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SURFACTANT STUDIES FOR BENCH-SCALE OPERATION

FIFTH QUARTERLY TECHNICAL PROGRESS REPORT: July 1, 1993 - September 30, 1993

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ABSTRACT

A phase II study has been initiated to investigate surfactant-assisted coal liquefaction, with the objective of quantifying the enhancement in liquid yields and product quality. This report covers the fifth quarter of work. The major accomplishments were 1) Completion of coal liquefaction autoclave reactor runs and related analysis with Illinois #6 coal at 400 °C with and without surfactant and/or catalyst at pressures of 1700 psig, 2) A literature search into the effect that lignin has in the coprocessing of coal 3) Presentation of a report summarizing the first year of work on this task at the Annual Liquefaction Contractors Review Conference.

Results from this quarter show that lignosulfonate surfactant continues to increase overall MAF conversion of Illinois # 6 coal at temperatures up to 400 °C and produces an improvement in light boiling fraction distillate over the base case of no surfactant addition.

CONTENTS

	Page
I. INTRODUCTION	5
II. EXPERIMENTAL SYSTEM	6
III. EXPERIMENTAL RESULTS	6
IV. LIGNIN COPROCESSING LITERATURE SEARCH	10
V. SUMMARY	11
VI. REFERENCES	12

I. INTRODUCTION

The liquefaction of coals is a promising technology for producing alternate fuels that may eventually replace petroleum-based fuels. This technology has implications toward the goal of attaining self sufficiency in the Nation's energy needs. However, in order to make coal liquefaction technology competitive with existing energy sources, high carbon conversion without subjecting the coal to extensive processing steps is desired. The fact that the operating conditions (such as solvent type and structure, the hydrogen to carbon (H/C) ratio, temperature etc.) play a significant part in the dissolution of the organic coal matter is long known^{1,2}. The possible effects of the lowering of the viscosity and the surface tension of the liquid phase in a reactor have mostly been speculated and not systematically investigated. Further, the research emphasis in coal liquefaction has recently shifted away from intensive processing to maximize liquid yields toward milder processing to obtain a more economically attractive slate of products.

A Phase I study³ using the surfactant approach for milder processing in liquefaction was completed at the Jet Propulsion Laboratory (JPL) in December 1990. This study, though preliminary and of a limited scope, identified sodium lignosulfonate as the surfactant additive which appeared most promising based upon viscosity tests. A few coal liquefaction autoclave test runs carried out with a small amount of the lignosulfonate additive showed an increase in light soluble solids. These preliminary tests also indicated a possible increase in the liquid yields.

The present work effort relates to an investigation of surfactant-assisted coal liquefaction with the objective of quantifying the enhancement in liquid yields and the product quality. Optimum conditions for a surfactant assisted coal liquefaction run were to be determined through a set of comprehensive batch autoclave tests and verified in a continuous-flow bench scale test. The economic advantage of such a surfactant-assisted coal liquefaction process will also need to be evaluated.

The technical progress made during the year of this effort was summarized in the first four quarterly technical progress reports^{4,5,6,7}. The results included in these reports showed a favorable effect of the surfactant addition in terms of an increase in overall coal conversion and an increase in the low boiling fractions for the filtrate at process temperatures up to 375 °C.

Accomplishments

The major accomplishments during the last three months were 1) Completion of coal liquefaction autoclave reactor runs and related analysis with Illinois #6 coal at 400 °C with and without surfactant and/or catalyst at pressures of 1700 psig, 2) A literature search into the effect that lignin has in the coprocessing of coal 3) Presentation of a report summarizing the first year of

work on this task at the annual Department of Energy Liquefaction Contractors Review Conference.

II. EXPERIMENTAL SYSTEM

The surfactant assisted coal liquefaction experimental reactor system consists of a Parr series 4500 autoclave and accessories. A schematic of the reactor system is shown in Figure 1. The reactor consists of a one liter stainless steel pressure vessel with a maximum operation pressure of 1900 psig at 375 °C. The reactor contents are mixed by a belt driven stirrer with a six blade turbine-type impeller with a rotation speed from 0 to 1000 rpm. The reactor shaft assembly includes a cooling water loop. The reactor system has gas lines and flow valves for nitrogen and hydrogen, and a vent line with burst reservoir. For safety, the reactor has a pressure relief valve rated at 1910 psig, and a burst valve rated at 2200 psig. Pressure is measured by a 3000 psig pressure gauge, and temperature by a thermocouple inserted into a thermowell within the reactor. Temperature is controlled by an automatic temperature controller.

The primary coal being used in this study is Illinois # 6 obtained from the Penn State Coal Data Bank (PSCD) with PSCD designation DECS-2. The coal particle size is -60 mesh and is stored in a sealed, dry container. The coal is used in as-received condition. The solvent used is SRC-2 recycle solvent obtained from Hydrocarbon Research Inc. (HRI). For the 400 °C runs, fresh recycle solvent was obtained from HRI. The surfactant is Sodium Lignosulfonate obtained from Pfaltz and Bauer, Catalogue No. S05950.

The experimental run procedures and analysis scheme have been presented in detail in previous quarterly reports^{5,6}. They have been developed over the last year to produce consistent and reproducible experimental results.

III. EXPERIMENTAL RESULTS

The mass balances at various mixing and separation steps were found to all close within 3 percent. The detailed operating conditions and run identifications for runs completed this quarter are summarized in Table 1. Detailed results for previous runs are included in the Second, Third and Fourth Quarterly Technical Progress reports^{5,6,7}. All runs reported here were made on Illinois #6 coal with sodium lignosulfonate as the surfactant. The results for the yields of the liquid filtrate, the solid filter cake, and the corresponding mass balance for each test run are given in Table 2 for Runs 36 to 40. Run 38 made use of one gram of dispersed finely ground iron oxide as a catalyst. Runs 39 and 40 each used one gram of finely ground Shell 317 nickel-molybdenum catalyst obtained from HRI. Run 40, in addition, used 1% of the lignosulfonate surfactant.

Coal Conversions and Liquid Product Quality

Coal conversions were obtained based on the conversion of the moisture and ash-free carbonaceous material to either the coal-derived liquid or the

Figure 1: Autoclave Reactor System Schematic

fraction that is soluble in solvents used in the extractions with the filter cake. The conversion was obtained using the relationship:

$$\text{Fractional Conversion} = (W_{\text{init}} - W_{\text{fin}})/W_{\text{init}}$$

where W_{init} is the initial weight of the coal on moisture and ash-free basis subjected to liquefaction, and W_{fin} is the final weight of the carbonaceous residue obtained from the treated slurry that is not soluble in THF. Note that W_{fin} is to be corrected by subtracting the ash in the initial sample as well as subtracting the soluble part of the surfactant in the runs where surfactant was added.

To obtain accurate measurement of overall MAF conversion it is necessary to understand the stability of the lignosulfonate surfactant at the processing temperatures used in this study. Runs 32, 33, and 35 were conducted to determine the fraction of surfactant that is retained in the filtercake as a solid and the fraction that is transferred into the liquid phase in the temperature range 350 to 400 °C.. During the liquefaction processing, the surfactant may either be hydrogenated and become liquid product or may decompose into smaller organic species. By processing the surfactant in the recycle solvent without coal and completing a hydrogenation process cycle, the stability of the surfactant could be determined. In these runs, the thermally processed surfactant was filtered at the end of the run and twice extracted with THF. The remaining residue was dried at 100 °C and weighed to determine the fraction of the surfactant that does not get liquefied and, hence, will stay in the filter cake. At temperatures of 350 to 375 °C, approximately 50 % surfactant is transferred into the liquid phase while at 400 °C, approximately 70 % of the surfactant ends up in the liquid phase. Taking this into account, the coal conversions for work completed this quarter are presented in Table 3 and the previously reported values for conversions in Quarterly Reports 2, 3 and 4 were corrected and summarized in Table 4.

The trend of increasing overall MAF conversion with temperature continued at the 400 °C batch autoclave tests conducted in this quarter. Figure 1 shows the comparison of the 1.0 % surfactant addition case to the baseline case without surfactant addition for the temperature range from 300 to 400 °C. Note that the surfactant addition increases the coal conversions by about 10 to 20 percent, generally increasing with temperature with the largest absolute increase occurring at the temperature of 350 °C. Closer analysis of the stability of the surfactant has provided new insight into the amount of surfactant that is needed to provide a significant step increase in overall conversion. As seen in Figure 2, only a small amount of surfactant (on the order of 0.5 %) is required to increase conversion.

The trend of improvement in the quality of the liquid yields by the addition of the surfactant is still seen at 400 °C. Figure 3 shows the increase in preasphaltenes with processing temperature. The production of preasphaltenes was determined from the THF extraction that succeeded the hexane and toluene washes. There is a greater increase in the amount of preasphaltenes with the

addition of the surfactant. This would appear to be due to high molecular weight fragments (preasphaltenes) from the coal entering the liquid product.

The HRI two-stage ebullated bed liquefaction process makes use of catalyst addition to produce an improvement in product slate quality. Selected tests were conducted to determine the effect of catalyst interaction with the surfactant. Figure 4 shows a comparison at 400 °C between the a) baseline case of thermal processing of coal alone, b) coal with 1% surfactant, c) coal with 1% HRI Ni-Mo catalyst, and d) coal with 1% HRI Ni-Mo catalyst and 1% surfactant. It is seen that the addition of either the surfactant or the HRI catalyst improves the conversion significantly over the base case, but the HRI catalyst is slightly more effective. However, when both the catalyst and the surfactant are added together at 400 °C, the conversion is decreased slightly compared to the catalyst alone.

The filter cake analysis for these cases showed that the yield of light oils was nearly the same for the runs where the additives were HRI catalyst alone (case c) and HRI catalyst mixed with the surfactant (case d), respectively. However, the yield of asphaltenes was higher and preasphaltenes lower for case d compared to case c. This indicates that at 400 °C, even though surfactant addition to HRI catalyst lowered the conversion by a small amount, it still improved the product slate due to generation of increased amounts of lighter components.

In previous work during this task³ the effect of disposable Fe₂O₃ catalyst was considered as an alternative process additive. During this quarter, the addition of Fe₂O₃ was tested at 400 °C processing temperature. The addition of the iron oxide increased the overall conversion to 89.6 % over the base case of no surfactant, at 84.1 % conversion. The Fe₂O₃ addition had a lower overall conversion than the case of the surfactant alone, and significantly less conversion than the HRI Ni-Mo catalyst.

Figure 5 shows the percent increase in light boiling fraction distillate (20 to 300 °C) that is produced by the addition of 1 % surfactant compared to the base case of no surfactant. The greatest percentage increase is still seen at a processing temperature of 350 °C with a 22 % improvement, but there is still a 15 % enhancement in light distillate quality at 400 °C.

DISCUSSION

The observed increase in the overall coal conversion due to the addition of the surfactant, sodium lignosulfonate, appears to result mainly from the breakage of crosslinks of the associated coal molecules. This, in turn, appears to lead to greater access of hydrogen to the coal fragments and thus a significant increase in the hydrogenation rate and subsequent solubilization rate. Table 4 shows that overall conversions are relatively independent of surfactant concentrations from 0.5 to 2.0 %. The observation that overall coal conversions are relatively independent of surfactant concentration is consistent with a recent study on the kinetics of adsorption of surfactants on mineral matter. Marbrel and Somasundaran⁸ have reported a study of the surfactant adsorption on a mineral

at the solid-liquid interface by electron spin resonance spectroscopy. This study showed that 40% of the total ultimate surfactant adsorption occurred during the first 5 seconds of contact, independent of the initial surfactant concentration (provided sufficient surfactant was present). The second stage of adsorption was much slower and occurred on the order of one to three hours. In our case, where the coal is a mineral-containing solid with preferential acid sites for the surfactant, close to 100% of the total surfactant adsorption may take place during the first minute of contact, even with very low surfactant concentrations.

While the favorable effect of surfactant addition has been well illustrated, there was a concern that the observed improvement in liquefaction yields may be due to its decomposition to lignin-type products and their participation in the liquefaction process. To address this question, a literature search of the effect of lignin addition in liquefaction or coprocessing of coal and lignin was made.

IV. LIGNIN COPROCESSING LITERATURE SEARCH

Study of simultaneous coal and lignin liquefaction has been conducted broadly by two groups of investigators: Lalvani, et. al.^{9,10} at Southern Illinois University, and Coughlin, et al.^{11,12} at the University of Connecticut, Storrs. The main findings of these studies are summarized below.

Lalvani, et. al. found that lignin-derived liquids when reacted with coal at about 375 °C enhance the rate of coal depolymerization by up to 30 percent. The lignin liquid-assisted coal depolymerization liquid products were observed to contain a significant amount of the lighter and desirable pentane soluble fraction. It was hypothesized that the enhancement in coal depolymerization rates can be explained by a reaction pathway involving intermediates formed from lignin derived liquids. For their work, a caustic lignin was obtained from steam-exploded aspen. Lignin was added to tetralin and heated to 200 °C in the presence of hydrogen gas. After reaction for a certain time, the reacted lignin was filtered. The filtrate was referred to as the lignin-derived liquid.

A follow up study indicated that the liquid product from the coal lignin mixture contains a lower fraction of the undesirable benzene insolubles than the liquid product from coal alone. The weight-averaged molecular weight for the overall liquid product (derived from the coal-lignin mixture) was lower than the molecular weight obtained by reacting coal or lignin alone. A 22% enhancement in coal conversion was seen to result.

Coughlin, et al. also observed that adding lignin to a mixture of coal and solvent caused more extensive depolymerization of the coal at lower temperatures (about 300 °C). The coal conversions were strongly dependent upon the ratio of lignin to coal. For processing temperatures of 300 °C and pressures around 1500 psi, coal conversion without lignin addition was about 5%. With a lignin to coal ratio of 1 to 4, the coal conversion increased to about 20%. With a lignin to coal ratio of 2 to 1, the coal conversion was about 43%. The mechanism of the lignin effect was investigated. Thermal depolymerization of the

lignin at relatively low temperatures is believed to form resonance-stabilized phenoxy radicals, which appear to attack the coal causing scission of aliphatic carbon-carbon bonds in the coal.

In a later study by Altieri and Coughlin, the coliquefaction of lignin and bituminous coal was investigated at 400 °C. The filterable solids from coliquefaction were about 30% benzene soluble compared to about 10% soluble when the same amounts of coal and lignin were reacted individually.

The above studies can be summarized by the general conclusion that addition of lignin or lignin-derived liquids to coal during liquefaction assists in coal depolymerization and hence results in increased conversions even at low processing temperatures. However, significant improvement appears to result only if the ratio of lignin additive to coal is large enough (from 0.25 to 2.5).

Run 34 was planned to investigate the effect of sodium lignosulfonate or its thermal decomposition products on coal conversion which may run parallel to the surfactant action. In this run, 10.0 grams each of coal and the sodium lignosulfonate surfactant were subjected to liquefaction with 200. ml of recycle solvent at 400 °C. The treated slurry was filtered and the filter cake was twice extracted with THF. Knowing that the surfactant liquefaction under these conditions is 70 %, the final dried residue was corrected to obtain the coal generated MAF residue. This number corresponds to overall coal conversion of 84.1 %, which is the same conversion for the coal alone with no surfactant addition. This indicates that the thermal decomposition products of the sodium lignosulfonate behaves differently than the lignin-derived liquid and did not aid the liquefaction process. This result is consistent with the earlier observation that a significantly favorable effect of the surfactant is seen by addition of a small amount (0.5 %), and addition of a significantly larger amount does not produce further enhancement.

It is clear from the analysis of the test runs in this experimental work where only the surfactant was processed with the recycle solvent (without coal), that a part of the surfactant is converted to liquid products. These liquid products may be likely to cause some enhancement in coal conversions due to lignin generated intermediate species formation as discussed by Coughlin^{11,12} However, such enhancement in conversions in this work should be very small as the amount of surfactant used is small. Further, the overall conversions observed here are relatively independent of the surfactant concentration, whereas, the lignin induced improvement in conversion seen by Coughlin is strongly dependent upon the lignin concentration. Hence, the improvement due to addition of sodium lignosulfonate would appear to be uniquely due to the surfactant effect and relatively free of the artifacts of its decomposition to lignin type products.

V. SUMMARY

The major accomplishments for this quarter included autoclave test runs and analysis with Illinois #6 coal to determine the effect of processing at 400°C. The results obtained and the data analysis indicate that the surfactant is highly

effective in improving liquefaction yields even at 400 °C and that only a small amount of surfactant is required to produce an effect. The improvement in liquefaction yields is seen both as an increase in overall conversion and as an improvement in light boiling fraction distillate. The surfactant approaches the effectiveness of the Ni-Mo catalyst in overall conversion. A rigorous comparison of the product quality in comparison to the Ni-Mo catalyst will be made during the next quarter.

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Table 1 Processing conditions for the liquefaction runs completed this quarter.

RUN NO	AVERAGE TEMP. °C	AVERAGE PRESSURE psig	PROCESS TIME hr.	SURFACTANT CONC. wt %	CATALYST CONC. gm.
32	375	1700	1.0	2.0 ^A	0.0
33	400	1690	1.0	2.0 ^A	0.0
34	400	1700	1.0	10 gm Coal/10 gm Surf.	
35	350	1670	1.0	2.0 ^A	0.0
36	400	1710	1.0	2.0	0.0
37	400	1745	1.0	0.0	0.0
38	400	1740	1.0	1.0	1.0 Fe ₂ O ₃
39	400	1680	1.0	0.0	1.0 Ni-Mo
40	400	1730	1.0	1.0	1.0 Ni-Mo

Note: A: Surfactant Only, No Coal

Table 2. Mass balance distribution of the liquid filtrate and the filter cake.

RUN NO.	LIQUID FILTRATE g	FILTER CAKE g	OVERALL MASS BALANCE (%)
36	169.66	98.59	97.8
37	160.28	109.19	97.4
38	158.87	115.02	99.3
39	164.96	106.91	98.5
40	164.88	106.60	97.5

Table 3. Overall coal conversions for the various liquefaction runs conducted this quarter.

RUN No.	TEMP. °C	PRESSURE PSIG	SURFACTANT CONC. wt %	CATALYST CONC. gm.	OVERALL CONVERSION (%)
36	400	1710	0.0	0.0	84.1
37	400	1745	1.0	0.0	92.9
38	400	1740	1.0	1.0	89.6
39	400	1690	0.0	1.0	95.6
40	400	1730	1.0	1.0	93.8

Table 4: Test matrix results of Illinois #6 coal conversion (MAF basis) processed for one hour with varying amount of sodium lignosulfonate surfactant.

<u>Temperature</u>	<u>H₂ Pressure</u> (Psig)	<u>Surfactant Concentration</u>			
		0%	0.5 %	1.0 %	2.0 %
300 °C	1800	21.4 %	24.7 %	24.6 %	24.5 %
325 °C	<1800				24.2 % (A)
325 °C	1800	25.4 %	29.8 %	36.5 %	29.2%
350 °C	<1800		65.9 % (B)		60.0 % (C)
350 °C	1800	54.4 %		62.5 %	63.1 %
375 °C	<1800	77.0 % (B)			82.5 % (C)
375 °C	1800	83.1 %	86.0 %	85.9 %	87.4 %
400 °C	1700	84.1 %		92.9	

Notes: A: 1050 Psig, B: 1300 Psig, C: 1500 Psig

Figure 1: Temperature dependence of conversion with and without surfactant.

Figure 2: Effect of surfactant concentration on MAF conversion.

Figure 3: Yield of preasphaltenes (as determined from THF extraction) as a function of temperature with and without surfactant.

Figure 4: Comparison of MAF conversion of catalyst and surfactant interactions at 400 °C.

Figure 5: Percent increase in light boiling fraction of distillate after 1 % surfactant addition compared to 0.0 % surfactant.

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