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EXPLORATORY COPROCESSING RESEARCH

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SUMMARY

The objectives of this project are to: (1) study the scope of hydrothermal pretreatment of coal on subsequent conversion, (2) identify and study the chemical or physical causes of this effect, and (3) attempt to elucidate the chemistry responsible for any coal-resid synergisms. This project is divided into three tasks. This quarter we concentrated on Task 1 as described below.

Task 1: Scope of Aqueous Pretreatment

The objectives of this quarter's work were to conduct coprocessing experiments in our new microreactor system, where the reactors are agitated by an electric reciprocating saw. Since Wyodak coal was shown to be more susceptible to pretreatment in the larger, 300-mL autoclaves, we decided to begin with this coal. Coprocessing experiments were conducted using pretreatments at 250°C and at 350°C, where a ratio of 1 part coal and 2 parts Maya ATB and 1200 psig of hydrogen was heated at 425°C. In each case the pretreatment increased the conversions, in agreement with the experiments in the larger autoclave. Based on hexane insoluble material, coal conversions ranged from 40% for conversions with no pretreatment, to 60% conversion with pretreatment at 350°C. The 350°C pretreatment gave the greatest degree of conversion which is consistent with FIMS pyrolysis data described in the previous quarter. In future work pretreatment by other methods will also be conducted, as well as a more thorough evaluation of the aqueous pretreatment.

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INTRODUCTION

Recent studies show that mild hydrothermal treatment of an Illinois #6 coal substantially enhanced conversion into soluble products. For instance the convertibility of an Illinois No. 6 coal into toluene-soluble products increased from ~ 35% to almost 70% when the coal was treated for 30 minutes with water at 250 °C under nitrogen, and then subjected to conversion in CO/water systems.¹ Similar favorable effects of mild hydrothermal pretreatment have been reported for conversions in pyrene² and for rapid hydropyrolysis.³⁻⁴

Under the present contract, we wish to determine whether the beneficial effects of mild hydrothermal pretreatment can be exploited in the context of coprocessing. From the proposed research we expect to achieve an understanding of coal-resid chemistry and the basis for a practical advance in the process. In our three-task research program we will first determine the degrees to which coals known to benefit from such pretreatment for conventional liquefaction will benefit for coprocessing. We will further determine how coals of different rank respond to the brief hydrothermal action. In this part of Task 1 we will use a single, well-characterized resid that has been found to be an effective coprocessing feedstock.

In the second task we will conduct experiments designed to lead to a better understanding of the effect and then to apply those findings as a probe into resid-coal chemistry. Using a single coal from Task 1, we will examine the compositional and morphological changes in coal after brief hydrothermal contact over a range of temperatures, and then correlate these results with subsequent coal-resid conversions. We expect that one focus of this task will be factors dealing with promotion and suppression of retrogressive reactions in both the coal and resid, as affected by the hydrothermal contact.

The third task centers on other earlier work in which we showed that coal liquefaction is not limited to simple thermal scission of weak bonds. Rather, that the likely critical route to reductive breakdown of the structure is cleavage of bonds too strong to break thermally by hydrogen atom transfer to critical Ar-X links. Our research has led to a substantial revision of the picture for coal liquefaction: the solvent should now be perceived

as an active reagent bringing about the necessary bond cleavage. Accordingly, we propose to apply this view of upgrading to coprocessing by examining the various observed synergies. Specifically, we will apply our scheme to the results from the first two tasks, augmenting that effort with a study of a bituminous and a subbituminous coal coprocessed in different or altered resids selected for variations in PCAH and hydroaromatic content. This effort will lead to the practical goal of optimizing coal-resid selection and processing parameters for maximum synergy.

TASK 1: SCOPE OF HYDROTHERMAL PRETREATMENT

The objective of this task is to determine how general the beneficial effect of hydrothermal pretreatment is regarding to the coal type (e.g., rank, mineral and moisture content) and the conditions of the subsequent conversion. In the previous quarters we evaluated the hydrothermal pretreatment in large 300 mL autoclaves with a slow heat-up period. Our results were encouraging for the lower rank coals, namely Wyodak. However, to have better temperature control and facilitate the experiments we decided to change the evaluation procedure and to utilize a agitated microautoclave reactor system. The following describes the results for this quarter.

EXPERIMENTAL

The configuration of the reactor system was described last quarter. The reactor (43mL in volume) was charged with 2.25 g of argonne Wyodak coal and 4.5 g of Maya and filled with 1200 psig of hydrogen (cold). The reactor was then shaken at 425 °C for 1 hour in a fluidized sandbath. Before opening the reactor, it was cooled in dry ice to prevent volatiles from escaping. For the experiments where the coal was pretreated thermally with water, the reactor was charged with 2.25 g of coal, 10 mL of water, and 500 psig of nitrogen. The mixture was then heated and agitated in the sandbath for 30 minutes at the desired temperature. The reactor was cooled in sand, carefully opened, and the excess water removed. Coal that was removed along with the water was weighed to determine the actual amount that was used. The Maya ATB was then added and the reactor charged with 1200 psig of hydrogen and reacted as described above.

RESULTS AND DISCUSSION

Tables 1 presents data from the coprocessing studies with Argonne premium samples of Wyodak coals and Maya ATB from both the 300 mL reactors and the new microautoclaves. The experimental methods were quite similar in that both reactors were charged with 1200 psig of hydrogen at room temperature, and then heated to 425 °C for one hour. Both types of reactors were filled with 10% reactor volume of Maya ATB. The differences in the methods were that the 300 mL autoclave had a slow heat-up period of approximately 45 minutes, while the 43 mL reactors had virtually no heat-up period.

Another difference is that the ratios of coal to Maya were different. The coprocessing experiments in the 300 mL reactors utilized a 1:3 ratio of coal to Maya whereas in the smaller reactors, a 1:2 ratio was used. The increased proportion of coal to Maya was used in the smaller reactors so that we could assess the impact of various coal pretreatments. Additionally, we are no longer conducting detailed fractionation steps, and are evaluating the pretreatments primarily on the weight of hexane-insoluble portions.

The first line of Table 1 represent base-line values and are conversions of Maya alone with no coal added. From these values we can determine the theoretical conversions of coal assuming that there is no interaction between the coal and and resid. For instance, for the 300-mL autoclave run 11% by weight of THF insoluble material was obtained after treating Maya under coprocessing conditions. If coal was added (10g for the 300 mL autoclave standard conditions), then we would have obtained a yield of 8% if all of the coal had been converted to THF soluble material. In contrast, if none of the coal had been converted, a value of 31% insoluble material would have been obtained. As shown in the table the results ranged from 16 to 19% THF insoluble material, indicating that a significant portion of the coal had been converted. In order to estimate the degree of conversion, we used the following correlation:

$$\text{Conversion} = 100 - [(THFI - 8)/(33 - 8)] \times 100$$

Thus we have a positive correlation, in that the addition of coal has increased the amount of THF soluble material.

Positive correlations were also obtained the the microautoclave. For these coprocessing experiments, the conversions were evaluated in terms of hexane insoluble material and coal conversions were calculated in an analogous to the method above. Both the 250°C and 350°C pretreatments gave greater conversions to hexane soluble material than did the nonpretreated coal. Figure 1 illustrates the effect of pretreatment on the conversions of coal, showing that higher temperature pretreatment of 350°C gives a greater conversion than the 250°C pretreatment. A similar effect of pretreatment at these temperatures was observed for volatility as observed by FIMS, and was discussed in QR 5. These results are promising, and in future work we will attempt to further investigate the temperature profile of this pretreatment, and also investigate other types of pretreatment.

Table 1

**COAL CONVERSION FROM COPROCESSING MAYA ATB AND
WYODAK COAL IN 300 mL AUTOCLAVE AND MICROAUTOCLAVE^a**

Pretreatment ^b	300-mL Autoclave		43-mL Microautoclave	
	THFI (wt%)	Coal Conversion	HI (wt%)	Coal Conversion ^c
Maya (no coal)	11	--	18	--
None	16	68	32	40
250 °C	19	56	26	57
250 °C	16	68	27	54
350°C	--	--	22	69
350°C	--	--	25	60

- a. Reactions of coal and Maya ATB at 425°C for 1 h at and 1200 psi H₂. THFI refers to THF insoluble, HI refers to hexane insoluble fractions.
- b. Pretreatment refers to treating coal with water at either 250°C or 350°C for 30 minutes under 500 psi of nitrogen.
- c. Coal conversion calculated assuming that the insoluble material from the Maya remains the same during the coprocessing experiment.

Figure 1. Effect of Pretreatment on Coal Conversion.

Reaction of 2.25 g Wyodak coal and 4.5 g Maya ATB with 1200 psig H_2 in 43-mL microautoclave. Reactor heated for 1 h at 425°C.

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