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# Surfactant Studies for Bench-Scale Operation

## Second Quarterly Technical Progress Report: October 1, 1992–December 31, 1992

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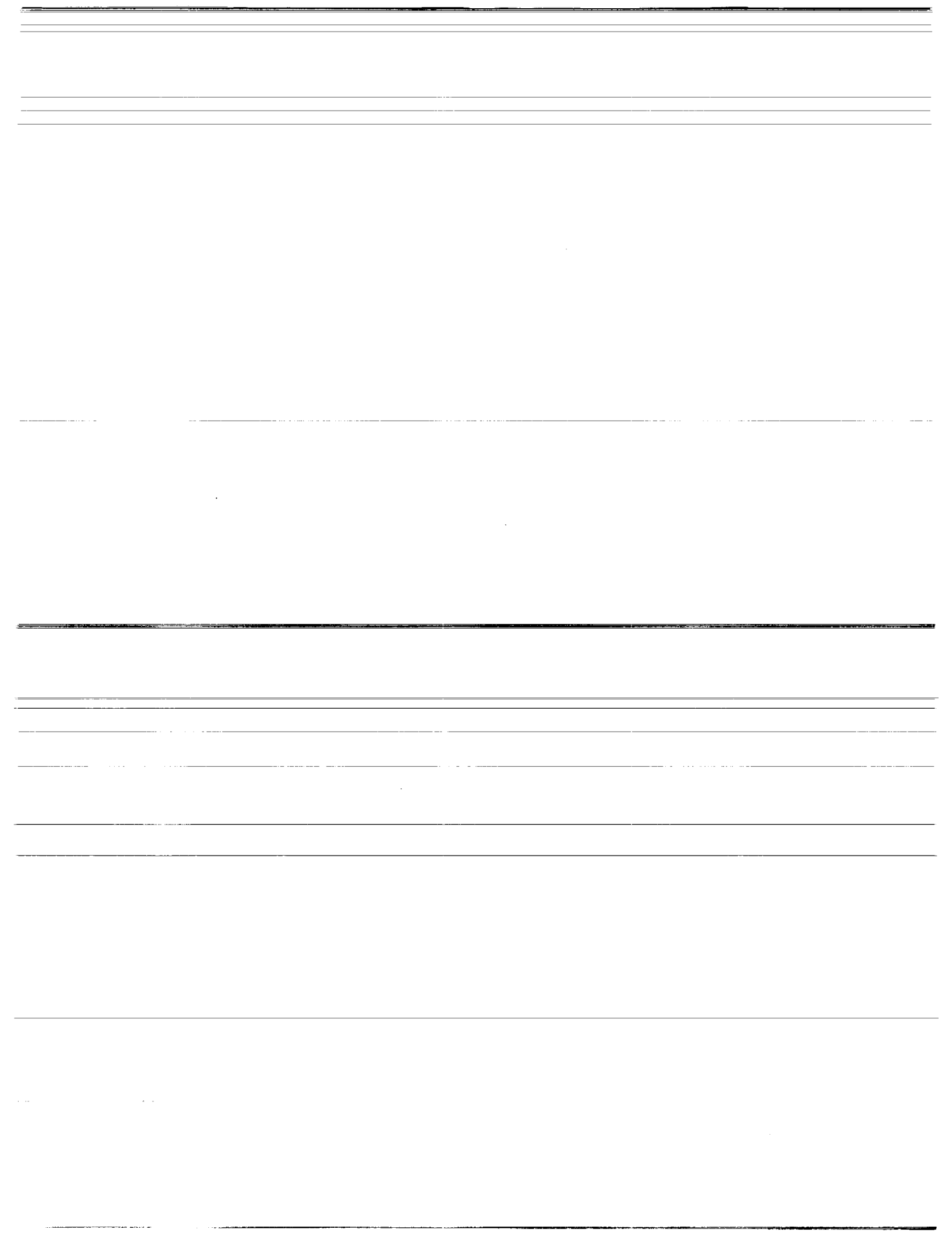
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## ABSTRACT

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 second quarter of work. The major accomplishments were: 1) completion of coal liquefaction autoclave reactor runs with Illinois #6 coal at processing temperatures of 300, 325, and 350 °C, and pressures of 1800 psig; 2) analysis of the filter cake and the filtrate obtained from the treated slurry in each run; and 3) correlation of the coal conversions and the liquid yield quality to the surfactant concentration. An increase in coal conversions and upgrading of the liquid product quality due to surfactant addition was observed for all runs.





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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 has long been known 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<sup>1,2</sup>. The possible effects of lowering the viscosity and the surface tension of the liquid phase in a reactor have mostly been speculated upon 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 study<sup>3</sup> 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 the 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 be evaluated.

The technical progress made during the first three months of this effort was summarized in the *First Quarterly Technical Progress Report*<sup>4</sup>. This report contained a description of liquefaction tests made with Pittsburgh #8 coal at a processing temperature of 280 to 300 °C, both in the presence of a surfactant and in its absence. The test results showed relatively low coal conversions of 25 to 28% due to the low processing temperatures. But these runs also 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 accomplishments during the last three months of this task were: (1) completion of selected reactor runs with Illinois #6 coal with processing temperatures of 300, 325, and 350 °C, at a pressure of 1800 psig and surfactant concentrations varying from 0 to 2.0 wt%; (2) analysis of the filter cake and the filtrate from these runs to obtain coal conversions and the yield of low-boiling cuts in the liquid product; and (3) correlating the surfactant concentration to the improvement in the product quality.

## II. EXPERIMENTAL SETUP

The surfactant studies 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 350 °C. The system is 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 a 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.

Two coals are planned to be used in this study. The primary coal to be used 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. An alternate coal, Pittsburgh #8, was used in preliminary experiments. This coal was obtained from Consol, Inc. as -28 mesh, and was ground and sieved to obtain samples of -100 mesh particles for testing.

The solvent used is SRC-2 recycle solvent obtained from Hydrocarbon Research Inc. (HRI). The surfactant is sodium lignosulfonate obtained from Pfaltzer 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 g of coal are 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 are mixed with it. The reactor is sealed by a split ring closure with a teflon gasket. The reactor is flushed three times with 300 psig dry nitrogen gas to remove the 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 900 and 1000 psig of hydrogen, so that at the processing temperature (300 to 350 °C), the system pressure will be 1800 to 1900 psig. A lower initial pressure is used for the 1000 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.

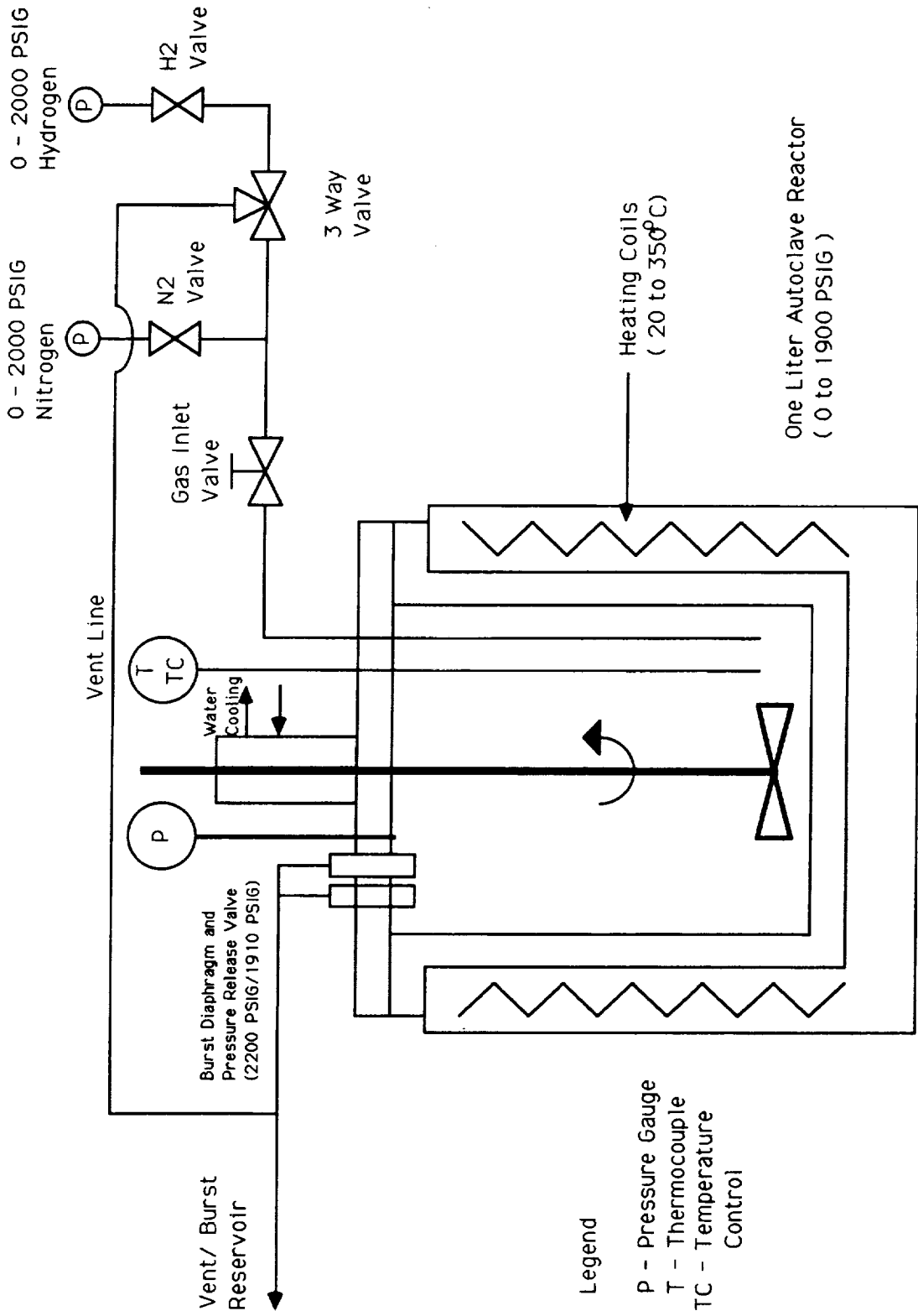


Figure 1. Autoclave reactor system schematic.

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 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. This procedure is the minimum level of analysis for each reactor run. A more detailed analysis will be conducted on specific future runs on the gas, liquid, and filter cake product samples. 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.

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- $\mu\text{m}$  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 distillation using the procedure outlined in ASTM D 246-89<sup>5</sup>. Distillation fractions are taken for the following cuts: room temperature to 200 °C, 200 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 gm 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- $\mu\text{m}$  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 hr. 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 hr. The final filter cake is then extracted with THF. At the completion of the THF extraction, the THF insoluble solids are dried for 16 hr at 60 °C in air to drive off any residual solvent before a final weight is determined.

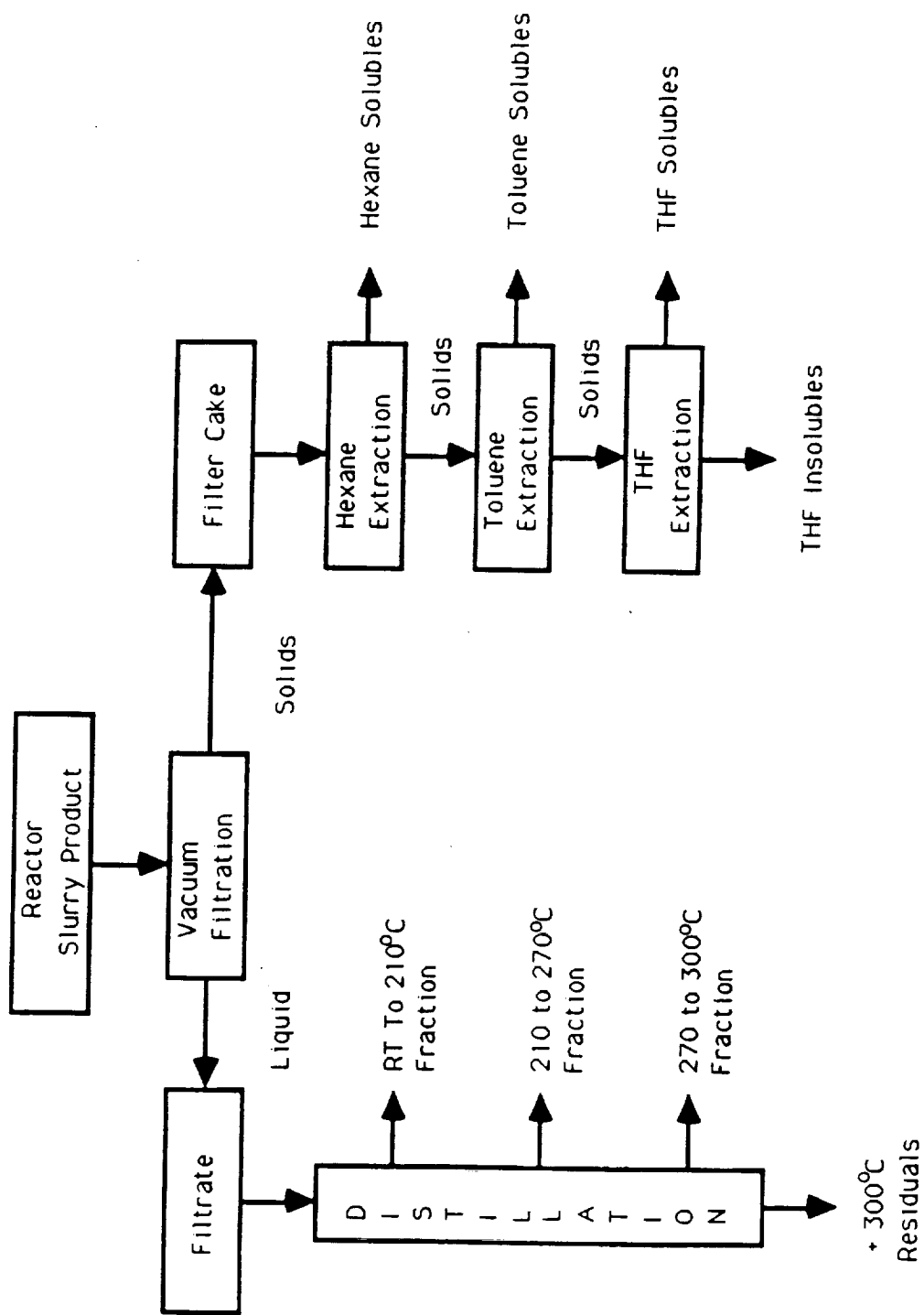


Figure 2. Baseline analysis schematic.

## IV. RESULTS

During storage of the treated slurry (for a period of about 2 to 3 days) obtained from a typical liquefaction run, it was found that the slurry separated into two layers. The upper layer contained very few solids while the lower layer was like a paste and contained most of the solids. A photograph of the stored slurry illustrating such a separation is shown in Figure 3.

The mass balances at various mixing and separation steps were found to all close within 3 percent. The operating conditions for various runs are summarized in Table 1. All runs reported here were made on Illinois #6 coal with sodium lignosulfonate. 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.

The results on the fractionation (by atmospheric distillation) of the solid-free filtrates for various runs are provided in Table 3. 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 Table 3 is the sum of the lower boiling fractions that are obtained below 300 °C.

In order to quantitatively compare the surfactant effect at the processing temperature of 325 °C, note that Run 12 (no surfactant) should be compared with Runs 9, 11, and 13. Similarly, at the processing temperature of 350 °C, Run 15 (no surfactant) should be compared with Runs 14, 16, 17, and 18.

The results on the soluble solids for various filter cake samples are reported in Table 4 on the 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  $W_{\text{init}}$  is the initial weight of the coal on a moisture- and ash-free basis subjected to liquefaction and  $W_{\text{fin}}$  is the final weight of the carbonaceous residue obtained from the treated slurry that is not soluble in hexanes, toluene, and THF. Note that  $W_{\text{fin}}$  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 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.





Figure 3. Separation of the treated slurry into two layers upon storage.

Table 1. Processing conditions for the various liquefaction runs.

RUN NO.	AVERAGE TEMP., °C	AVERAGE PRESSURE, psig	PROCESSING TIME, hr	SURFACTANT CONC., wt %
5	300	1800	1.0	1.0
6	300	1800	1.0	0.5
7	300	1700	1.0	0.0
8	300	1800	1.0	2.0
9	325	1800	1.0	1.0
10	325	1050	1.0	2.0
11	325	1850	1.0	0.5
12	325	1800	1.0	0.0
13	325	1700	1.0	2.0
14	350	1850	1.0	1.0
15	350	1800	1.0	0.0
16	350	1500	1.0	2.0
17	350	1850	1.0	2.0
18	350	1300	1.0	0.5

Table 2. Yields of the liquid filtrate and the filter cake in various runs.

RUN NO.	LIQUID FILTRATE, g	FILTER CAKE, g	OVERALL MASS BALANCE, %
5	128.53	141.64	97.13
6	148.55	128.20	98.33
7	147.84	126.98	98.29
8	139.92	139.42	98.07
9	127.23	150.40	97.98
10	136.67	141.54	98.13
11	134.99	136.72	96.63
12	136.66	137.77	97.79
13	134.81	146.05	98.00
14	153.12	120.44	97.10
15	153.23	118.16	97.40
16	150.26	123.97	98.00
17	147.94	127.03	98.00
18	140.56	127.88	97.90

Table 3. Results on fractionation 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
9	1.0	0.67	5.61	9.14	34.04	15.42
11	0.5	0.92	7.13	9.28	32.09	17.33
12	0.0	0.24	6.16	7.95	34.65	14.35
13	2.0	0.98	6.97	10.49	30.87	18.44
14	1.0	1.29	5.60	9.33	33.57	16.22
15	0.0	0.98	4.00	8.30	36.15	13.28
16	2.0	1.08	5.13	8.47	35.14	14.68
17	2.0	1.28	5.72	10.12	32.67	17.12
18	0.5	1.06	5.45	8.27	34.98	14.78

Table 4. Results on fractionation of the filter cake for various runs.

RUN NO.	SURFACTANT CONC., wt%	HEXANE SOLUBLES, wt%	TOLUENE SOLUBLES, wt%	THF SOLUBLES, wt%
5	1.0	33.7	2.7	6.7
6	0.5	29.3	2.8	5.8
7	0.0	26.9	2.5	6.3
8	2.0	31.4	2.2	5.6
9	1.0	38.2	3.4	11.7
10	2.0	31.8	2.9	9.4
11	0.5	32.4	2.9	9.7
12	0.0	32.1	2.7	8.4
13	2.0	33.9	3.2	9.6
14	1.0	23.9	6.2	33.2
15	0.0	25.0	5.7	28.0
16	2.0	24.6	8.6	28.2
17	2.0	26.3	9.0	29.1
18	0.5	29.8	11.2	27.0

The coal conversion results for various runs as dependent upon the operating conditions (temperature, pressure, and surfactant concentration) are described in Table 5. The uncertainty in the conversion values is estimated to be less than 2 percent. From an examination of the data presented in the 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 4. 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 dependence is that of the increase in the light distillate fractions (compared to the base case of no surfactant) as dependent upon the surfactant concentration at an operating temperature of 350 °C. This dependence is illustrated in Figure 5. No such clear trend was obtained at a temperature of 325 °C even though the test runs where surfactant had been added showed a substantial increase in the light boiling fractions. This is probably due to the overall conversions being rather low.

It is of significant interest to compute how much of the increased coal conversion due to the surfactant addition ends up in the light-boiling fractions in the liquid filtrate. In order to qualitatively assess this effect, one can compare the runs at 350 °C with no surfactant and 2.0 wt% surfactant, i.e., Runs 15 and 17. Both the runs started with 100 g as-received coal (75.6 g on a moisture- and ash-free [MAF] basis), the increase in conversion from 54.4 to 66.8 percent corresponds to about 9.4 g of additional coal liquid due to the surfactant. The distillation results on these runs based upon 50 g of liquid filtrate showed that the total light fraction (boiling below 300 °C) increased from 13.28 g to 17.12 g, i.e., an increase of 3.84 g. As the total liquid filtrate for this run was about 148 g, the total increase in the light-boiling fractions is  $3.84 \times 148/50 = 11.3$  g. This number compares quite well with 9.4 g of additional coal liquid due to the surfactant. Thus, it would appear that a major part of the increased liquid yield due to the surfactant is seen in the light boiling fractions. This analysis is preliminary because the differences in the filter cakes (i.e., the hexane and toluene solubles) have not been taken into account. Nevertheless, this is a highly encouraging result with potential implications toward significantly improving the slate of products in coal liquefaction by surfactant addition.

## 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. Processing temperatures of 300, 325, and 350 °C and surfactant concentrations from 0 to 2.0 wt% have been covered. Product analysis indicated that coal conversions at processing temperatures of 300 and 325 °C were rather low. However, a significant increase in the overall coal conversions and upgrading of the liquid product quality (in terms of an increase in lighter boiling fractions) are observed for all processing temperatures for this coal due to surfactant addition. At processing temperatures of 350 °C, surfactant addition increased coal conversions in excess of 20 percent. The data from the liquefaction runs at 350 °C indicate that a fair part of the surfactant-assisted increase in the conversion corresponds to an increase in the light boiling fractions for the liquefaction products.

During the next reporting quarter, we plan to conduct additional runs using Illinois #6 coal at 350 °C and a limited number of runs at 375 °C. We will also recommend test conditions for a few promising autoclave tests at PETC. In addition, we will initiate the task of determining the mechanism of surfactant-assisted improvement in liquefaction.

Table 5. Overall coal conversions for the various liquefaction runs.

RUN NO.	TEMP., °C	PRESSURE, psig	SURFACTANT CONC., wt%	OVERALL CONVERSION, %
5	300	1800	1.0	26.0
6	300	1800	0.5	25.5
7	300	1700	0.0	21.4
8	300	1800	2.0	24.5
9	325	1800	1.0	38.1
10	325	1050	2.0	31.0
11	325	1850	0.5	30.6
12	325	1800	0.0	25.4
13	325	1700	2.0	32.5
14	350	1850	1.0	64.3
15	350	1800	0.0	54.4
16	350	1500	2.0	63.7
17	350	1850	2.0	66.8
18	350	1300	0.5	66.8

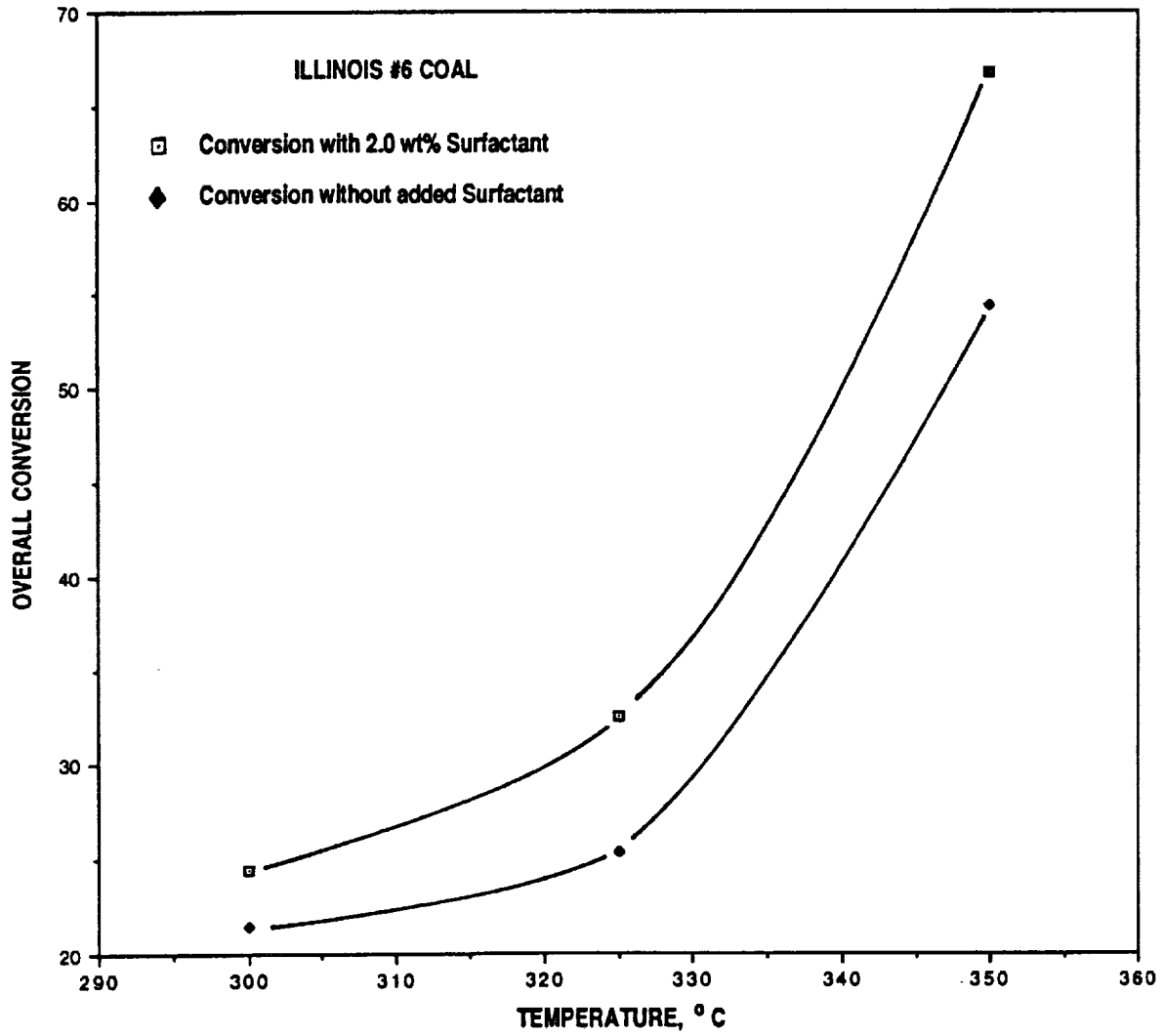


Figure 4. Overall conversion as dependent upon processing temperature without and with 2 wt% surfactant at 1800 psig.



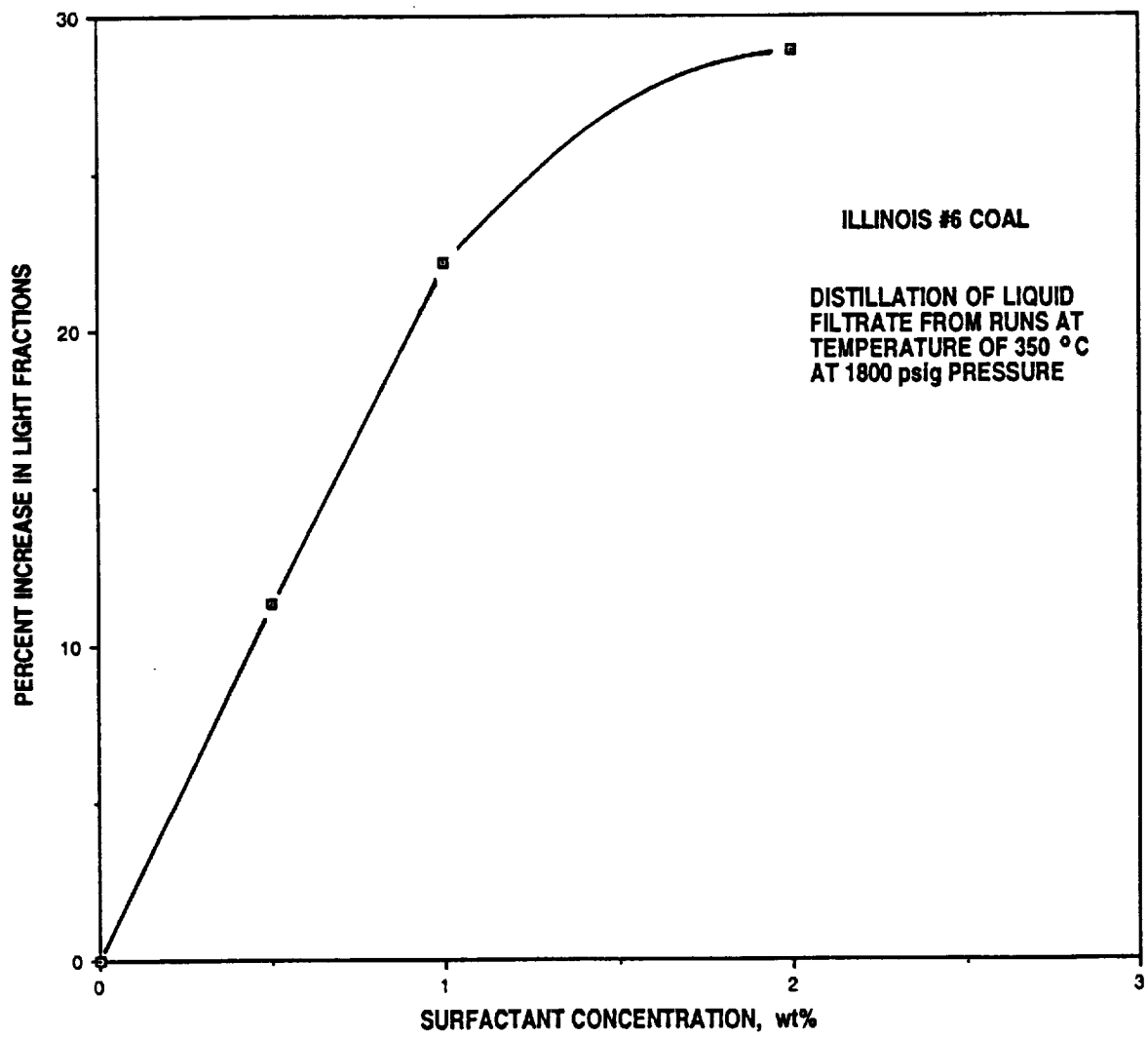


Figure 5. Increase in light boiling fractions as a result of surfactant concentration compared to the baseline case of no surfactant.

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