EXPLORATORY COPROCESSING RESEARCH

Quarterly Report No. 9
For the Period September 1, 1990 to November 30, 1990

By: Albert S. Hirschon, Doris T. Tse, Ripudaman Malhotra, Donald F. McMillen, and David S. Ross

May 1991

Prepared for:
U.S. DEPARTMENT OF ENERGY
Pittsburgh Energy Technology Center

Work Performed Under Contract No. DE-AC22-88PC88802

333 Ravenswood Avenue • Menlo Park, CA 94025-3493 • (415) 326-6200 • FAX: (415) 326-5512 • Telex: 334486

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03 June 1991
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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 2 and 3 as described below.

Task 2: Chemistry of Pretreatment

This Quarter we continued our investigation of the chemistry of pretreatment using an iron catalyst, (ferrous sulfate), both with and without aqueous pretreatment on Wyodak coal. The combination of iron and hydrothermal pretreatment gave the best results, as long as the pretreated coal was not dried prior to conversion. However, the combination of iron and pretreatment gave similar conversions as with pretreatment alone.

Task 3: Chemistry of Synergy

To help provide a baseline for distinguishing between the benefits resulting from chemical and physical solvency factors, we decided to conduct some experiments in homogeneous systems, from which we can easily extract the impact due to chemical changes. We synthesized a series of benzyl aromatics and studied their cleavage in a mixture of anthracene and dihydroanthracene. Cleavage rates for the different substrates increase in the order diphenylmethane < benzynaphthalene < benzylphenanthrene < benzylpyrene. The log of observed first-order rate constants correlate linearly with the exothermicity of H-addition to the aromatic bearing the benzyl group, and are in excellent agreement with our previously modeled results. The experimental results further show the generality of induced bond cleavage, and buttress our view of the possible chemical basis of improvements resulting from increased aromaticity.
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. Similar favorable effects of mild hydrothermal pretreatment have been reported for conversions in pyrene and for rapid hydropyrolysis.

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 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.

In this study we used the method of Fouda et al. who added ferrous sulfate to Forrestburg subbituminous coal for coprocessing experiments. For the pretreatment investigations, we compared the effects of iron catalyst, (ferrous sulfate), both with and without aqueous pretreatment on Wyodak coal (See Table 1). The iron was impregnated in two different ways. In the first method, the coal was pretreated, iron added in an aqueous solution, and then dried under vacuum. Maya ATB was then added, and the mixture was subjected to the normal coprocessing experiment. The effect of the combination of iron and pretreatment appeared to be minimal, giving the same conversions as without pretreatment.

For the second method, the excess water was removed from the pretreated coal and then iron and the Maya were directly added. The coal was not dried prior to conversion. In this experiment, the conversions were improved, giving less insoluble material. We suspect that the lower conversions of the first method were due to the drying of the coal reversing the benefits of pretreatment.

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EFFECT OF IRON AND HYDROTHERMAL PRETREATMENT IN COPROCESSING MAYA ATB AND WYODAK COAL IN MICROAUTOCLAVE

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>% Hexane Insoluble</th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Without FeSO₄</td>
<td>With FeSO₄</td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>32</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>Hydrothermal 350°C</td>
<td>--</td>
<td>28ᵃ</td>
<td></td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>22ᵇ</td>
<td></td>
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</tbody>
</table>

ᵃ. Method 1, coal dried before conversion
ᵇ. Method 2, coal not dried.
TASK 3: CHEMISTRY OF SYNERGY

This task is based on earlier work in which the solvent can be perceived as an active reagent bringing about bond cleavage. In this previous work we have suggested that increased aromaticity may be beneficial because the PCAH species are better H-shuttlers, and can utilize hydrogen from aliphatic structures of the resid for inducing cleavage of strong bonds. This cleavage results from transfer of hydrogen to critical ipso positions via several pathways, including radical hydrogen-transfer.

To help provide a baseline for distinguishing between the benefits resulting from chemical and physical solvency factors, we conducted some experiments in homogeneous systems, from which we can easily extract the impact due to chemical changes. We synthesized a series of benzyl aromatics and studied their cleavage in a mixture of anthracene and dihydroanthracene. Cleavage rates for the different substrates increase in the order diphenylmethane < benzynaphthalene < benzylphenanthrene < benzylpyrene. The log of observed first-order rate constants correlate linearly with the exothermicity of H-addition to the aromatic bearing the benzyl group, and are in excellent agreement with our previously modeled results. The experimental results further show the generality of induced bond cleavage, and buttress our view of the possible chemical basis of improvements resulting from increased aromaticity.

Recent introduction of a recycle loop by UOP in their coprocessing has resulted in marked improvement in yield and processability. While the improvement has been attributed to physical factors, namely greater turbulence, chemical factors may also be important. This recycle stream substantially increases the aromatic content of the reaction mixture. It is noteworthy that HRI's reactor, which has substantial internal recycle, also results in increased aromatic content, as does addition of anthracene oil, a practice known to enhance conversion during coprocessing. Thus, increased aromaticity is associated with improved conversion. We suggest the basis of the synergy may in fact lie in the types of hydroaromatic species present in the resid or recycle solvent.
REFERENCES


