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HIGHLY DISPERSED CATALYSTS FOR COAL LIQUEFACTION

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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.

Task 1. Analytic Support

This task is in support of Task 2, and involves the analyses of the liquefaction products and catalysts involved in the liquefaction runs. As found last month, the fractionated products from the coal liquefaction experiments conducted in Task 2 exhibited a very low H/C ratio, most likely due to the low H/C ratio of the Black Thunder recycle vehicle used in these liquefaction experiments. Wilsonville has reported the recycle vehicle as approximately 20% distillable material (1100°F at one atmosphere), 20% insoluble material (CI) and 40% resid. We are now in the process of fractionating this material in order to determine its contribution to our liquefaction results. We also analyzed some of the sulfated iron catalysts for surface areas, finding that the calcined catalyst had surface areas of 76 m²/g, compared to 6 m²/g for the iron oxide used by Wilsonville.

Task 2. Laboratory Scale Operation

During this quarter we synthesized two more catalysts, the sulfated iron catalyst, and a thiolato iron carbonyl catalyst. We hope to be able to screen these catalysts for liquefaction experiments in the 300 mL autoclaves during the next quarter. This quarter we studied iron carbonyl as a catalyst using atmospheres of hydrogen and of hydrogen and carbon monoxide at total cold pressures of 1000 psia. The comparisons are not yet completed, but it appears that pure hydrogen gave slightly higher conversions into preasphaltenes, but similar conversions into asphaltenes and oils.

As found in the last quarter, when a carbon monoxide/hydrogen atmosphere was used, all of the carbon monoxide was accounted for as either unconverted carbon monoxide or as carbon dioxide. No evidence of conversion of the carbon monoxide to methane or Fischer-Tropsch type reactions were observed.

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. During this quarter the fractionated products for the coal liquefaction experiments were analyzed for C, H, and N content. We are also preparing an ASTM distillation apparatus for evaluation of the products obtained from a simulated two-stage liquefaction conversion. In addition, in combination with another DOE project, an automated TGA is being built to evaluate some of the smaller scale runs.

Analyses from Coal Conversions

Table 1 lists the analyses of fractionated products derived from conversions of Black Thunder Coal and the corresponding recycle vehicle. The fractions listed in this table are THF-insoluble, THF-soluble/Toluene-insoluble, referred to as preasphaltenes, and Toluene-soluble/Hexane-insoluble fractions, referred to as asphaltenes.

Unlike last quarter, where the coal conversions were conducted under an pressure of 850 psi, these conversions were conducted at 1000 psi, and the conversions to soluble products are correspondingly higher. However, since these conversions were conducted with a poor solvent such as Black Thunder recycle vehicle with a low H/C ratio of 1.0 and iron based catalysts, there is a very poor hydrogen utilization and a low H/C ratio as observed in Table 1. The approximate solvent properties as reported from Wilsonville for the Black Thunder recycle vehicle are 40% distillate (1100°F), 20% CI (cresol insoluble) and 40% resid, so much of the insoluble material obtained during these coal liquefaction experiments are most likely from the heavy solvent. We are in the process of fractionating the recycle vehicle to help us determine the contribution of this solvent in our liquefactions experiments. We hope to incorporate this data in future reports.

Table 2 lists the light gas slate from these runs as determined by GC analysis. We have improved our analysis conditions so that we can get a better hydrogen analysis than we were able to get last quarter. The hydrogen consumption during this conversion was found to be quite high, with a final hydrogen content in the range of 160-200 mmoles compared to 550 mmoles in the initial charge. Also, as seen in this table, the majority of the gas formed during these conversions consists of methane (approximately 150 mmoles), with small amounts of carbon dioxide, ethane and other gases. Last quarter when we conducted a conversion using iron oxide (from Wilsonville) using an atmosphere of

hydrogen and carbon monoxide, (120 mmoles), the equivalent amount of carbon dioxide was formed, with no evidence of hydrogenation of the carbon monoxide to methane, or any types of Fischer-Tropsch type chemistry to form higher hydrocarbons. This quarter we conducted a similar conversion using $\text{Fe}(\text{CO})_5$ as a catalyst (25.5 mmoles). As seen in Table 2, much more CO and CO_2 was observed (for a total of 280 mmoles of carbon oxides) than for the Fe_2O_3 H_2 /CO reaction. The additional amounts of carbon oxides suggest that the $\text{Fe}(\text{CO})_5$ decomposed during the conversion to provide additional amounts of CO (130 mmoles in theory), with the remaining carbon oxides produced from the coal itself.

Catalyst Characterization

The surface areas of the iron oxide obtained from Wilsonville and the sulfated iron oxide produced by the method of Pradham et al,^{11,12} were determined by BET methods to be 6.1 and 76 m^2/g , respectively. The relative acidities of these iron oxides were determined by ammonia adsorption and desorption by TGA. The sulfated iron oxide was found to adsorb 58.4 mg/g or 3.43 mmoles NH_3/g of catalyst whereas the Wilsonville iron oxide adsorbed essentially no ammonia, indicating a very low acidity. Thus we may have two opposing factors in the coal liquefaction scheme. On one hand the sulfated iron oxide has a high surface area, and but on the other hand it has a high acidity, which may be detrimental to conversions due to the acid promoted retrogressive reactions. Next quarter we plan to compare conversions using these catalyst on the Black Thunder coal.

Table 1. Analyses of Conversion Products^a

Conversion	Atmosphere	% C	% H	H/C
Black Thunder		63.56	4.96	0.930
Recycle vehicle ^b		88.08	7.09	1.055
Fe ₂ O ₃	850 psi H ₂			
THF-Insol		72.97	2.89	0.471
Preasphaltene		71.49	4.73	0.788
Asphaltene		81.31	6.56	0.961
Fe(CO) ₅	850 psi H ₂			
THF-Insol		64.56	2.70	0.499
Preasphaltene		89.32	4.20	0.560
Asphaltene		83.46	6.00	0.856
Fe ₂ O ₃ ^c	1000 psi CO/H ₂			
THF-Insol		51.50	2.16	0.501
Preasphaltene		90.75	4.72	0.619
Asphaltene		85.89	6.40	0.887
Fe ₂ O ₃	1000 psi H ₂			
THF-Insol		41.39	1.90	0.548
Preasphaltene		89.67	4.27	0.568
Asphaltene		87.71	6.65	0.903
Fe(CO) ₅ ^c	1000 psi CO/H ₂			
THF-Insol		36.31	1.76	0.577
Preasphaltene		88.46	4.89	0.657
Asphaltene		87.06	6.44	0.880

^aReaction conducted in a 300-mL autoclave with 20g Black Thunder Wyodak coal, 1.4 g iron metal in catalyst, 50 g Recycle solvent and at 425°C. Atmosphere contained 3% H₂S in either H₂ or CO/H₂.

^bApproximately 40% distillate, 20% CI, and 40% resid.

^cCO/H₂ mixtures contained 3% H₂S, 79% H₂, and 18% CO.

Table 2. Gas Analyses^a

Catalyst	CO₂	CO	CH₄	C₂H₆	atm
None	37	–	148	48	850 psi H ₂
Fe ₂ O ₃	20	–	148	41	850 psi H ₂
Fe ₂ O ₃	116	44	130	44	1000 psi H ₂ /CO
Fe ₂ O ₃	36	–	112	39	1000 psi H ₂
Fe(CO) ₅	160	100	120	41	1000 psi H ₂ /CO

^aGases reported in mmoles.

TASK 2: LABORATORY SCALE OPERATIONS

The objectives of the first phase of this task are to evaluate the effects of dispersed catalysts and carbon monoxide atmospheres in the first stage of a 2-stage liquefaction process. We are continuing our work to evaluate the base-line first-stage reaction conditions, with experiments being run at 425°C for 1 hour in a 300 mL autoclave. The feedstock consisted of 2.5 parts by weight of recycle vehicle from Wilsonville run #263 to 1 part Black Thunder coal. The coal was dried at 76°C under <1 torr vacuum to reduce the water content, since the Wilsonville coal facility dries their coal prior to conversion.

Last quarter we compared the conventional catalysts Fe_2O_3 (received from Wilsonville) using an atmosphere of 850 psi of H_2 , with a conversion where an additional amount (18% CO) was added to give a total pressure of 1000 psi, and found the conversion to liquid products was much greater. This quarter we found similar enhanced conversions with when iron carbonyl was used as a catalyst. As seen in Table 3, the conversions based on THF insolubles (100 - % THF insol) increased from 40% to 74% for the iron oxide conversion and 65% to 81% for the iron carbonyl catalyzed run. However, as seen in the conversion with Fe_2O_3 , simply increasing the H_2 pressure to 1000 psi and without CO addition gave almost equivalent conversions. Conversions based on THF increased by approximately 4%, and were apparently accounted for in increased amounts of asphaltenes. However, since we dried the coal and only residual water or water generated during the conversion was present, we may not have had the full effect of hydrogen from the CO generated by the WGS reaction. Nevertheless, an important aspect of this project was to see the effect of CO without water in the expectation that the CO can react with OH groups in the coal itself, and by so doing remove oxygen. Also, the presence of water might increase the total pressure of the conversion system. However, a careful water/CO balance may be able to minimize the pressure during the conversion process.

As shown in Table 2 in Task 1, the addition of the carbon monoxide was essentially converted to carbon dioxide and not to methane or any higher hydrocarbons. Thus even though the coal was dried prior to use and no additional water was added, the carbon monoxide can be effectively utilized in coal conversion.

During this quarter we synthesized two more catalysts, the sulfated iron catalyst, and a thiolato iron carbonyl catalyst. We hope to be able to screen these catalysts for liquefaction experiments in the 300 mL autoclaves during the next quarter.

Table 3. Wt% Yields of Fractionated Products^a

Catalyst	Atmosphere	THF Insol	Preasphaltene	Asphaltene	Oils
Fe ₂ O ₃	850 psi H ₂	59.9	0.2	2.4	4.0
Fe(CO) ₅	850 psi H ₂	35.1	5.9	27.1	12.9
Fe ₂ O ₃	1000 psi CO/H ₂	26.0	9.3	25.5	16.2
Fe ₂ O ₃	1000 psi H ₂	21.5	11.5	32.8	16.6
Fe(CO) ₅	1000 psi CO/H ₂	18.6	10.6	43.6	12.9

^aReaction conducted in a 300-mL autoclave with 20g Black Thunder Wyodak coal, 1.4 g iron metal in catalyst, 50 g Recycle vehicle and at 425°C. Atmosphere contained 3% H₂S in either H₂ or CO/H₂.

^bCO/H₂ mixtures contained 3% H₂S, 79% H₂, and 18% CO.

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