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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 third quarter of work. The major accomplishments were 1) completion of coal liquefaction autoclave reactor runs and related analysis with Illinois #6 coal at a processing temperature of 375 °C, and pressures of 1800 and 1500 psig, 2) completion and analysis of two autoclave reactor runs to observe the synergistic effect of the surfactant and an iron catalyst, and 3) setting up a subcontract with HRI Inc. to test the surfactant enhanced liquefaction process in a continuous flow reactor.

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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 are 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 to be evaluated.

The technical progress made during the first six months of this effort was summarized in the first and the second quarterly technical progress reports^{4,5}. The results included in these reports showed a favorable effect of the surfactant addition in terms of an increase in coal conversion and an increase in the low boiling fractions for the filtrate.

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 a processing temperature of 375 °C, and pressures of 1800 and 1500 psig, 2) completion and analysis of two autoclave reactor runs to observe the synergistic effect of the surfactant and an iron catalyst, and 3) setting up a

subcontract with HRI Inc. to test the surfactant enhanced liquefaction process in a continuous flow bench-scale facility.

II. EXPERIMENTAL SETUP

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). The surfactant is Sodium Lignosulfonate obtained from Pfaltz and Bauer, Catalogue No. S05950.

Batch Run Procedures

A batch run procedure has been developed with an emphasis on reproducibility and safety. For each run, 100 gm of coal is weighed and mixed with the appropriate concentration of surfactant (0.0, 0.5, 1.0 or 2.0 wt%). The coal is added to the autoclave and 200 ml of recycle solvent is mixed with it. The reactor is sealed by a split ring closure with Teflon gasket. The reactor is flushed three times with 300 psig dry nitrogen gas to remove air, and is then pressurized to 1000 psig for 30 minutes to check for leaks. If there are no leaks, the system is vented slowly and purged two times with 50 psig hydrogen, followed by two purges at 300 psig hydrogen to remove the nitrogen. The reactor is then pressurized to between 850 and 1000 psig of hydrogen, so that at the processing temperature (300 to 375 °C), the system pressure will be 1800 to 1900 psig. A lower initial pressure is used for the 1500 psig experimental runs. The gas inlet valve is closed and the system is heated to the test temperature, and held at that temperature for the appropriate duration of time.

Upon completion of the run the power is turned off to the heater, and the reactor is cooled. The slurry in the reactor is allowed to settle overnight, then the system is vented. If a gas sample is to be collected, it is collected in an evacuated gas sample cylinder before the system is vented. The reactor is then opened and the treated slurry is collected for subsequent filtration and analysis. Great care is taken to collect all liquids and solids by scraping the interior of the

Figure 1: Autoclave Reactor System Schematic

reactor, the impeller shaft and supports. Material losses remaining are determined to be generally less than 1 percent. At this point, the reactor is thoroughly cleaned with isopropanol solvent and prepared for the next reactor run.

III. ANALYSIS PROCEDURES

A detailed analysis procedure has been developed to characterize the coal liquefaction solid and liquid products. A schematic is shown in Figure 2. The definition for conversion is the mass fraction of the carbonaceous material that either is directly converted to liquid during the reaction or is extracted during solvent treatments. By definition, conversion is on a moisture and ash free (MAF) basis.

The reactor product slurry is allowed to settle out for a minimum of three days. The product slurry usually separates into two fractions, the top fraction being mostly liquid while the bottom fraction contains the major part of the solids. The top fraction is decanted, filtered and put in a collection vessel, and the remaining wet solids are vacuum filtered for 15 minutes to remove the filterable liquids from the filter cake. The filtration is conducted with a buchner funnel with 5 μm pore size filter paper. The filtered liquid is added to the original filtrate. The filtrate and the filter cake are weighed and the mass balance closure during the filtration step is verified.

In order to characterize the liquid obtained as the filtrate, 50 ml of the filtrate are removed for atmospheric distillation using the procedure outlined in ASTM D 246-89⁶. Distillation fractions are taken for the following cuts: room temperature to 210 °C, 210 to 270 °C, 270 to 300 °C, and residual bottoms.

The filter cake is subjected to a series of extractions to determine the preasphaltenes, asphaltenes and light oil fractions. The solvents used for successive extractions are hexanes, toluene and tetrahydrofuran (THF). All solvents are reagent grade. For the extraction, 10 grams of filter cake are added to 30 ml of hexanes, stirred, and allowed to sit overnight. The slurry is then vacuum filtered using a conical funnel and 2.5 μm pore size filter paper (Whatman 42). The mixture is washed with solvent until the filtrate is clear. The remaining filter cake is then dried by vacuum for 10 minutes to remove a part of the solvent. The remaining solvent is removed by heating the filter cake in an oven maintained at a temperature of about 100 °C for 4 to 8 hours. The dried filter cake is weighed and then mixed with 30 ml of toluene for the toluene extraction and the extraction procedure is repeated and the sample is dried at 125 °C for 4 to 8 hrs. The final filter cake is then extracted with THF. At the completion of the THF extraction, the THF insoluble solids are dried 16 hrs at 60 °C in air to drive off any residual solvent before a final weight is determined.

Overall conversions were also determined by THF extraction alone. In this alternative approach, 10 g of the filter cake were extracted with 30 ml of THF

Figure 2: Baseline Analysis Scheme

over a period of 24 hrs. After filtration, the extraction with THF was repeated. The final extracted residue was separated by filtration, dried and then weighed.

IV. RESULTS

The mass balances at various mixing and separation steps were found to all close within 3 percent. Table 1 shows a generalized test matrix of the completed runs to date. The detailed operating conditions and run identifications for runs completed this quarter are summarized in Table 2. Detailed results for previous runs are included in the Second Quarterly Technical Progress report⁵. All runs reported here were made on Illinois #6 coal with sodium lignosulfonate as the surfactant and a processing time of one hour. The results on the yields of the liquid filtrate and the solid filter cake together with the corresponding mass balance closure for each test run are given in Table 3.

The results on the fractionation (by atmospheric distillation) of the solids-free filtrates for various runs are provided in Table 4. For each distillation, the initial filtrate sample was 50 g. The various cuts reported are weights of distilled fractions obtained at the specified temperature ranges. The last column in this table is the sum of the lower boiling distillate fractions that are obtained below 300 °C.

The results on the soluble solids for various filter cake samples are reported in Table 5 on a weight percent basis of the original weight of the filter cake. The total soluble solids are separated into hexane solubles, toluene solubles, and THF solubles, as obtained by step-wise extractions in that order.

Coal Conversions

Coal conversions were obtained based on the conversion of the ash and moisture-free carbonaceous material to either the coal-derived liquid or the fraction that is soluble in solvents used in the extractions with the filter cake. As it is generally believed that the treated coal fractions which are soluble in hexanes and toluene will also be soluble in THF, this method of computation of the overall conversion should be nearly the same as the result obtained if the treated slurry were washed with THF alone. Thus, 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 hexanes, toluene, and THF. Note that W_{fin} is to be corrected by subtracting the ash in the initial sample as well as subtracting the surfactant in the runs where surfactant was added. To validate that this extraction procedure only extracts reacted coal, the extraction sequence was performed on as-received Illinois #6 coal. The pseudo-conversion for raw coal (after successive washes with hexane, toluene, and THF) was similarly determined and was found to be only about 2.0 percent.

The coal conversions obtained by the successive extractions procedure described above were compared with the more conventional approach of THF extraction alone. The difference between the coal conversions obtained by these two procedures was within 3 percent.

The coal conversion results for runs completed this quarter with variable operating conditions of temperature, pressure, and surfactant concentration are described in Table 6. Table 7 provides a summary of conversion results for all runs to date with Illinois # 6 coal. The uncertainty in the conversion values is estimated to be less than 2 percent. From an examination of the data presented in above tables, some noteworthy trends are apparent. One such trend is the dependence of the conversion upon operating temperature with and without the surfactant. This dependence is illustrated in Figure 3. Note that the surfactant addition increases the coal conversions by about 15 to 25 percent, increasing with temperature with the largest absolute increase occurring at the temperature of 350 °C. Another important trend is that the addition of the surfactant increases the amount of the light distillates continues up to 375 °C. This trend is illustrated in Figure 4 comparing the 2.0 % addition versus the 0 % case. The production of preasphaltenes increases with reaction temperature. This is illustrated in Figure 5. The production of preasphaltenes was determined from the THF extraction that succeeded the hexane and toluene washes. There is also a greater increase in the preashaltenes 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.

Table 8 shows the results of preliminary work on the effect that Fe_2O_3 has on the conversion of coal to recoverable liquid products. Previous work by Cugini, *et. al.* at PETC has shown that the addition of iron oxide as a disposable catalyst increases conversion over the noncatalyzed process⁷. Their work focused on adding hydrated iron oxide (FeOOH) dispersed on coal by the incipient wetness precipitation approach. The results shown here are for the direct addition of finely ground iron oxide powder to the coal without further preparation. The 1.0 % surfactant addition at 375 °C, 1800 psig Hydrogen and one hour processing time was used as the base case. This had a conversion of 83.1 %. By adding the 1 wt % Fe_2O_3 to the coal with surfactant the MAF conversion increases to 93.5 % for the batch reactor run. A third run with 1 wt % Fe_2O_3 without surfactant had a conversion of 88.8 %. This preliminary work indicates that the addition of the iron oxide and surfactant would have a positive synergistic effect on coal conversion.

Gas samples were analyzed by mass spectroscopy to determine the primary gas products for selected runs. Samples were taken from runs # 9, 14, 19 and 20 after the runs had been completed and the reactor had cooled down. These runs correspond to 1% surfactant addition at 325, 350, and 375 °C and 375 °C without surfactant. The primary gas products, in addition to the hydrogen, were light gases consisting of methane, ethane, propane, and water vapor and their fragments. Sulfur containing species could be smelled, but were less than 1% of the reactor gases. The proportion of hydrocarbon gases increased with temperature, using the amount of water produced as a normalization factor.

Figure 3: Temperature dependence on conversion with and without surfactant.

Figure 4: Temperature dependence of light boiling fractions with and without surfactant.

Figure 5: Yield of preasphaltenes (as determined from THF extraction) as a function of temperature with and without surfactant.

Implication of Autoclave Test Results to the Proposed Bench-Scale tests

The bench scale tests will be carried out at HRI, Inc. using a continuous flow two-stage bench unit which incorporates two 2,000 cc ebullated-bed reactors in series. A subcontract with HRI has been set up for five days of bench scale operation to demonstrate the surfactant effect in the continuous flow bench unit. The recommendations for the operating conditions are made within the constraints of operation of this unit; which will directly follow the scheduled test run for PETC. It is recommended that we use 2.0 wt% surfactant addition with an initial operating temperatures no higher than 420 °C, to be followed by stabilized operation at 375 °C. The operating pressures and mass flow rates will remain unchanged from the last set of conditions of the PETC run. The reactor flow rates should be high enough such that the observed coal conversion before surfactant addition is not near the maximum; so the effect of the surfactant may be observed.

V. SUMMARY

In summary, the experimental runs and the analysis described here for the Illinois #6 coal constitute an important subset of the overall matrix of tests planned for this coal. A processing temperature of 375 °C and surfactant concentrations from 0 to 2.0 wt % have been covered. The temperature dependence of the coal conversion and the light boiling fractions in the filtrate have been illustrated. These results indicate that surfactant addition can lower (or even eliminate) catalyst requirements and, at the same time, enable the coal processing to be carried out at less intensive temperatures and pressures than currently used.

During the next reporting quarter, we plan to investigate the mechanism of the increase in liquefaction yield due to surfactant addition and investigate the dependence on processing time on conversion. During the next quarter the continuous flow bench scale reactor test run will be completed at Hydrocarbon Research, Inc.

Surfactant Studies Test Matrix

Coal: Illinois # 6
 Surfactant: Sodium Lignosulfonate
 Time: 1 hour

R: Run Completed
 A: Run Analysed

		Surfactant Concentration			
		0 %	0.5 %	1.0 %	2.0 %
TEMPERATURE	Psig				
	300 C	RA	RA	RA	RA
	1800				
	325 C	RA	RA	RA	RA
	<1800				
	1800		RA		RA
	350 C	RA			
	<1800			RA	RA
	1800	RA		R	RA
	<1800	RA	RA	RA	RA
	1800				

Table 1: Generalized liquefaction process test matrix

Table 2. Processing conditions for the liquefaction runs completed this quarter.

RUN NO.	AVERAGE TEMP. °C	AVERAGE PRESSURE psig	PROCESSING TIME hr.	SURFACTANT CONC. wt %
19	375	1800	1.0	1.0
20	375	1300	1.0	0.0
21	375	1500	1.0	2.0
22	375	1650	1.0	0.5
23	375	1800	1.0	2.0
24	375	1800	1.0	0.0
25	375	1800	1.0	1.0*
26	375	1800	1.0	0.0*

* With 1 wt% (based on coal) iron oxide addition

Table 3. Mass balance distribution of the liquid filtrate and the filter cake.

RUN NO.	LIQUID FILTRATE g	FILTER CAKE g	OVERALL MASS BALANCE (%)
19	155.40	121.03	98.4
20	156.80	119.42	98.0
21	154.06	121.49	97.5
22	158.10	118.12	98.4
23	158.16	120.51	98.1
24	157.35	117.77	98.4
25	160.26	118.07	97.9
26	162.28	115.59	98.5

Table 4. Distillation fractions of the liquid filtrate based on a 50 g sample.

RUN No.	SURFACT. CONC. wt %	210 °C CUT g	270 °C CUT g	300 °C CUT g	BOTTOMS > 300 °C g	TOTAL LIGHT UP TO 300 °C g
19	1.0	0.03	8.47	10.69	30.53	19.19
20	0.0	0.08	7.51	7.82	34.31	15.41
21	2.0	1.01	5.53	6.52	36.66	13.06
22	0.5	1.41	7.39	8.38	32.54	17.18
23	2.0	0.88	8.81	7.93	32.11	17.62
24	0.0	1.23	8.26	7.06	32.25	16.55
25	1.0*	0.71	6.92	6.05	36.13	13.68
26	0.0*	0.91	6.84	7.02	34.97	14.77

* With 1.0 wt% (based on coal) iron oxide addition

Table 5. Extraction fractions of the filter cake for various runs.

RUN No.	SURFACTANT CONC. wt %	HEXANE SOLUBLES wt%	TOLUENE SOLUBLES wt%	THF SOLUBLES wt%
19	1.0	31.3	10.4	35.9
20	0.0	31.2	7.1	34.0
21	2.0	29.5	7.2	36.6
22	0.5	30.5	7.2	38.1
23	2.0	29.9	9.7	38.1
24	0.0	29.5	8.0	37.8
25	1.0*	30.0	6.9	44.4
26	0.0*	29.0	8.0	41.2

* With 1.0 wt.% (based on coal) iron oxide addition

Table 6. Overall coal conversions for the various liquefaction runs.

RUN No.	TEMP. °C	PRESSURE PSIG	SURFACTANT CONC. wt. %	OVERALL CONVERSION (%)
19	375	1800	1.0	87.7
20	375	1300	0.0	77.7
21	375	1500	2.0	86.2
22	375	1650	0.5	86.9
23	375	1800	2.0	91.2
24	375	1800	0.0	83.1
25	375	1800	1.0*	93.5
26	375	1800	0.0*	88.8
* With 1.0 wt% (based on coal) iron oxide addition				

Surfactant Studies Test Results

Coal: Illinois # 6
 Surfactant: Sodium Lignosulfonate
 Time: 1 hour

		Surfactant Concentration			
		0 %	0.5 %	1.0 %	2.0 %
TEMPERATURE	300 C				
	< 1800	21.4 %	25.5 %	26.0 %	24.5 %
	1800				
325 C	<1800	25.4 %	30.6 %	38.1 %	32.5 %
	1800				
350 C	<1800	54.4 %	66.8 %	64.3 %	66.8 %
	1800				
375 C	<1800	77.0 %		---	86.2 %
	1800				
		83.1 %	86.9 %	87.7 %	94.5 %

Table 7: Generalized test matrix results.

Table 8: Effect of Iron oxide addition on coal conversion.

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