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REVIEW

STEAM PRETREATMENT FOR COAL LIQUEFACTION

Sixth Quarterly Report

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Robert A. Graff

Valeria Balogh-Nair

The City College of CUNY
Office of Research Administration
New York, NY 10031

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Arun C. Bose, Program Manager

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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.

Conversion of the autoclave apparatus to rapid heating liquefaction was carried out this quarter following redesign of the coal slurry injection system. The modified equipment and procedure was tested in a simulated liquefaction run without coal. Initial tests of slurried -20 mesh coal showed too rapid settling for successful operation. Coal ground to pass 200 mesh proved suitable, and an impact grinder was put into operation to grind the material under an inert atmosphere. A batch of Illinois No. 6 coal for the first rapid heating liquefaction tests has been prepared and stored under inert gas.

The steam pretreatment of α -benzyl-naphthyl ether was carried out using stainless steel and glass lined reactors. A preparative scale procedure for product separation was developed. The major components were identified and the average product distribution determined for both types of reactors.

Pretreatment of α -naphthylmethyl phenyl ether was also carried out using stainless steel and glass-lined reactors. Separation and analysis of the products has been started. The major components have been identified. Analyses and identification of the components will be continued next quarter.

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INTRODUCTION

This is the sixth 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

Slow heating liquefaction tests were completed last quarter. Conversion of the autoclave apparatus to rapid heating liquefaction was carried out this quarter.

The coal slurry injection system was redesigned. Instead of following the method used by Whitehurst, et al. (1976) using a floating piston and a solenoid valve, we have adopted the approach of Klein and Provine (1990) employing a rupture disc. The latter, we believe, will prove easier to construct and be more trouble free in operation.

In the revised scheme (Figure 1), a coal slurry injection line is added to the conventional reaction system in parallel to the gas inlet line. The coal slurry injection line contains a stainless steel reservoir holding the coal slurry. This reservoir is separated from the autoclave by a 1000 psia rupture disc.

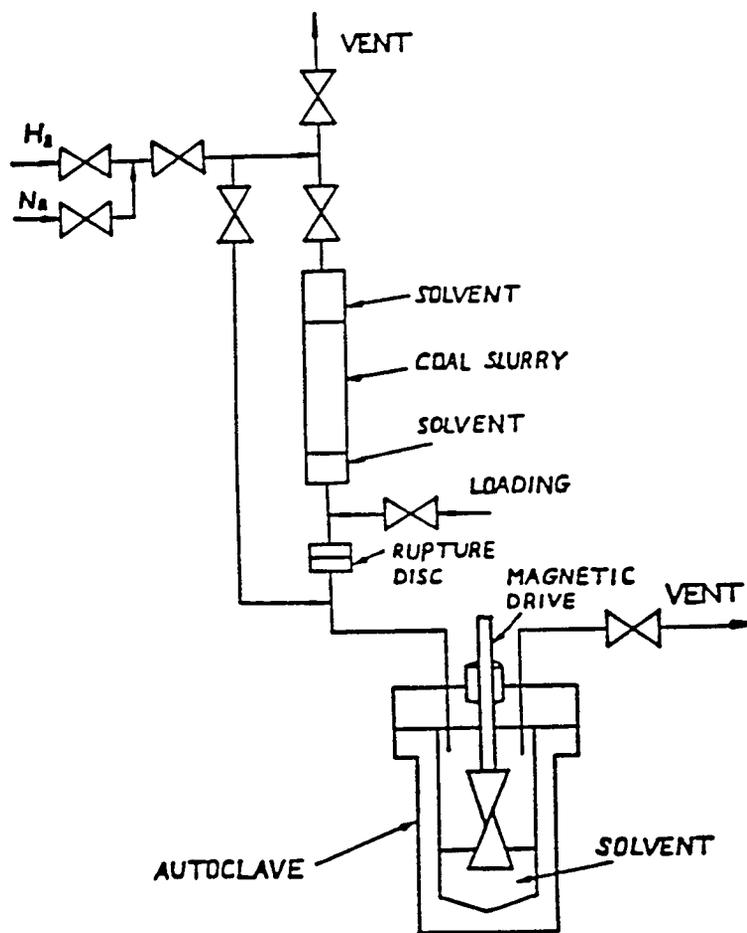


Figure 1. Stirred Autoclave with Coal Slurry Injection.

With this apparatus, the liquefaction procedure is as follows: Sixty grams of solvent (tetralin) is placed into the autoclave, and the vessel is sealed. After leak testing the autoclave with nitrogen, the reactor is flushed with hydrogen and then heated using an electric furnace. As the desired operating temperature is approached, the injection vessel is sequentially loaded with 15 g solvent, 40 g coal slurry containing 50 wt% of coal, and 5 g solvent using a glass syringe.

When the reaction temperature has been reached, coal slurry injection is executed by closing the gas bypass line and applying hydrogen at reaction pressure to the slurry reservoir. This causes the rupture disk to burst, sweeping the coal slurry into the reactor and pressurizing the autoclave. Thereafter, the liquefaction run and subsequent Soxhlet extraction is carried out as described in the previous Quarterly Report (Fifth Quarterly Report, 1 October 1991 to 31 December 1991).

Conversion of the autoclave system for rapid heating was completed and the entire system pressure tested to 3000 psia at room temperature. The system was then pressurized again to 1500 psia to test the action of the rupture disc.

A simulated liquefaction experiment was carried out to test the experimental procedure and the equipment at operating temperature. Coal was not used in this test; otherwise the procedure was identical to that described above with coal slurry replaced by an equal volume of solvent. It was found that before injection the autoclave will have to be heated about 60 C above the desired final temperature in order to avoid subcooling and prolonged thermal recovery. The test was otherwise totally successful.

Initial tests of 50 wt% slurry in tetralin were made with -20 mesh coal. Settling was too rapid to either allow syringe loading of the reservoir or to allow storage in the reservoir before injection. Tests were successful when -200 mesh coal was used. Consequently, our coal samples, which were received as -20 mesh, must be ground to pass 200 mesh. For this propose, a Trost Air Impact Pulverizer was put into operation. A batch of Illinois No. 6 coal for the first rapid heating liquefaction tests has been ground to pass 200 mesh. Grinding was carried out under nitrogen atmosphere and the sample is now stored under inert gas. Rapid heating liquefaction tests will be initiated next quarter.

MODEL COMPOUND STUDIES

Model Compound Preparation

An additional 0.7 grams of α -naphthylmethyl phenyl ether was synthesized for later use.

Steam Pretreatment of Model Compounds

α -benzyl naphthyl ether

The steam pretreatment of model compound α -benzyl naphthyl ether (α -BNE) was conducted at 320 C and 750 psia using two types of reaction vessels. In Run No. MK1-3, 0.2 grams of compound were pretreated in a stainless steel reactor. Runs No. MK1-4 and MK1-5 were carried out in glass lined vessels using 0.1 gram of material in each case. After pretreatment, gases in the reactor tubes were vented directly into the mass spectrometer for analysis. The liquids were then extracted from their reactors and frozen at -70C to prevent chemical transformations pending further analysis.

Work towards the separation and identification of reaction products formed by steam treatment of model compounds was carried out using analytical scale chromatographic separation (SPB5 Supelco column) as a guide to the development of a preparative scale separation scheme. Carbowax 20M and Tenax GC (Alltech) packed columns were tested as media for the separation. Preliminary chromatographic analyses were carried out using 1-naphthol, 2-naphthol, toluene, benzaldehyde, α -benzyl naphthyl ether, and α -naphthylmethyl phenyl ether to determine sample recovery, column characteristics related to sample size, and the ability to conduct the separation at temperatures above 250C. Tenax GC proved to be the best medium for separation.

Preparative GC separation of the reaction products from runs No. MK1-3 - MK1-5 was accomplished using the selected Tenax GC (Alltech) packed column. The GC profile is shown in Figure 2. Using a combination of ^1H , and ^{13}C nmr spectroscopy, CI-MS and EI-MS analyses, the structures of the major constituents labelled 2, 5, and 6, were determined to be 1-naphthol, 2-benzyl-1-naphthol, and 4-benzyl-1-naphthol, respectively. Prior to the above GC separation, the volatile compound, toluene, had also been detected (via MS) as a reaction product.

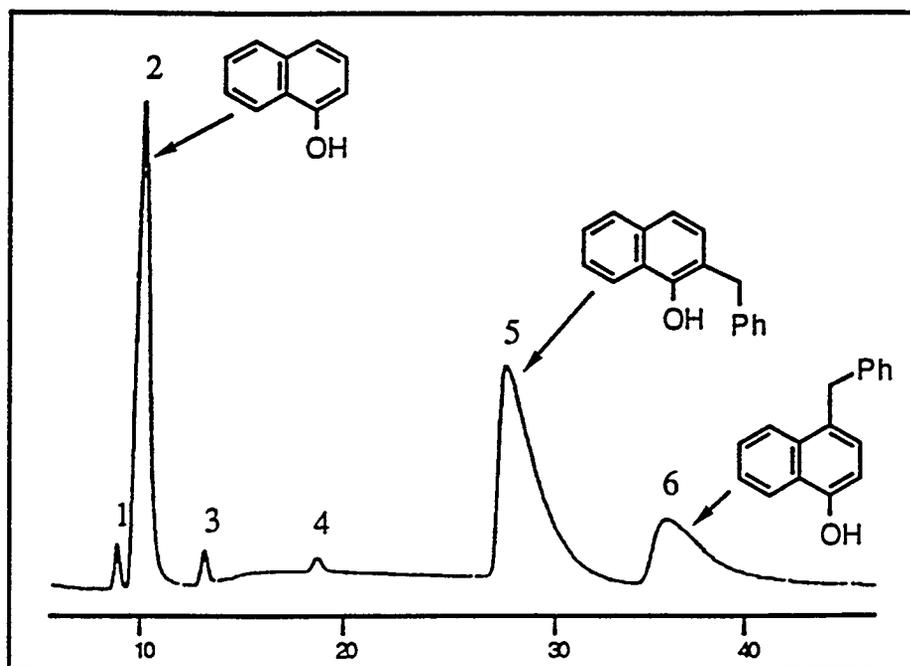


Figure 2. Steam pretreatment of α -benzyl-naphthyl ether. GC profile of product mixture (obtained from glass-lined vessel).

Complete structural identification of the isomeric starting materials 5, and 6, had not been previously reported. Work is now in progress to identify the minor products 1, 3, and 4.

Steam treatments were conducted in stainless steel and glass-lined reactors to explore the effect of the wall on product distribution. Experiments were replicated to establish reproducibility. Comparison of the product distributions (Table 1) shows a modest increase in the amount of compound 5 and a decrease in compound 2 produced when the glass-lined reaction vessel is used. These differences lie outside the limits of reproducibility and suggest a small effect of the wall on the course of reaction. Product recovery is lower for the stainless steel reactor which suggests a higher yield of gaseous and volatile species (the reproducibility of product recovery has not yet been established).

Table 1.
Comparison of product distributions obtained using
metal and glass-lined reactors

<u>Run No.</u>	<u>Vessel Type</u>	<u>Recovery (%)</u>	<u>Product Distribution (%)</u>					
			<u>Compound No.</u>					
			<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
MK1-3	metal	53	1.3	40.8	2.5	1.3	40.6	13.5
MK1-6	metal		2.6	40.9	2.9	1.3	39.2	13.1
Mean	metal		2	41	3	1	40	13
MK1-4, 5*	glass		1.5	36.3	1.2	0.8	43.8	16.4
MK1-7	glass	64	3.1	36.8	3.4	1.5	43.9	11.3
Mean	glass		2	37	2	1	44	14

*Products from runs MK1-4 and 5 were mixed for this analysis.

α -naphthylmethyl phenyl ether

Steam pretreatment of model compound α -naphthylmethyl phenyl ether (α -NMPE) was conducted at 328 C and 750 psi. In Run No. MK3-2, 0.2 grams of material were pretreated in a stainless steel reactor. Run No. MK3-3 was carried out in glass lined vessel using 0.1 gram of compound. After each pretreatment, gases in the reactor tube were vented directly into the mass spectrometer for analysis.

The condensed products were washed out of the reactor tube with methylene chloride. A preparative GC separation of the reaction products was accomplished using a Tenax GC (Alltech) packed column. The GC profile of the product mixture obtained from the steel vessel is shown in Figure 3. Using a combination of ^1H nmr spectroscopy and CI-MS analyses, the structure of the constituents labelled 1, 2, 3, 4, and 5 were determined to be phenol, 1-methyl naphthalene, 1-naphthaldehyde, o-naphthylmethyl phenol, and p-naphthylmethyl phenol, respectively. The relative distribution of these products will be determined next quarter. Duplicate runs will be made to check reproducibility.

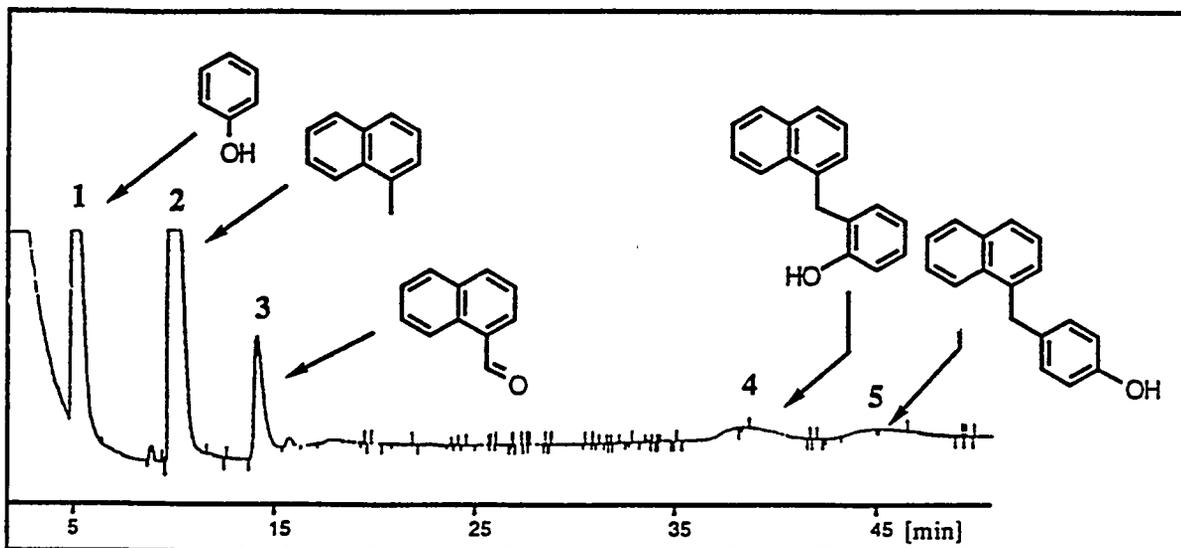


Figure 3. Steam pretreatment of α -naphthylmethyl phenyl ether. GC profile of product mixture obtained in a stainless steel reactor.

REFERENCES

1. Whitehurst, D. D., M. Farcasiu, and T. O. Mitchell (1976) "The Nature and Origin of Asphaltenes in Processed Coals," Annual Report, EPRI Project 410-1, EPRI AF-252, Electric Power Research Institute, Palo Alto, CA.
2. Klein, Michael, and W. Provine (1990), private communication.

WORK PLANNED FOR NEXT QUARTER

Rapid heating liquefaction tests with -200 mesh Illinois No. 6 coal will be carried out next quarter.

Additional pretreatments of the model compounds will be conducted in inert gas as well as steam. Identification of products and determination of product distributions will be made. Product distributions in steam and inert atmospheres, and in stainless steel and glass-lined reactors will be quantitatively compared.