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DE93 004930

Quarterly Report No. 4 - 5 November 1992

HIGHLY DISPERSED CATALYSTS FOR COAL LIQUEFACTION

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SRI Project 2760

Period Covering May 23, 1992 through Aug 22, 1992

Prepared for:

United States Department of Energy
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P.O. Box 10940
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Contract No. DE-AC22-91PC91039

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SUMMARY

The objectives of this project are to study the effect of pretreatment methods on the two-stage liquefaction process. In particular, the effects of dispersed catalysts and carbon monoxide atmospheres on a coal liquefaction process. The project is divided into three technical tasks. Task 1 and 2 deal with the analyses and liquefaction experiments, respectively, whereas Task 3 deals with the economic impact of utilizing the pretreatment methods. This quarter we concentrated on Tasks 1 and 2, which are summarized below.

Analytic Support and Laboratory Scale Operation

Samples of Black Thunder Subbituminous coal and the corresponding recycle solvent were received from Wilsonville. These particular samples were obtained from run # 263. The samples were analyzed for a proximate and ultimate analysis, as well as heat content. We have also received samples of the iron oxide used in the Wilsonville coal liquefaction runs as well as Shell 324 and molyVanL for use in future runs.

Base-line screening experiments were conducted in 300 mL autoclaves using 2.5 parts by weight of recycle solvent to 1 part Black Thunder coal at 425°C for one hour. In preliminary results for the comparison of iron oxide and iron carbonyl, the iron carbonyl appears to give higher yields to soluble products.

Also, we submitted a paper to Pittsburgh conference for October in this year. Although little work has been done due to the NEPA, we discussed past work on dispersed catalysts which is highly relevant to our new project.

INTRODUCTION

Integrated processes to liquefy coal have evolved to the current two-stage close coupled catalytic configurations now being used at Wilsonville.¹⁻⁴ Recent estimates (1990) indicate that two-stage conversion of coal to liquids has a product cost in the area of \$38 per barrel and the improved quality of the liquids makes them equivalent to oil costing \$33 per barrel. Several areas in the conversion technology have been identified that, if improved, should make coal converted to oil more cost competitive with petroleum products. These areas include pretreatment and cleaning methods, choice of feedstock, novel catalysts, and processes to improve hydrocarbon recovery. The objective of this project is to address possible methods of improving the efficiency of these and other steps in the integrated process so that the overall conversion will show increased cost effectiveness. This work will concentrate on individual steps and technoeconomic evaluations to provide information on their relative effectiveness toward the overall goal of \$25 per barrel.

So far, most work at Wilsonville has involved bituminous coals, which are much easier to convert than lower-rank coals such as Wyodak and lignites.⁵ The lower-rank coals are more abundant and cheaper, and conversions lead to a higher quality product with less heteroatom content.⁶ However, the yield of liquid products is low. The low conversion of these coals has been attributed to their high oxygen content, and the carboxyl groups are thought to cause retrograde reactions by free radical processes.^{7,8} Additionally, phenolics often are associated with retrograde reactions leading to polymeric furans.^{9,10} Developing a process for utilizing these coals in high conversions would greatly improve the economics of coal conversion. Several approaches, including highly dispersed catalysts and coal pretreatment techniques, have been suggested to overcome these detrimental reactions. In recent work we have studied both of these approaches to enhance the convertibility of coal and minimize the retrogressive reactions.

This project is designed to evaluate the feasibility of using low-rank coals such as Wyodak and lignite in a two-stage liquefaction pilot demonstration unit (PDU). The primary objectives are to (1) synthesize and impregnate coal with high activity, highly dispersed catalysts (dispersed on the molecular scale); (2) develop an understanding of these catalysts in terms of their reactivities toward hydrogenation and hydrogenolysis, especially in terms of removing phenolics and carboxylates, which are thought to cause

most retrogressive reactions; (3) monitor the activities and physical properties of these catalysts during coal liquefaction processes and compare them with those of other types of catalysts; and (4) evaluate process cost improvements that might be realized through the use of low-rank coals, dispersed catalysts, and CO/H₂ for coal liquefaction in a two-stage close coupled configuration.

TASK 1: ANALYTICAL SUPPORT

The objectives of this task are to provide analytic support for the laboratory conversion studies conducted in Task 2. In this task the coal liquefaction products and residues as well as the catalysts will be analyzed.

The following table lists the analyses of the Black Thunder Coal, the derived recycle solvent, as well as analyses of some of the base-line liquefaction runs.

Table. Analyses of Black Thunder Coal and Recycle Solvent

<u>Ultimate Analysis (Wt%)</u>	<u>Black Thunder (As Received)</u>	<u>Black Thunder (Dried at 76°C)</u>	<u>Recycle Solvent</u>
Carbon	55.07	63.56	88.08
Hydrogen	6.22	4.96	7.09
Nitrogen	0.79	0.80	0.99
Sulfur	0.34		
Chlorine	<0.07		
Ash	5.87		
Oxygen (by diff)	31.71		
<u>Proximate Analysis (Wt% As Received)</u>			
Moisture	21.21		
Volatile Moisture	35.30		
Ash	5.87		
<u>Ash Fusion Temperature</u>			
	<u>Oxidizing</u>	<u>Reducing</u>	
Initial	2280°F	2200°F	
H/W	2300°F	2240°F	
1/2 H/W	2320°F	2280°F	
Fluid	2340°F	2320°F	
<u>Heat Content (BTU/pound)</u>			
	<u>Gross</u>	<u>Net</u>	
As Received	9283	8707	
Dry Basis	11765	11035	

TASK 2: LABORATORY SCALE OPERATIONS

The objectives of this task are to evaluate the effects of dispersed catalysts and CO atmospheres in the first stage of a 2-stage liquefaction process. This quarter we have begun the first phase of this work and are developing the base-line to evaluate the first-stage reaction conditions. These evaluations are being run at 425°C for 1 hour in a 300 mL autoclave with a slow heat-up period (approximately 45 minutes) in order to incorporate any possible preconversion benefits at lower temperatures. The feedstock consisted of 2.5 parts by weight of recycle solvent from Wilsonville run #263 to 1 part Black Thunder coal. In conversations with Wilsonville we found that they dried the coal in-situ prior to the run and therefore the coal was dried at 76°C for 12 h under vacuum prior to use. For these initial screening tests we used conventional catalysts such as Fe₂O₃ (received from Wilsonville) and iron carbonyl. The reaction products were solvent fractionated to determine the product profile. The profile includes tetrahydrofuran insoluble material (THF-Insol), THF soluble-Toluene insoluble (Preasphaltenes), Toluene soluble-hexane insoluble (Asphaltenes), and hexane soluble (oils).

This quarter conversions were run comparing Fe₂O₃ and Fe(CO)₅ as catalysts. The amount of catalyst was 1.4 grams of iron, which is equivalent to 2% Fe₂O₃, a typical value used in the Wilsonville iron oxide catalyzed coal conversions. The reaction atmosphere was 850 psia of hydrogen containing 3% hydrogen sulfide. As shown in Figure 1, the iron carbonyl gives higher yields to soluble products. The higher yields using the Fe(CO)₅ is as expected, since many workers have shown that the carbonyl gives much higher conversions. However, we found that the iron oxide catalyzed reaction appeared to have an exotherm around 350°C, making the reactor momentarily overshoot the final temperature by about 25°C. The combination of the overshoot and the inability of the catalyst to efficiently utilize hydrogen most likely attributed to the low conversions. The on-line GC was not functional for these reactions, but we suspect that due to inefficient hydrogen utilization, the reactions may be hydrogen starved, and future runs will be conducted at higher hydrogen pressures.

We are also in the process of investigating the iron oxide-sulfate acid catalysts as described by Kotamigawa et al.¹¹ and Pradham et al.^{12,13} Several variations in the synthetic method for the production of the sulfated iron oxide were conducted in order to increase the surface area and vary the pore size distribution. Also, we have submitted a paper to Pittsburgh conference for October in this year. Although little work has been done

due to the NEPA, we will discuss past work on dispersed catalysts which is highly relevant to our new project. The paper is included in Appendix A.

Fig. 1 Conversion of Black Thunder Coal

Conversion in 300 mL autoclave at 425°C for 1 h with 850 psia (cold) of $\text{H}_2/3\%\text{H}_2\text{S}$

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