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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 Tasks 1 and 2 as described below.

Task 1: Scope of Aqueous Pretreatment

During the previous quarters we have investigated the Argonne Wyodak coal for the effects of aqueous pretreatment. This quarter other Argonne coals were investigated for this effect, including an Illinois #6 and a North Dakota lignite. The pretreatment conditions used were those found best for the Wyodak coal, namely 350°C. The coprocessing experiment utilized a ratio of 1 part coal and 2 parts Maya ATB under conditions previously described. The results showed that the aqueous pretreatment techniques at 350°C were most effective for the Wyodak coal, with the lignite showing a slight benefit, and the Illinois #6 coal showing essentially no benefit.

Task 2: Chemistry of Pretreatment

During this quarter we investigated other means of pretreating low rank coal to enhance conversions. In particular, the use of iron salts by the method of Fouda et al., who added iron sulfate to enhance the conversion of a subbituminous coal under coprocessing conditions. We found that the addition of iron increased the conversion, but not to the extent as the aqueous pretreatment. In future work we will investigate the combination of both methods to determine if the effect will be additive.

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 hydrolysis.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 and found pretreatment at 350°C to give the best conversions for Wyodak coal. During this quarter we compared coals of various ranks to determine the relative effect of the aqueous pretreatment method in order to further evaluate the benefits of hydrothermal pretreatment.

EXPERIMENTAL

The aqueous pretreatment was conducted at 350°C. The coals used in this study were Wyodak-Anderson seam subbituminous coal, Illinois #6 seam high volatile bituminous coal, and Beulah-Zap seam North Dakota lignite; all coals were obtained from the Argonne premium coal bank and used as received. The iron impregnated coal was prepared by the addition of 0.168g of $\text{Fe(II)SO}_4 \cdot 5\text{H}_2\text{O}$ dissolved in 20 mL of water to 2.25g of Wyodak coal. The water was then removed at 50°C under rotary evaporation using water aspirator pressure. The coprocessing and pretreatment methods have previously been described in Quarterly Reports 6 and 7.

RESULTS AND DISCUSSION

Table 1 presents data from the coprocessing studies with Argonne premium samples of Wyodak, Illinois #6, and North Dakota coals and lignite. The first line of Table 1 represents base-line values and are conversions of Maya alone with no coal added. The theoretical conversions of coal was calculated assuming that there is no interaction between the coal and and resid. As shown in Table 1 the results ranged from 22 to 34% hexane insoluble material, indicating that a significant portion of the coal had been converted. Although bituminous coals are generally more easily converted than subbituminous coals, as seen from this data, the Wyodak and Illinois #6 coals that were not pretreated were converted to about the same extent, yielding 32-34% hexane insoluble material. However, although the pretreatment of Wyodak gave a significant enhancement of conversion, no benefit for the Illinois #6 coal was observed, and only a moderate effect for the lignite was

detected. Figure 1 illustrates these differences in conversion. It should be remembered that we had optimized the pretreatment conditions using the Wyodak coal; and a priori have no reason to assume that these conditions are optimal for other coals as well. The lignite may show a more pronounced effect with a lower temperature hydrothermal pretreatment. However, exploration of optimal conditions for all coals is beyond the scope of the present work. Nevertheless, these results show the beneficial effects of hydrothermal pretreatment are not specific to the Wyodak coal and that other low rank coals also show qualitatively similar enhancement in conversion.

We have suggested that water can mitigate retrogressive reactions of phenolics and carboxylates, and have shown this to be true in models such as dihydroxyphenolics as described in our earlier Quarterly Reports (1-3). Low rank coals such as the Wyodak and lignite have a relatively higher proportion of phenolics and carboxylates than the higher ranking Illinois #6 coal, and therefore we would predict that these lower rank coals would have the most benefit from the aqueous pretreatment. Thus our work is consistent with this prediction, and shows the generality of the pretreatment effect. However, the actual reason for the benefit is not understood. In quarterly report 7 we showed that simple thermal pretreatment in the absence of water is detrimental, presumably since many retrogressive reactions take place that limit conversion. On the other hand, the presence of water during conversion is not necessarily beneficial, since both the Wyodak and lignite already have a high moisture content (ca 30%). Thus, we only see the benefit when the conversion solvent or resid is not present during pretreatment. The larger effect of the pretreatment on the Wyodak coal compared to the lignite is also not fully understood. Most of our work on pretreatment concentrated on the Wyodak coal, and perhaps other pretreatment conditions would enhance the conversion of the lignite. The relative types of functionalities in these coals are most likely different, with the lignite having a higher carboxylic acid content than the Wyodak. Thus a thorough study of the effect of the pretreatment on different types of functionalities present in coals of varying ranks should be conducted in order to more fully understand the nature of the effects, and to predict optimal processing conditions.

Table 1

**COPROCESSING OF COALS OF DIFFERENT RANK WITH MAYA ATB
IN MICROAUTOCLAVE^a**

Experiment	Coal	Pretreatment	Hexane Insoluble	Coal Conversion ^b
1	None	None	18	--
2	Wyodak	None	32	40
3	Wyodak	350°C	22	69
4	Wyodak	350°C	25	61
5	Illinois #6	None	34	33
6	Illinois #6	350°C	35	30
7	Lignite	None	28	52
8	Lignite	350°C	24	64

- a. Reactions of coal and Maya ATB at 425°C for 1 h at and 1200 psi H₂.
 b. Coal conversion calculated assuming that the insoluble material from the Maya remains the same during the coprocessing experiment.
 c. % Conversion = $100 - [(HI - 12)/(33)] \times 100$ (derived in QR 7)

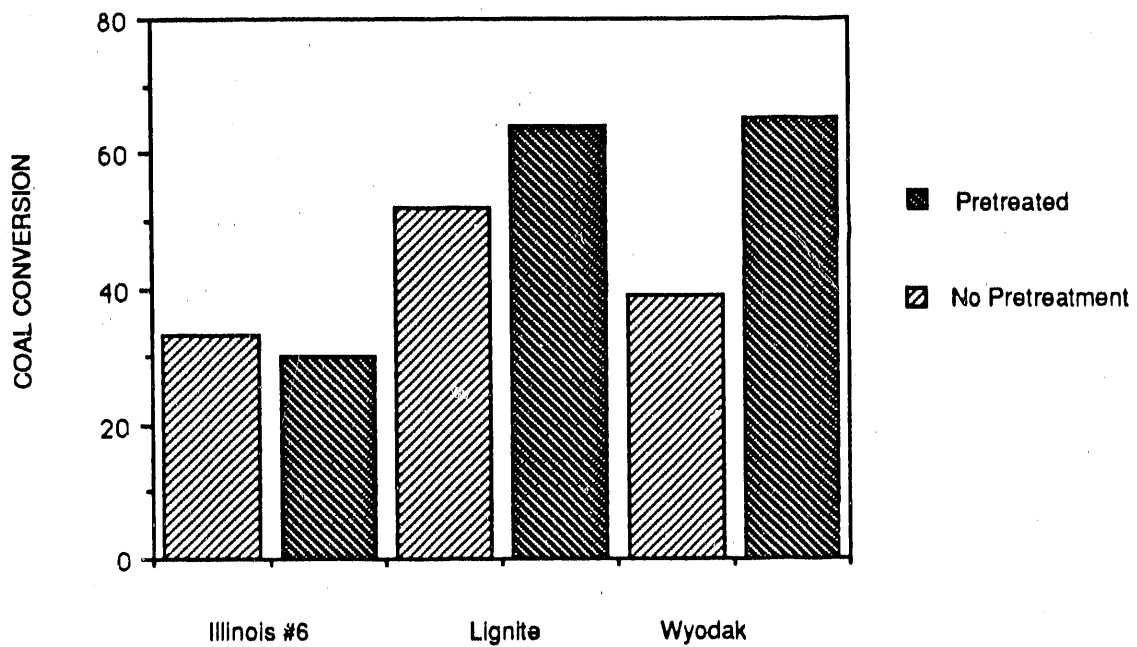


Figure 1. Effect of 350°C Pretreatments on Coals of Varying Ranks.

Reaction of 2.25 g coal and 4.5 g Maya ATB with 1200 psig H₂ in 43-mL microautoclave. Reactor heated for 1 h at 425°C.

TASK 2: CHEMISTRY OF PRETREATMENT

The goal of this task is to help understand the phenomena of pretreatment and how it relates to the ultimate convertibility of coal. Various factors could be involved, including morphological changes affecting mass transfer rates, and specific chemical changes brought about in the coal. An additional factor in pretreatment is the effect of iron in the convertibility of low rank coals. In this quarter we investigated the effects of this additional pretreatment.

EXPERIMENTAL

The iron impregnated coal was prepared by the addition of 0.168g of $\text{Fe(II)SO}_4 \cdot 5\text{H}_2\text{O}$ dissolved in 20 mL of water to 2.25g of Wyodak coal. The water was then removed at 50°C under rotary evaporation using water aspirator pressure. The coprocessing and pretreatment methods have previously been described in Quarterly Reports 6 and 7.

RESULTS AND DISCUSSION

Iron salts or oxides have often been used to enhance the conversion of low rank coals. One of the functions of the iron is to help cleave or remove some of the oxygen functionalities in the coal, which are thought to cause retrogressive reactions. Low rank coals tend to have a low natural iron content. Table 2 lists the pyrite contents of the coals used in Task 1. Note that the low rank coals have a pyrite content of 0.1 to 0.3%, whereas the Illinois #6 coal has a contains 5.5% pyrite. Thus any effect of iron should be most easily observed in the lower rank coals such as the Wyodak studied here. In this study we used the method of Fouda et al. who added ferrous sulfate to Forrestburg subbituminous coal for coprocessing experiments. As shown in Table 2, the addition of iron enhanced conversion, as we had anticipated; however, we did not observe as great an enhancement as with the aqueous pretreatment. There can be several reasons for these differences in reactivity, based on how and when the pretreatment works. The mechanism of the aqueous pretreatment has not been well understood, but we have evidence that it prevents retrogressive reactions at temperatures at least as low as 300°C. In contrast, workers have

shown that the most active form of the iron is pyrrhotite; however, the iron does not transform into pyrrhotite until much higher temperatures, in the range of 400°C. Thus the iron sulfate could not prevent any retrogressive reactions at low temperatures. During the next quarter we will determine the effect of a combination of both iron and aqueous pretreatment methods.

Table 2

**EFFECT OF IRON IN COPROCESSING MAYA ATB AND WYODAK
COAL IN MICROAUTOCLAVE^a**

Experiment	Pretreatment ^b	Hexane Insoluble	Coal Conversion ^b
2	None	32	40
3	Aqueous 350°C	22	69
4	Aqueous 350°C	25	60
9	Iron(II) Sulfate	27	55
10	Iron(II) Sulfate	29	49

- a. Reactions of coal and Maya ATB at 425°C for 1 h at and 1200 psi H₂.
b. Coal conversion calculated assuming that the insoluble material from the Maya remains the same during the coprocessing experiment.
c. % Conversion = $100 - [(HI - 12)/(33)] \times 100$ (derived in QR 7)

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