MAR 21 1994

A-2

SRI International

Quarterly Report No. 8 - 1 November 1993

HIGHLY DISPERSED CATALYSTS FOR COAL LIQUEFACTION

By: Albert S. Hirschon and Robert B. Wilson

SRI Project 2760

Period Covering May 23, 1993 through August 22, 1993

Prepared for:

United States Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, PA 15236

Contract No. DE-AC22-91PC91039

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

RECEIVED
USDOE/NETC
94 MAR 14 11:09
ACQUISITION & ASSOCIATE DIV.

MASTER

30 no issues

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

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

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. This quarter we analyzed products derived from liquefaction experiments using the $\text{Fe}(\text{CO})_5$ catalysts, under process conditions where carbon monoxide atmospheres and water contents were varied.

Task 2. Laboratory Scale Operation

During this quarter we compared coal conversions using $\text{Fe}(\text{CO})_5$ with CO and CO/H₂ atmospheres and determined the product distributions. In particular, the effect of a 20% CO/H₂ atmosphere and 50% CO/H₂ atmosphere. These conversions were conducted with and without the presence of additional water. We found that the $\text{Fe}(\text{CO})_5$ under a pure hydrogen atmosphere gave better conversions than under a CO/H₂ atmosphere in terms of THF solubility, but the addition of CO seemed to give good yields of oils with reduced oxygen contents. Interestingly when water was added to attempt to increase the effectiveness of the CO by utilizing the water-gas-shift reaction, less oils were observed. It is not obvious at the moment if this reduction is due to emulsions in the work-up or differences in chemical reactivities. We will try and repeat some of these reactions in the next quarter.

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 from the coal liquefaction experiments and for C, H, and N content, and in selected cases, the oxygen content. The gas analysis of the coal liquefaction products was also analyzed to determine differences in light gases as a function of catalyst and process conditions.

Elemental Analyses

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, toluene-soluble/hexane-insoluble fractions, referred to as asphaltenes, and hexane solubles, referred to as oils. For comparison, the recycle vehicle with and without treatment under coal conversion conditions was fractionated as described above to compare with the results obtained from the coal liquefaction experiments. With the exception of the oils, no notable differences in H/C ratio were observed for these fractionated products as a function of the catalyst. Oils were slightly more difficult to compare, in that they are somewhat volatile and more difficult to analyze. Currently we use a DSC pan to encapsulate the oils and avoid most of the volatiles from escaping. Comparison of the H/C ratios of these oils suggests that the $\text{Fe}(\text{CO})_5$ catalyst, especially in conjunction with CO appears to give higher H/C ratio. We plan to analyze these differences more closely after the screening portion of this project. We also analyzed selected asphaltene and oil samples for oxygen content by submitting them for direct oxygen analysis. These oxygen analyses showed a definite effect of CO in reducing the oxygen content in the products. For instance, for the $\text{Fe}(\text{CO})_5$ and H_2 reaction, the oxygen content of the asphaltene and oil fractions were 4.78% and 2.37% respectively. For the reactions conducted in the presence of 50% CO the oxygen contents were 2.74% and 1.74% respectively. When water was present, in the 50% CO run, the oxygen contents were similarly low. Thus the presence of CO appears to reduce the oxygen functionalities in the coal fractions, although the overall THF solubilities are not increased. We expect that with higher hydrogen partial pressures, or treatment of these first stage products in the second stage reactor, should give enhanced conversions and better quality products.

Gas Analysis

Table 2 lists the light gas slate from these runs as determined by GC analysis. At 1000 psi the atmosphere consists of 645 mmoles gas (H_2 or H_2/CO). As seen in the table, the majority of the gas formed during the hydrogen conversions consists of methane with small amounts of carbon dioxide, ethane, and other gases, and as observed from the treatment of the recycle vehicle, most of these gases appeared to arise from the vehicle itself.

When $Fe(CO)_5$ was used as a catalyst, carbon oxides were observed due to the CO decomposition in the catalyst, and under an atmosphere of CO/H_2 more CO and CO_2 gases were detected, as expected. As seen in the table, with 20% CO atmospheres the ratio of CO_2 to CO was only 62%, and with the 50% CO atmosphere the ratio was only 52%, suggesting that we could potentially improve the effectiveness of the CO by reacting it either with water to generate H_2 and CO_2 , (all though we would prefer it to react by deoxygenating phenols to form aromatics and CO_2). Note that the coal was previously dried and so only water generated during the coal conversion would be available. (For instance the condensation of phenolics to produce an ether and water). This quarter we added some water (1 mL) during this reaction in order to determine if the presence of water earlier in the reaction will aid the CO conversion and perhaps improve the yields to soluble products. The total amount of CO and CO_2 observed in the 20% CO and water reaction seems quite low and may be low due to a smaller sample aliquot for GC analysis. However, we saw no significant increase in CO_2/CO ratio for any of the water runs, and surprisingly, saw a decrease in oil production for both the 20% CO experiment and the 50% CO experiment.

Table 1. Analyses of Conversion Products^a

Conversion	Atmosphere	%C	%H	H/C	O
Black Thunder		63.56	4.96	0.930	
Recycle Vehicle ^b		88.08	7.09	1.055	
Fractionated Recycle Vehicle					
THF-Insol		42.55	2.59	0.726	
Preasphaltene		85.61	5.76	0.801	
Asphaltene		87.21	9.58	1.309	
Oils		89.37	10.54	1.404	
Recycle Conversion Products	1000 psi H ₂				
THF-Insol		30.62	1.62	0.632	
Preasphaltene		86.32	4.62	0.637	
Asphaltene		87.84	6.21	0.842	
Oils		84.20	8.10	1.145	
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	6.000	
Oils		84.07	7.76	1.099	
Fe ₂ O ₃	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	
Oils		83.07	8.02	1.149	
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	
Oils		84.76	7.46	1.148	
Fe(CO) ₅	1000 psi H ₂				
THF-Insol		36.92	1.82	0.587	
Preasphaltene		86.86	4.94	0.676	
Asphaltene		86.71	6.49	0.891	4.78
Oils		88.66	8.93	1.199	2.37
Fe(CO) ₅	1000 psi				
THF-Insol	20% CO	36.31	—	—	
Preasphaltene	—	—	—	—	
Asphaltene		89.05	7.10	0.949	
Oils		88.39	12.11	1.632	
Fe(CO) ₅	1000 psi				
THF-Insol	20% CO	47.48	2.37	0.594	
Preasphaltene	1 mL H ₂ O	90.43	4.85	0.639	
Asphaltene		88.58	7.16	0.962	
Oils		84.61	7.90	1.112	
Fe(CO) ₅	1000 psi				
THF-Insol	50% CO	47.17	—	—	
Preasphaltene		85.02	—	—	
Asphaltene		89.14	7.14	0.954	2.74
Oils		84.06	11.06	1.566	1.74
Fe(CO) ₅	1000 psi				
THF-Insol	50% CO	45.81	—	—	
Preasphaltene	1 mL H ₂ O	80.18	4.85	0.720	
Asphaltene		88.03	7.95	1.076	2.68
Oils		88.93	10.04	1.345	1.76

^aReaction conducted in a 300-mL autoclave with 20 g 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 37% distillate, 18% CI, and 45% resid.

Table 2. Gas Analyses^a

Catalyst	CO₂	CO	CH₄	C₂H₆	C₃	atm
Recycle Only	–	–	67	28	16	1000 psi H ₂
Fe(CO) ₅	69	17	79	27	10	1000 psi H ₂
Fe ₂ O ₃	116	44	130	44	8	20% CO
Fe ₂ O ₃	36	–	112	39	7	1000 psi H ₂
Fe(CO) ₅	160	100	120	41	9	20% CO
Fe(CO) ₅	85	41	70	23	15	20% CO /H ₂ O
Fe(CO) ₅	220	200	116	38	13	50% CO
Fe(CO) ₅	240	189	118	38	18	50% CO/H ₂ O

^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 containing 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 solvent from Wilsonville run #263 (50g) to 1 part Black Thunder coal (20g). The total gas content that we now use is 1000 psi cold charge. 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.

This quarter we were also able to compare the effect of the iron carbonyl catalyst with carbon monoxide concentrations of 20% and 50%, and the effect of added water. We are now comparing our product fractions in terms of MAF basis. For instance, as seen in Table 3, the recycle solvent produces 6.9% THF insoluble material. Since the conversions contain 50 g of recycle solvent and 20 g of coal, we would expect 4.9% THF insoluble material if all of the coal reacted to soluble products and 33.5% THF insoluble material if none of the coal reacted to soluble products. (Of course there are many possible interactions between the coal and the solvent which could invalidate this assumption). From the above method we can use equation (1) to estimate the coal conversions as calculated in the last column of Table 3. Based on THF insoluble values, the best conversions into soluble products were found for those using $\text{Fe}(\text{CO})_5$ as a catalyst and either a pure H_2 atmosphere or H_2/CO atmospheres.

$$100 - [(\text{Wt fraction} - 4.9)/28.6^*] \times 100 \quad (1)$$

* = % Coal in feed

In comparison to the recycle vehicle which had been subjected to conversion conditions, anything above 22% oils would be considered a positive oil yield. Thus, under our conversion conditions, the only positive yields were obtained from the experiments

with $\text{Fe}(\text{CO})_5$ and 50% CO. We have also fractionated the unreacted recycle vehicle to compare with the recycle vehicle treated under our processing conditions to determine if a significant loss of oils is occurring from the recycle vehicle itself or the combination of coal and recycle vehicle. As shown in Table 3, the conversion conditions actually increased the oil yields from the recycle vehicle. We suspect that the increase in oils may have come from disproportionation reactions rather than actual upgrading of the vehicle. In an actual coal conversion process we expect much better yields by using higher partial pressures of hydrogen in the presence of CO. Further optimization of the CO/H₂ ratio and addition of a second stage to the reaction should give us improved conversions and quality of product.

Table 3. MAF Yields of Fractionated Products^a

Catalyst	Atmosphere	THF Insol	Preasphaltene	Asphaltene	Oils	% Conv^b
Recycle	as received	8.7	7.5	60.9	23.2	–
Recycle	1000 psi H ₂	6.9	4.6	53.2	30.9	–
Fe ₂ O ₃	1000 psi H ₂	12.4	13.3	37.8	19.1	73.8
Fe ₂ O ₃	1000 psi CO/H ₂	19.6	10.4	28.6	18.1	48.6
Fe(CO) ₅	850 psi H ₂	21.9	6.8	31.3	14.9	40.6
Fe(CO) ₅	1000 psi H ₂	5.8	7.5	54.9	21.7	96.9
Fe(CO) ₅	20% CO/H ₂	9.9	5.0	40.1	21.5	82.5
Fe(CO) ₅ /H ₂ O	20% CO/H ₂	14.2	11.9	54.9	4.6	67.5
Fe(CO) ₅	50% CO/H ₂	15.4	19.2	35.8	26.1	63.3
Fe(CO) ₅ /H ₂ O	50% CO/H ₂	14.3	14.4	47.6	7.4	67.1
Fe ₂ O ₃ ·SO ₄	1000 psi H ₂	12.4	11.6	41.2	17.7	73.8

^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.

^bCoal Conversion = 100 - [(THF Insol - 4.9)/28.6]x100

REFERENCES

1. S. N. Rao, H. D. Schindler, and G. V. McGurl, ACS Fuel Preprints, (1988) **33**(3), 145-156.
2. J. M. Lee, O. L. Davies, T. E. Pinkston, and J. R. Gough, ACS Fuel Reprints, (1988) **33**(3), 157-171.
3. D. Gray and G. Tomlinson, ACS Fuel Preprints (1988) **33**(3), 172-179.
4. S. V. Gollakota, J. M. Lee, O. L. Davies, and T. E. Pinkston, DOE Direct Liquefaction Contractors' Review Meeting, Pittsburgh, Pennsylvania, October 1988.
5. R. Neavel, Phil. Trans. R. Soc. Lond. A, (1981) **300**, 141.
6. E. C. Moroni, ACS Fuel Preprints, (1986) **31**(4), 294-299.
7. E. M. Suuberg, D. Lee, and J. W. Larsen, Fuel, (1985) **64**, 1668.
8. G. V. Deshpande, P. Solomon and M. A. Serio, ACS Fuel Preprints, (1988) **33**(2), 310.
9. E. C. Moroni, ACS Fuel Preprints, (1988) **33**(1), 384-386.
10. C.-L. Li, Z.-r Xu, and B. Gates, Ind. Eng. Chem. Prod. Res. Dev., (1985) **24**, 92-97.

DATE

FILMED

6 / 2 / 94

END