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SURFACTANT STUDIES FOR BENCH-SCALE OPERATION

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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 fourth quarter of work. The major accomplishments were 1) Completion of coal liquefaction autoclave reactor runs and related analysis with Illinois #6 coal with time as a variable at 375 °C, and pressures of 1800 psig, 2) An investigation into the mechanism of the effect that the lignosulfonate surfactant has in enhancing liquefaction yields 3) Completion of a bench-scale test with the surfactant in the continuous flow Catalytic Two Stage Liquefaction Process (CTSL) reactor at HRI.

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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 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 first nine months of this effort was summarized in the first three quarterly technical progress reports^{4,5,6}. 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 with processing time as a variable at a temperature of 375 °C, and pressures of 1800 psig, 2) an investigation into the mechanism of the effect that the lignosulfonate surfactant has in enhancing liquefaction yields, and 3)

completion of a bench-scale test with the surfactant in the continuous flow Catalytic Two Stage Liquefaction Process (CTSL) reactor at HRI.

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). 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 and Third Quarterly Technical Progress reports^{5,6}. All runs reported here were made on Illinois #6 coal with sodium lignosulfonate as the surfactant and processing time as the variable. 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 2 for Runs 27 to 31.

Coal Conversions

Coal conversions were obtained based on the conversion of the moisture and ash-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. The conversion was obtained using the relationship:

Figure 1. Autoclave reactor system schematic.

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

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 surfactant in the runs where surfactant was added. The conversions are based on THF extraction only for this set of results.

The coal conversion results for runs completed this quarter are described in Table 3. The dependence of conversion on the processing time is shown in Figure 2. The conversion increases with longer processing. For the case with the added surfactant, the conversion approaches close to its maximum after 60 minutes of processing, with only incremental increase by maintaining the reaction at 375 °C for an additional 30 minutes. For the runs without any surfactant, the longer processing times continue to improve conversion.

FIGURE 2: Conversion dependence on time, with and without the addition of surfactant.

IV MECHANISM STUDY

The structure of coal has been investigated by many researchers and it is generally agreed to consider coal as a highly crosslinked amorphous polymer, which consists of a large number of stable aggregates connected by relatively weak crosslinks. Figure 3 shows one possible structure. At high temperatures in the presence of a hydrogen donor solvent, the fragments will break up into radicals that are capped by the solvent to form stable species before reaction. These species consist of aggregates, or groups of aggregates with molecular weights ranging from 300 to 3000. In the absence of a hydrogen donor solvent, the radicals will react to form either char or coke. These coal derived fragments are primarily preasphaltene and asphaltene particles. They consist of high molecular weight polyaromatic or polycyclic molecules with links to heteroatoms of N, O and S.

The coal liquefaction process occurs in three stages: 1) the solubilization and breakage of the crosslinks of the coal in the solvent into smaller fragments, 2) the reaction of hydrogen with the coal fragments by hydrogen transfer to lower molecular weight molecules, and 3) the rehydrogenation of the solvent. All three processes are important to occur to have a functional, self-sustaining continuous industrial process. The three primary considerations for the sustainability and high reactivity of the system are the hydrogen donor capability of the liquid solvent produced, the physical solubilization of the coal particles within the solvent, and the hydrogen transfer for reaction within the system.

SELECTION OF THE SURFACTANT AND ITS EFFECT

Coal fragments typically disperse poorly in nonpolar and mildly polar solvents, and tend to agglomerate into aggregates of high molecular weight. The motive for adding a surfactant with an "asphaltene-like" structure was to better disperse the particles and prevent them from aggregating. Sodium lignosulfonate surfactant was chosen because it is an oil-compatible colloidal surfactant that is commercially available as an inexpensive by-product from waste paper and pulp processing. It has an approximate structure shown in Figure 4. It has a molecular weight in the 300 to 1000 range. At mild processing temperatures it readily disperses in hydrocarbon solvents as molecular units. It is typically used in industry as a dispersion agent for solids, and as an oil-water emulsion stabilizer. It is relatively stable at the processing temperatures up to 375 °C. The lignosulfonate may act as an aid in dissolution of the coal particles into asphaltene and preasphaltene units, as micelles and colloids, without the formation of radicals which can recondense and react to form char or coke.

The ability to disperse the coal particles in a slurry would be seen as a reduction in viscosity. The effect of viscosity reduction with the addition of the surfactant at temperatures up to 100 °C was shown in previous work by Hsu³. The sodium lignosulfonate was found to act better in viscosity reduction over other anionic, cationic, and nonionic surfactants at these lower processing temperatures. Based upon these results, a systematic analysis of the effect of sodium lignosulfonate on coal liquefaction was carried out.

Effect Of Surfactant Addition On Coal Liquefaction Conversion

As seen from the data presented in this report and the earlier data, the addition of the surfactant increased conversions at all temperatures and pressures. Some representative results from temperature dependence of overall conversion are shown in Figure 5 which shows the MAF conversions with and without the addition of the surfactant. The highest conversion was 92% for the addition of 2 wt % surfactant at 375°C processing temperature, compared to 83.1 % conversion without the surfactant. In addition to the overall conversion, the amount of light boiling fraction distillate (up to 300°C) was determined. Figure 6 shows the increase in light boiling fraction with the addition of the surfactant.

INVESTIGATION OF THE SURFACTANT MECHANISM

Figure 7 shows one possible mechanism for the reaction of the coal with the surfactant. Without the surfactant, the coal would agglomerate and only the outer peripheral groups would react. This would lead to increased gas production and lower conversion. If the preasphaltene coal fragments are separated by the surfactant, larger coal fragments could react with the hydrogen and give higher conversion.

To further evaluate the role of the surfactant, a series of analytical evaluations were made of the processed coal filtercake, filtrate and residue. The primary objectives of the analytical work were to determine the distribution of the surfactant in the product streams, and to quantify changes in the liquefaction product due to the addition of the surfactant.

Sodium Analysis on Filtercake and Extracted Residue

Two residues from 375°C processing runs, one with 2% surfactant, and the other without any surfactant were analyzed by SEM/EDS to determine if any surfactant was retained in the residue after successive extractions with hexane, toluene and THF. The surfactant contains 7.0 % sulfur by weight and 5.9% sodium by weight. Since the coal has 4.5% sulfur initially, the presence of sodium was used to qualify the presence of surfactant. Sodium was found evenly dispersed in the residue of the surfactant added sample by SEM/EDS analysis. Flame atomic absorption was conducted on the two residues to determine the total sodium. From a mass balance based on the increase in sodium content of the samples where the surfactant was added, it was determined that 53% and 47% of the surfactant was retained in the filtercake and extracted residue, respectively.

FTIR Analysis

The filtrates, filtercakes and residues were characterized by Fourier Transform Infrared Spectroscopy (FTIR) to determine structural differences between samples with and without surfactant. The 0% and 2.0% surfactant

added runs at 375°C were analyzed by the diffuse reflectance method, as were the pure surfactant and recycle solvent. The surfactant was seen in the 2.0% sample of the filtrate, filtercake and residue as a distinctive sulfonate group stretch at wavenumber 1145 cm⁻¹. The filtrates, filtercakes and residues were all multifunctional group structures. With the exception of the surfactant presence, there was only a little difference between the two filtrates and residues. The filtercake from the surfactant added sample showed some additional C-H stretching at around 2900 to 3000 cm⁻¹ and some additional aromatic stretches near 1000 cm⁻¹. Since there was a significant difference in the light boiling fractions of the filtrates from the 350 °C runs, the 0% and 2.0% surfactant added filtrate products were analyzed by FTIR. These two samples showed more differences than the 375°C filtrates. The filtrate corresponding to 2.0 % surfactant showed much stronger C-H stretches and aromatic stretches than the 0% surfactant added filtrate product. FTIR analysis was also conducted on successive hexane, toluene and THF extracts from the 0% and 2% surfactant added filtercake products. No significant structural differences were found between the extracts with and without the surfactant.

NMR Analysis

Proton NMR and ¹³C NMR were conducted on the two 350°C filtrates. For these two filtrates, their structures were very similar, consisting of aliphatic, polycyclic and polyaromatic compounds. While no clear structural differences with and without the surfactant were observed, the analysis indicated that the majority of the aromatics were of the structure shown in Figure 8.

GC/MS Analysis

To better quantify the filtercake products, gas chromatography (GC) was conducted on successive hexane, toluene and THF extracts from the 0% and 2.0% surfactant added filtercake products from the 375°C processing temperature runs. Samples of the extracts were injected into the GC (a 25 m length DB5 capillary column) and separated by the column. Selected compounds were routed to a mass spectrometer for species identification. Reference samples of C₁₀ to C₃₀ compounds were also tested to provide a baseline for determining average molecular weights.

The hexane extracts were mainly saturated and unsaturated hydrocarbons. The extract from the 2% surfactant added product showed the presence of a larger number of species and an average molecular weight of 250 compared to a molecular weight of 230 for the extract without surfactant. The toluene extracts were primarily saturated and unsaturated hydrocarbons with some aromatic species. Both samples had an approximate molecular weight of 260. The THF extracts were mostly aromatic species. Though these species had a longer column retention time, they had a lower average molecular weight. The surfactant added THF extract had an average molecular weight of 150 compared to 125 for the 0% extract. There was good qualitative agreement regarding species structure between the GC/MS and FTIR analyses.

XPS Surface Analysis of the Filtercakes

Surface analysis of the hexane-washed filtercakes from the 0% and 2% surfactant added processed coals was conducted using X-ray Photoelectron Spectroscopy (XPS). The technique analyzes only the top 50 Å of the surface. The analysis indicated only a trace level of the sodium on the surface for both the samples. This result is at odds with the quantitative sodium determination by atomic absorption. However, a possible explanation is that a majority of the surfactant migrated to macropores beneath the top surface. As macropore surface area is expected to be significantly greater than the external geometric surface, it is conceivable that the sodium concentration on the external surface dropped below the detection level of the XPS.

Surface Morphology by SEM Analysis

The surface morphology of the coal after processing was examined by SEM. Samples of the filtercake were extracted with hexane to remove absorbed oils. Examples of the surface morphology are shown in Figure 9. The processed coal where surfactant had been added has a more open structure, with greater surface area than the coal processed without surfactant. The addition of the surfactant appears to have opened up the pore structure of the coal, producing larger macropores. This provides evidence that the surfactant action is being facilitated by opening up the structure of the coal during processing. The coal hydrogenation occurs at the surfaces (internal pore and external) of a coal particle. If one considers the reactions on a macropore surface, in the presence of the surfactant, such reactions will be significantly enhanced due to the open structure of the coal fragments. Thus the macropore will be enlarged relative to its size (or opening) when no surfactant is present. This enlarging of the macropore was observed from the SEM morphological analysis of the hexane washed filter cakes.

DISCUSSION

The batch autoclave tests indicate a significant increase in overall coal conversions at all operating temperatures in the range from 300 to 375°C. The increase in light boiling fractions of the filtrate, on the other hand, is significant up to 350°C only. Analytical test results on the structure and functional groups of organic compounds in the filtrate, filtercake and extracted residues show only minor differences in the samples processed with and without surfactant. The same is also true of the structure and functional groups for the successive extracts obtained by washing the filtercakes with hexane, toluene, and THF. The only significant differences obtained for the hexane and THF extracts are in the average molecular weights, which were higher in the 375°C processing run with 2.0 % surfactant than for the case with no surfactant added.

The above results suggest that this surfactant does not significantly alter the three stage progression of coal liquefaction described earlier. The surfactant appears to speed up the first stage, the breakage of the crosslinks in the coal. If this process was rate controlling, the remaining two stages, i.e., the reaction of

the hydrogen with coal fragments and the rehydrogenation of the solvent, would also speed up.

The following discussion will help visualize how the surfactant may help in the breakage of the crosslinks of the coal. Let the coal be represented by R-O-H. Without the surfactant, coal molecules (represented as R-O-H and R'-O-H in Figure 7) are associated by hydrogen bonding between the H-atom of one coal molecule and the O-atom of the other. Due to its anionic polar nature, the surfactant attaches itself to the acid site (H atom) on the coal. Thus it breaks the association with the O-atom between different coal molecules, increasing the favorable hydrogenation reactions. Because the lignosulfonate is a Lewis acid and a partially hydrogenated aromatic compound, it is possible that it could act as a hydrogen donor in the reaction. This is a possible additional avenue of increase in favorable liquefaction processes due to the surfactant.

The addition of the surfactant at 375°C processing temperature increased coal conversion from 83% to higher than 90%. The increase was primarily related to the increase in the THF extracted species from the filtercakes. As the THF extracted species are expected to be preasphaltenes and the GC/MS analysis indicate that these species to be polyaromatic compounds, the increase in the average molecular weight of the THF extract was not surprising. The species that converted to a THF soluble product due to the surfactant are expected to be bigger than those that did not require the surfactant.

The effects of the surfactant on the quality of the filtrate (i.e. the light boiling fractions) are clearly dependent on processing temperature. The surfactant increases the straight chain (lower boiling) hydrocarbons (C-H stretch) as well the molecular weight of the polyaromatics. At 350 °C, the increase in straight chain hydrocarbons appears to dominate, resulting in an increase of lighter fractions. At 375°C, the production of aromatics appears to counter the production of aliphatic hydrocarbons. Hence, a significantly smaller increase in lighter fractions is observed.

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, would lead to greater access of hydrogen to the coal fragments and thus a significant increase in the hydrogenation rate and subsequent solubilization rate.

Figure 3: Representative structure of coal.

Figure 4 Representative structure of sodium lignosulfonate surfactant.

Figure 5: Temperature dependence of coal conversion, with and without surfactant.

Figure 6: Temperature dependence of light boiling fractions, with and without surfactant.

Figure 7: Representative mechanism for the role of the surfactant.

Figure 8: Representative functional groups of coal liquids that were seen by NMR.

9 a)

9 b)

Figure 9: SEM micrographs of hexane extracted filtercakes a) with and b) without the surfactant added during processing.

V. HRI BENCH SCALE TEST

All previous work completed under this research program has evaluated the effect that surfactant addition would have on thermal liquefaction processes. It had been hoped that a continuous bench scale run could be conducted in a completely thermal operation. At present, there is no available outside subcontractor that is capable of conducting a bench-scale continuous operation with recycle of a completely thermal liquefaction within the scope and funding of this research contract. The only alternative was to utilize an industrial catalytic liquefaction bench-scale facility

Hydrocarbon Research, Inc. (HRI) has been under contract to conduct bench-scale test of coal liquefaction by PETC utilizing their Catalytic Two Stage Liquefaction (CTSL) process. In the month of May of this year, they had a scheduled operation (Run 227-78 (CMSL-2)) to evaluate the impact of lower coal ratios (0.9 - 1.1) on Illinois #6 coal. This was a 17 $\frac{2}{3}$ day operation, of which the last 4 $\frac{2}{3}$ days were devoted to evaluating the effect of sodium lignosulfonate surfactant addition on operation and process performance.

Run 227-78 was carried out using Illinois #6 Burning Star mine No. 2 coal and Shell-317 (Ni-Mo/Al₂O₃) catalyst (1/32" extrudates) in both reactors. The startup oil was L-769. The first three and $\frac{1}{3}$ days of operation were at high stage temperatures (first stage 775 °F and second stage 810 °F) and one and $\frac{1}{3}$ days of operation at reduced temperatures (first stage 750 °F and second stage 810 °F). The lignosulfonate surfactant was added to the feed slurry at 2 weight % (relative to the coal). A summary of the operation conditions are given in Table 4. In this table, periods 10, 12, and 13 represent operating conditions and performance before adding the surfactant while periods 16 and 18A/B represent operating conditions and performance after adding the surfactant.

By a comparison of period 16 to period 13, it is seen that the overall coal conversion increased by only 1 percent. Other performance parameters were somewhat lower. This degradation in these performance parameters was the same as would be expected due to the aging of the catalyst. Thus, it appears that no improvement in the process run due to surfactant addition was seen.

There are several reasons for the absence of a process performance improvement due to the surfactant addition. It is possible that the baseline overall conversion for this coal was already close to the maximum before adding the surfactant. The non-reactive carbon imacerals in the coal are not expected to liquefy. Also, the surfactant may decompose appreciably at the high operating temperatures used in the bench-scale run, thus losing most of its effectiveness. Finally, one or more of the decomposition products from the surfactant may interfere with the supported Ni-Mo catalyst and thus degrade its performance.

HRI Batch Microautoclave Tests

HRI also conducted six batch microreactor tests to determine coal conversions at temperatures of 750, 800, and 825 °F with and without surfactant addition. There was a modest increase observed in coal conversion due to the surfactant addition at temperatures of 750 and 800 °F, respectively. HRI's results on the coal conversion and the percent increase in coal conversion (due to the surfactant) as a function of processing temperature are plotted in Figure 10 along with JPL's results (at lower processing temperatures) with 1% surfactant (based on total slurry) addition. The left part of Figure 10 shows the JPL data while the right part shows the HRI data. It is seen that the HRI results fit the trend established by the JPL results on overall coal conversions. The conversions appear to saturate when they approach 92 percent. Further, at temperatures higher than 375 °C, the increase in conversion due to surfactant addition gradually decreases to zero due to saturation of the conversion.

Figure 10: Comparison of JPL and HRI autoclave data.

VI. MASS SPECTROMETRIC STUDY OF SURFACTANT DECOMPOSITION AT HIGH TEMPERATURES

A small quantity of the surfactant (about 50 mg) was placed in a quartz sample holder flask and was connected to a mass spectrometer sampling system. The quartz flask was heated at a rate of approximately 4 °C per minute to a final temperature of 420 °C. The vapor emanating from the flask was analyzed by the mass spectrometer at temperature increments of 25 °C.

The decomposition products from the surfactant, sodium lignin sulfonate, were seen to be given out at temperatures above 150 °C. A majority of these decomposition products appeared to be miscellaneous hydrocarbons. At temperatures up to 350 °C, the most pronounced set of peaks were in the molecular weight range of 60 to 65, though smaller amounts of hydrocarbon species of molecular weight up to 138 were also seen. Two peaks, corresponding to atomic-mass-units (amu) of 91 and 94 appeared at temperatures above 300 °C. Above 350 °C, the majority of the hydrocarbon peaks diminished rapidly with the increase of temperature, but the two peaks corresponding to atomic-mass-units of 91 and 94 increased in intensity. These peaks were present even at 420 °C. It is interesting to note that these peaks would correspond to the mass spectra contributions from the functionality $\text{CH}_2\text{-SO}_3$. This observation suggests that the functionality $\text{CH}_2\text{-SO}_3$ may detach itself from the surfactant at temperatures above 300 °C and the resulting unstable species may attack the catalyst, thus lowering its performance.

VII. SUMMARY

The major accomplishments for this quarter included autoclave test runs and analysis with Illinois #6 coal to determine the effect of processing time on liquefaction. An investigation into the mechanism of surfactant-assisted liquefaction was carried out by a systematic analysis of various processed product fractions, i.e. the filtrate, the filter cake, the various solvent extracts from the filter cake, and the extracted residues both for the surfactant added and the surfactant-free test runs. In particular, FTIR, NMR, GC/MS, XPS and SEM/EDS analyses were made on selected product fractions. This analyses indicated that the improvement in overall conversions due to the surfactant addition is probably due to the break up of cross linkages (associations) in coal molecules. Recently, an additional avenue of observed improvement due to phenoxyl radicals generated from possible lignin decomposition has been brought to our attention. This possibility will be explored in future tests.

A bench scale test run was carried out at HRI to determine the surfactant effect in a continuous flow reactor. The results of this test run showed only a small increase in overall conversion and no improvement in other process performance parameters. The lack of any noticeable improvement appears to result from the decomposition of the surfactant at the relatively high temperatures used in the bench-scale test and interference of the decomposition products with

the supported catalyst. A mass spectrometer analysis of the decomposition products of the surfactant (generated during heating it under a vacuum) was made and indicated the possibility of the functionality $\text{CH}_2\text{-SO}_3$ detaching from the surfactant and its interference with the catalyst.

While the bench-scale test run results were disappointing, it should be pointed out here that the surfactant selection in the present research program was primarily geared toward a thermal liquefaction process. It should be possible to come up with a relatively inexpensive surfactant that will be effective at the HRI test conditions and will function suitably in presence of their catalyst.

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

RUN NO.	AVERAGE TEMP. °C	AVERAGE PRESSURE psig	PROCESSING TIME hr.	SURFACTANT CONC. wt %
27	375	1800	1.0	1.0
28	375	1800	0.5	2.0
29	375	1800	1.5	2.0
30-	375	1820	0.5	0.0
31	375	1800	1.5	0.0

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

RUN NO.	LIQUID FILTRATE g	FILTER CAKE g	OVERALL MASS BALANCE (%)
27	146.82	129.59	97.5
28	149.38	129.77	98.5
29	159.49	118.98	98.9
30	152.71	123.84	98.7
31	161.33	112.54	96.6

Table 3. Overall coal conversions for the various liquefaction runs.

RUN No.	TEMP. °C	PRESSURE PSIG	SURFACTANT CONC. wt %	OVERALL CONVERSION (%)
27	375	1800	1.0	71.9
28	375	1800	2.0	81.4
29	375	1800	2.0	93.3
30	375	1820	0.0	68.8
31	375	1800	0.0	90.1

TABLE 4
RUN 227-78 (CMSL-2) OPERATING SUMMARY
EVALUATION OF LOW SOLVENT-TO-COAL RATIOS

COAL : ILLINOIS NO. 6 HRI-6107
CATALYST : SHELL-317 HRI-5394 (BOTH STAGES)

Period Number	9	10	11	12	13	14	15	16
Date (Start of Period)	4/27/93	04/28/93	04/29/93	04/30/93	05/01/93	05/02/93	05/03/93	05/04/93
Hours of Run (End of Period)	208.	232.	256.	280.	304.	328.	352.	376.
Stage 2 Catalyst Age, Lb Dry Coal/Lb Cat	270.	295.	333.	376.	422.	458.	495.	535.
1st Stage Temperature (°F)	751.	751.	767.	775.	777.	776.	776.	776.
2nd Stage Temperature (°F)	801.	802.	811.	812.	812.	811.	812.	811.
Unit Back Pressure (PSIG)	2502.	2503.	2503.	2503.	2500.	2501.	2501.	2502.
Space Velocity, Lb Coal/Hr/Ft ³ Catalyst (per stage)	42.3	41.0	60.2	66.7	74.2	56.7	57.5	63.5
W% OF DRY COAL								
PFL Recycle	90.1	90.1	90.1	90.1	90.2	90.1	90.0	88.5
PFL to Buffer to Stage 1	4.9	4.5	3.3	2.6	2.6	4.7	3.2	3.0
PFL to Buffer to Stage 2	4.8	4.4	3.4	2.9	2.6	4.5	3.1	3.5
Make-up Oil	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
SOLVENT-TO-COAL (DRY) RATIO	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
MATERIAL BALANCE (%) (GROSS)	95.46	99.25	95.63	97.91	97.28	95.81	99.3	97.69
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED								
C ₁ -C ₃ in Gases		5.22		5.89	4.73			5.21
C ₄ -C ₇ in Gases		3.80		3.46	3.36			3.25
IBP-390°F in Liquids		15.89		15.83	14.75			11.12
390-500°F in Liquids		11.13		8.61	8.09			8.78
500-650°F in Liquids		27.52		21.14	20.52			20.01
650-850°F in Liquids		7.36		10.60	12.34			14.37
850-975°F in Liquids		1.04		2.41	3.36			3.73
Toluene Soluble 975°F ⁺ Oil		1.95		3.73	5.66			8.15
Toluene Insoluble 975°F ⁺ Oil		0.02		0.06	0.12			0.17
Unconverted Coal		6.28		6.28	6.69			5.98
Ash		12.04		12.04	12.04			12.04
Water		10.18		10.16	10.14			8.66
CO		0.10		0.17	0.15			0.16
CO ₂		0.04		1.72	0.12			0.15
NH ₃		1.40		1.34	1.31			1.23
H ₂ S		3.40		3.29	3.29			3.21
Total (100 + H ₂ Reacted)		107.37		106.74	106.67			106.21
PROCESS PERFORMANCE								
=====								
C4-975°F Distillates, W% of MAF Coal		75.9		70.6	71.0			69.6
975°F ⁺ Conversion, W% MAF		90.6		88.6	85.8			83.7
Coal Conversion, W% MAF		92.9		92.9	92.4			93.2
HDS, W%		80.1		77.3	77.5			75.6
HDN, W%		91.7		87.5	85.8			80.1

TABLE 4
RUN 227-78 (CMSL-2) OPERATING SUMMARY
EVALUATION OF LOW SOLVENT-TO-COAL RATIOS

COAL : ILLINOIS NO. 6 HRI-6107
 CATALYST : SHELL-317 HRI-5394 (BOTH STAGES)

Period Number	17	18A/B
Date (Start of Period)	05/05/93	05/06/93
Hours of Run (End of Period)	400.	416.
Stage 2 Catalyst Age, Lb Dry Coal/Lb Cat	570.	597.
1st Stage Temperature (°F)	763.	752.
2nd Stage Temperature (°F)	801.	796.
Unit Back Pressure (PSIG)	2506.	2500.
Space Velocity, Lb Coal/Hr/Ft ³ Catalyst (per stage)	57.1	63.6
W% OF DRY COAL		
PFL Recycle	90.3	88.6
PFL to Buffer to Stage 1	3.3	2.4
PFL to Buffer to Stage 2	4.7	2.8
Make-up Oil	0.0	0.0
SOLVENT-TO-COAL (DRY) RATIO	0.9	0.9
MATERIAL BALANCE (%) (GROSS)	98.96	92.96
ESTIMATED NORMALIZED YIELDS, W% DRY FRESH FEED		
C ₁ -C ₃ in Gases		4.32
C ₄ -C ₇ in Gases		3.26
IBP-390°F in Liquids		8.32
390-500°F in Liquids		7.34
500-650°F in Liquids		15.76
650-850°F in Liquids		18.16
850-975°F in Liquids		6.02
Toluene Soluble 975°F* Oil		15.58
Toluene Insoluble 975°F* Oil		0.32
Unconverted Coal		7.28
Ash		12.04
Water		2.33
CO		0.20
CO ₂		0.29
NH ₃		1.00
H ₂ S		3.03
Total (100 + H ₂ Reacted)		105.24
PROCESS PERFORMANCE		
=====		
C ₄ -975°F Distillates, W% of MAF Coal		66.9
975°F* Conversion, W% MAF		73.6
Coal Conversion, W% MAF	93.0	91.7
HDS, W%		71.4
HDN, W%		65.6

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