0.03. Otherwise, the procedure was the same as previously used.

Results for the entire series of runs with Blind Canyon coal are listed in Table 2. Yields are based on daf raw coal charged. The results for run FBE 8 are consistent with the conclusions reached in the previous report. The observed volatiles yields increase and extraction yields decrease with increasing sulfur loading. Both determinations may be masked by residue from the decomposition of phenyl disulfide. The apparent decrease in extraction yield might be entirely due to this residue. On the other hand, the increase in

volatiles must be real and is considerably larger than reported if residue is indeed present.

Table 2.
Steam Pretreatment of Blind Canyon Coal
at 340 C and 750 psi.

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
FBE 8	steam pretreated with Fe + S disulfide/coal=0.03*	12.15	4.34	16.49

* weight ratio of phenyl disulfide to coal.

MODEL COMPOUND STUDIES

Model Compound Purification

Purification of the second batch of α -naphthylmethyl phenyl ether was continued and will be completed next quarter.

Steam Pretreatment of Model Compounds

α -benzyl-naphthyl ether

Chromatographic separation and product analysis of the previously steam pretreated α -benzyl-naphthyl ether (α -BNE) continued. Washing the residue in the reactor with methylene chloride produced 73 mg of extractable material (100 mg of the compound had been used for pretreatment). GC-MS analysis of the methylene chloride extract revealed the presence of three major components as described in an earlier report. The ion chromatogram is somewhat deceiving as the integrated areas of the GC-MS trace may not reflect the product distribution. Development of a GC separation scheme to effect efficient separation of the methylene chloride extract was accomplished using a linear temperature program. The conditions are as follows:

HP 5890.TCD (N₂)
Column: Supelco SPB 5, 30 m, 0.75 mm ID
Temperature Program: 30 C to 160 C,
rate= 10 C/min.

Three major components were observed (Figure 1).

A significant observation was made while performing the GC separation of the extract. Figure 1 and Table 3 show a complete shift in the proportions (integral areas) of peaks 2 and 3 in the sample. It appears that component 2 is being transformed into component 3. This transformation will be investigated further.

Table 3.
Product Distribution Change During Separation.

	PEAK 1, %	PEAK 2, %	PEAK 3, %
WEEK 1	6.70	64.00	29.20
WEEK 2	6.07	27.95	65.97

A comparison of the ¹H nmr spectrum (5.5 ppm to 2.5 ppm) of the products of steam pretreatment in the glass lined reactor and in the stainless steel reactor revealed considerable differences (Figure 2). Despite the observation of near identical GC-MS data (Cl mode using ammonia), a simpler spectrum (cleaner reaction) and a significant change in the product distribution (peak intensities) were obtained using the glass lined reaction vessel.

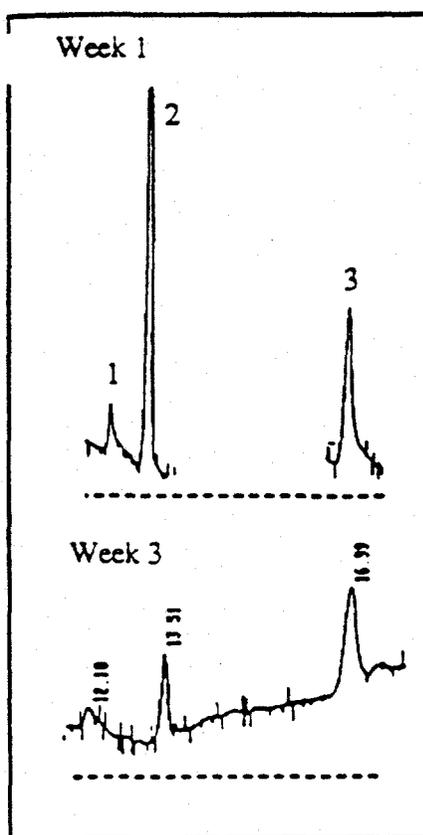


Figure 1. Steam pretreatment of α -benzyl-naphthyl ether. GC analysis of methylene chloride extract of products obtained in a glass lined reactor.

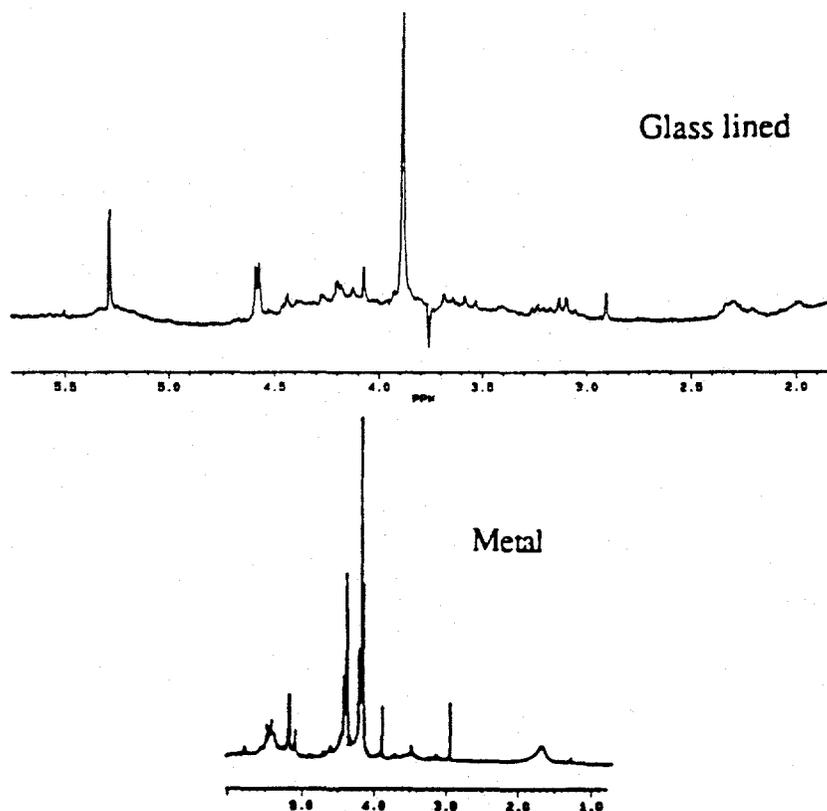


Figure 2. Steam pretreatment of α -benzyl-naphthyl ether. Comparison of ^1H nmr spectra of CH_2Cl_2 extracts.

To verify the structural identities of the components 1-3, collection and subsequent GC-MS, and NMR analyses are at present being done on the collected fractions. Continued efforts are being made to separate and quantify the components of the steam treatment product, verify the structural integrity of the separated components by other spectroscopic methods and further investigate the observed transformation of the recovered product.

α -naphthylmethyl phenyl ether

A steam pretreatment of the model compound α -naphthylmethyl phenyl ether (α -NMPE) was conducted at 320 C and 750 psia in a glass lined reaction vessel (run MK3-1). This parallels the procedure used for α -BNE reported previously (Fourth Quarterly Report, 1 July to 30 September 1991). One hundred mg of the compound were used. After pretreatment, gases in the reactor tube were vented directly into the mass spectrometer for analysis.

The products were then removed from the reactor with methylene chloride and subjected to GC-MS analysis. Both chemical ionization (CI) with NH_3 and electron ionization (EI) were used. The ion chromatogram showed six major components whose molecular masses are shown in Figure 3.

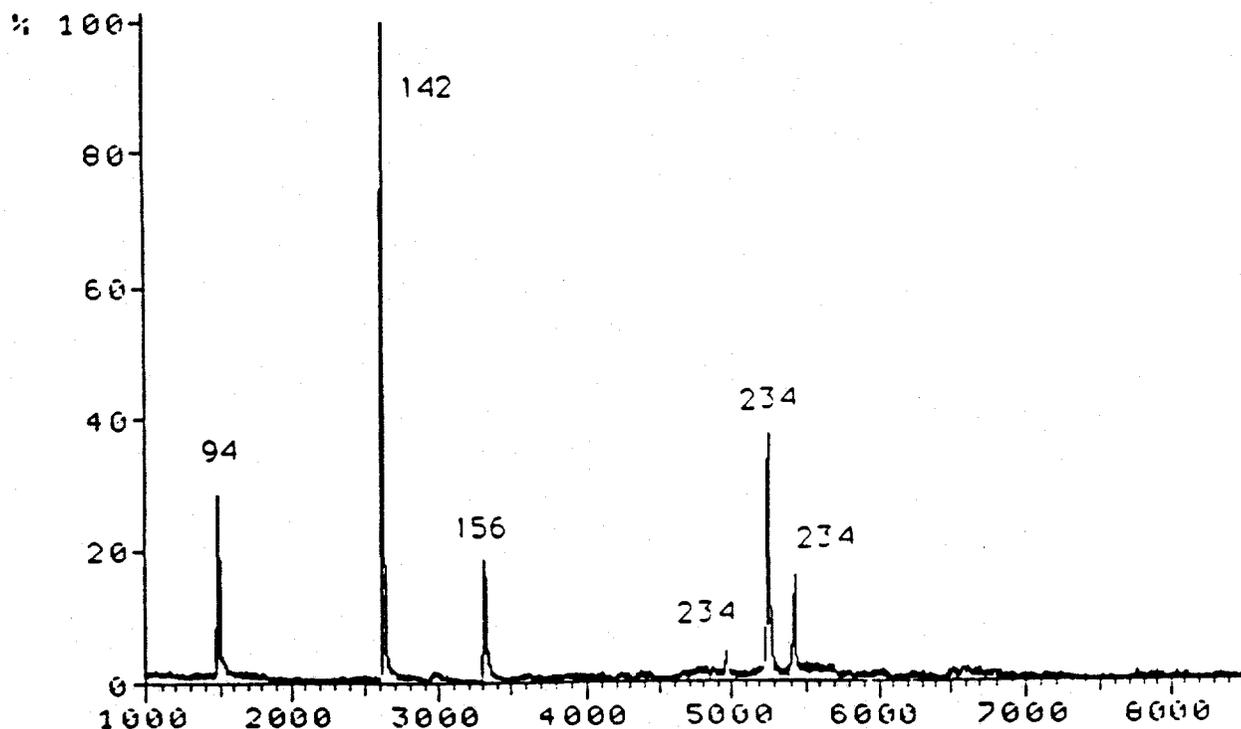


Figure 3. Steam pretreatment of α -naphthylmethyl phenyl ether. GC-MS (CI mode using ammonia) ion chromatogram.

A preliminary identification of these products is given in Figure 4.

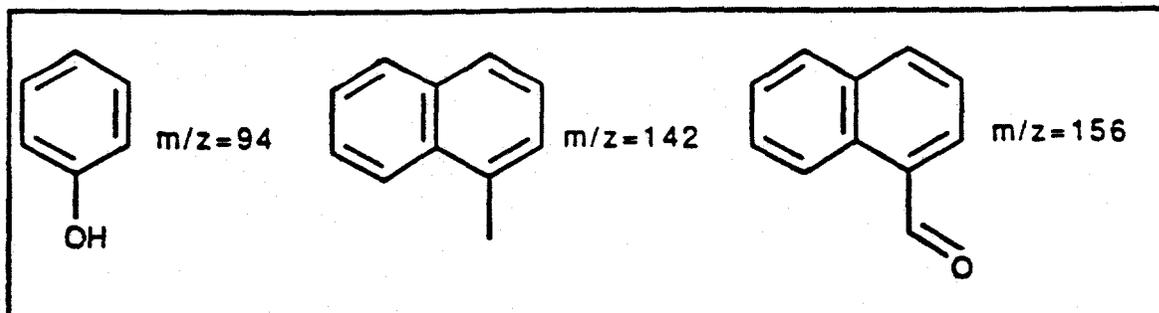


Figure 4. Steam pretreatment of α -naphthylmethyl phenyl ether. Structural assignments to GC-MS components.

A proton nmr spectrum of the methylene chloride extract was also taken (Figure 5). The presence of the aldehyde proton at 10.15 ppm correlates with the GC-MS peak with m/z of 156. The near absence of starting material (5.5 ppm) supports the identification of the three components with m/z of 234 as rearranged starting material.

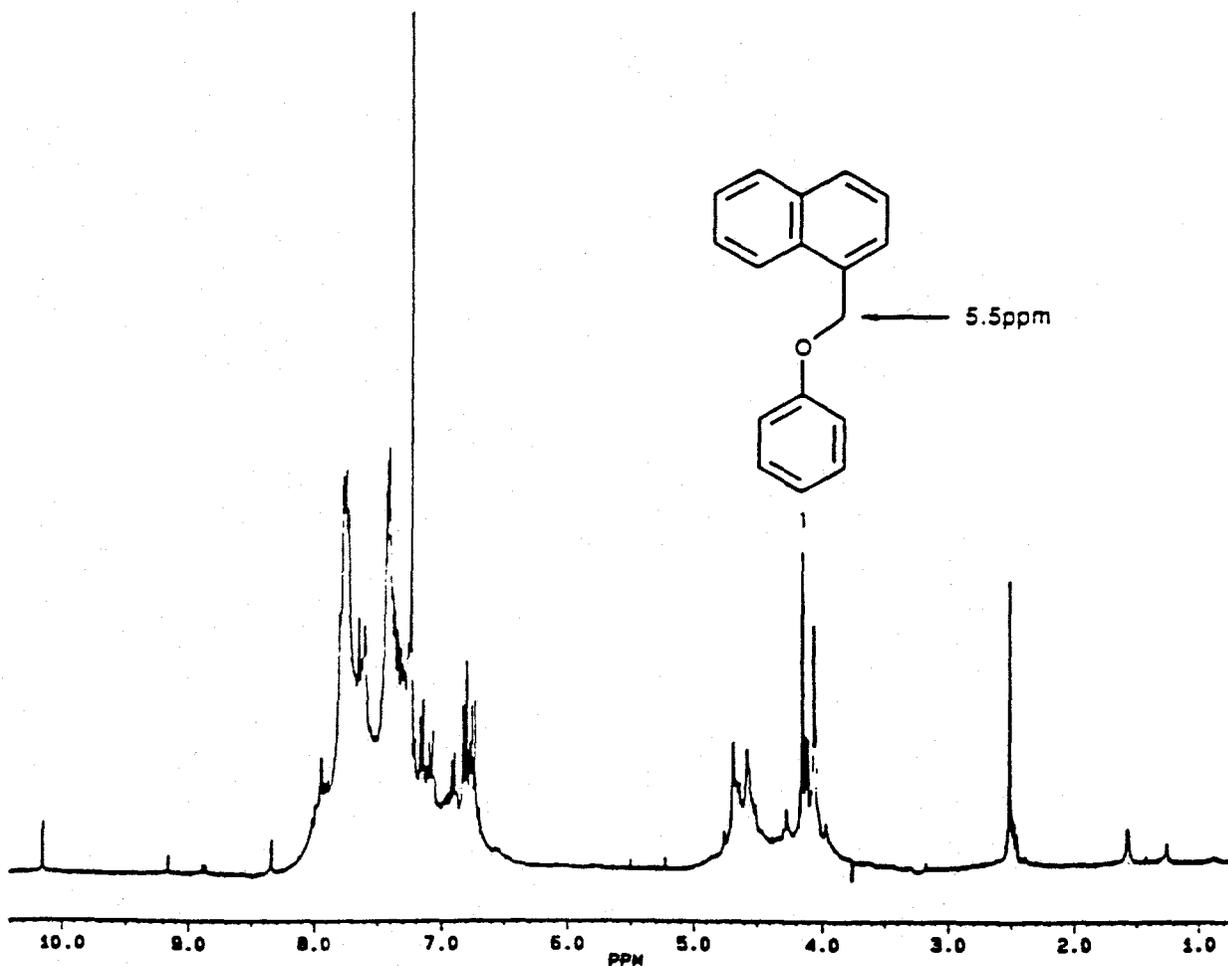


Figure 5. Steam pretreatment of α -naphthylmethyl phenyl ether. ^1H nmr (CDCl_3) of CH_2Cl_2 extract.

Analysis of this mixture will be continued to fully identify the three major rearrangement products.

Keeping in mind the difficulty encountered in the purification of α -NMPE and the interconversion of the α -BNE extract, careful monitoring and understanding of the mechanisms involved in any changes in the structural integrity of the sample are now an important concern.

REFERENCES

Joseph, J.T. (1991), "Liquefaction Behavior of Solvent Swollen Coals," Fuel, 70, 139.

WORK PLANNED FOR NEXT QUARTER

Modification of the reaction system for coal slurry injection and rapid heating will be carried out next quarter.

Analysis of α -naphthylmethyl phenyl ether products will be continued. Steam pretreatment of α -benzyl naphthyl ether will be repeated in order to further investigate the reactions of this model compound.