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Surfactant Studies for Bench-Scale Operation

First Quarterly Technical Progress Report: July 1, 1992 – September 30, 1992

Gregory S. Hickey
Pramod K. Sharma

December 30, 1992

Prepared for
U.S. Department of Energy
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Through an agreement with
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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 publication covers the first quarter of work. The major accomplishments were: (1) the refurbishment of the high-pressure, high-temperature reactor autoclave, (2) the completion of four coal liquefaction runs with Pittsburgh #8 coal, two each with and without sodium lignosulfonate surfactant, and (3) the development of an analysis scheme for the product liquid filtrate and filter cake. Initial results at low reactor temperatures show that the addition of the surfactant produces an improvement in conversion yields and an increase in lighter boiling point fractions for the filtrate.

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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, 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 study[3] 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 that were 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 will 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.

Accomplishments

The accomplishments during the first three months of this task were: (1) refurbishing the high-pressure high-temperature autoclave and accessories for the batch parametric tests, (2) completion of a series of four coal liquefaction runs (with and without surfactant), (3) analysis of the filtrate and the filter cake from above runs to quantify the surfactant effect, and (4) visiting Hydrocarbon Research Inc. (HRI) and initiating discussions on planned bench-scale runs.

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

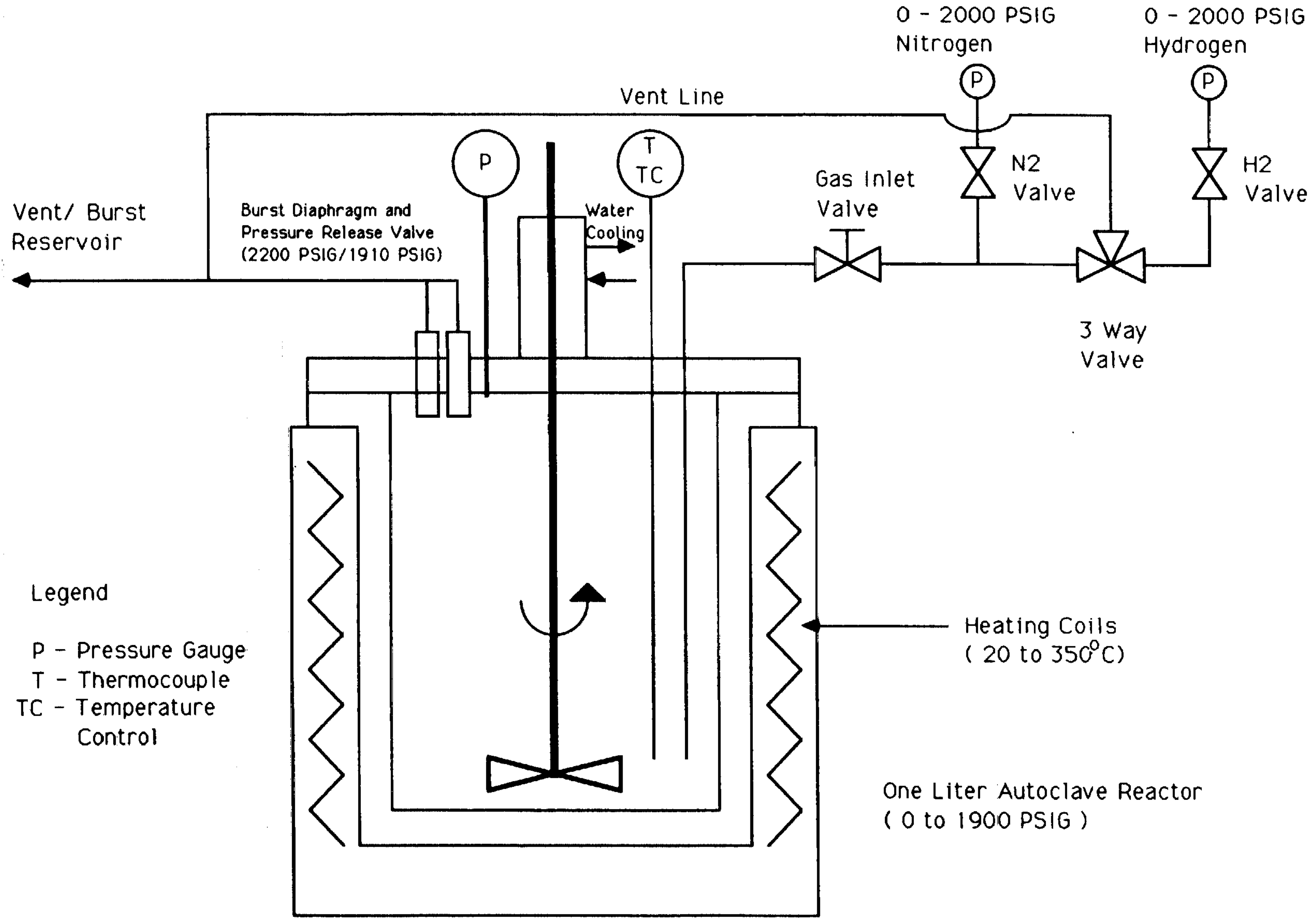

Figure 1. Autoclave Reactor System Schematic

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 a PSCD designation of 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 grams 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 is mixed with it. The reactor is sealed by a split ring closure with a teflon gasket. The reactor is flushed three times with dry nitrogen gas at 300 psig 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 hydrogen at 50-psig, followed by two purges with hydrogen at 300-psig to remove the nitrogen. The reactor is then pressurized to between 900 and 1000 psig with hydrogen, so that at the reaction temperature (300 to 350°C) the system pressure will be 1800 to 1900 psig. A lower initial pressure will be 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.

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, 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. 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 carbon 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 filtrate 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 50 ml of the filtrate are removed for distillation using the procedure outlined in ASTM D-246-89[4]. Distillation fractions are taken for room temperature to 200°C, 200-270°C, 270-300°C, and residuals.

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 20 ml of hexanes 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 the remaining solvent. The new filter cake is weighed and then mixed with 20 ml of toluene for the toluene extraction and the extraction procedure is repeated. The final filter cake treatment is with THF for the THF extraction. The same filtering procedure is used to determine the toluene soluble fraction and the THF soluble fraction. At the completion of the THF extraction, the THF insoluble solids are dried 16 hr at 60°C in air to drive off any residual solvent before a final weight is determined.

IV. RESULTS

All mass balances at various mixing and separation steps were found to close within 2 percent. The operating conditions for various runs are summarized in Table 1 because of their relevance to all data. All runs reported here were made using Pittsburgh #8 coal.

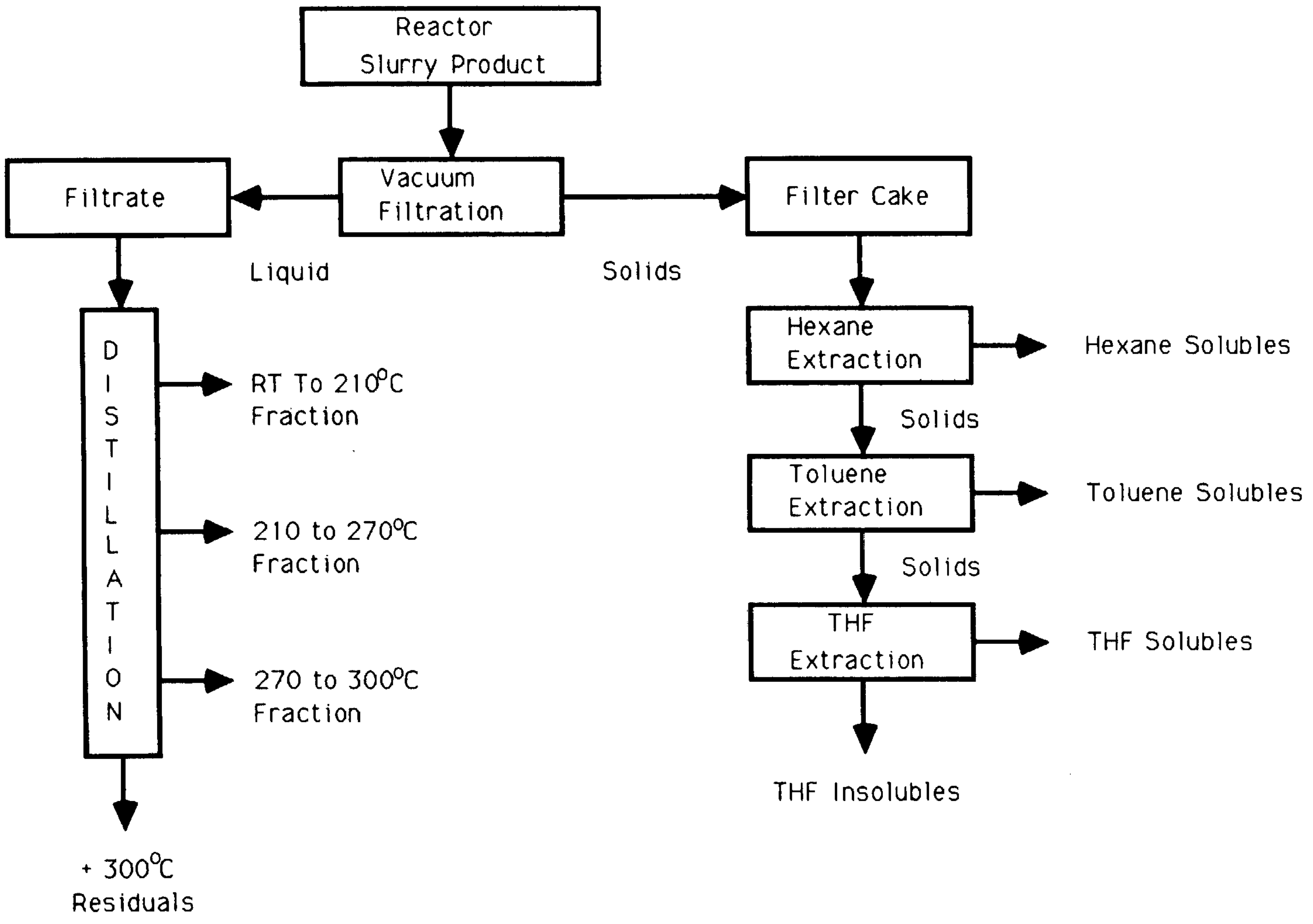

Figure 2. Baseline Analysis Schematic

Table 1. Liquefaction Run Summary

Run No.	Average Temp., °C	Average Pressure, psig	Processing Time, hr	Surfactant Concentration wt %
1	280	1300	1.0	0.0
2	300	1600	1.0	0.0
3	280	1300	1.0	2.0
4	300	1600	1.0	2.0

The measured weights of the clear filtrate for above runs showed an increase of about 10 percent in the filtrate for the runs where surfactant was present. For example, Run 3 compared to Run 1 showed an increase of about 10 percent in the yield of the clear filtrate. A similar trend was seen for Runs 2 and 4.

The results on the atmospheric distillation of the clear filtrates for various runs are provided in Table 2 below. For each distillation, the initial filtrate sample was 50 g. The various cuts reported are weights of distilled fractions obtained at the specified temperatures. The last column in this table is the sum of the lower boiling fractions that are obtained below 300°C.

Table 2. Liquefaction Run Distillation Results

Run No.	Surfactant Concentration, wt %	210°C Cut, g	270°C Cut, g	300°C Cut, g	Total Dist. Up to 300°C, g
1	0.0	0.71	4.80	7.90	13.41
2	0.0	2.33	4.91	8.08	15.32
3	2.0	1.30	5.36	8.84	15.50
4	2.0	2.28	4.97	10.71	17.96

In order to quantitatively compare the surfactant effect, note that Run 3 should be compared with Run 1, and Run 4 should be compared with Run 2. By comparing these runs in the last column, it is seen that the surfactant addition increased the light boiling fractions by about 15 percent. This indicates a substantial upgrading in the product quality due to surfactant addition.

The results on the soluble solids for various filter cake samples are reported on the basis of the original weight of the filter cake. Table 3 gives a summary of the extracted solids.

Table 3. Liquefaction Extraction Results

Run No.	Surfactant Concentration, wt %	Hexane Solubles, wt %	Toluene Solubles, wt %	THF Solubles, wt %
1	0.0	27.6	7.4	15.4
2	0.0	24.7	6.9	14.5
3	2.0	25.2	4.6	13.8
4	2.0	22.4	4.6	16.2

It is seen that the hexane and toluene solubles in the filter cakes decreased slightly for the runs where the surfactant was present. The THF solubles, on the other hand, showed no clear trend. This is not surprising because an upgrade in the quality of the light boiling fractions in the filtrate may well correspond to some decrease in the hexane and toluene solubles. Further, the THF solubles for all four of these runs are quite large. This indicates that a significant amount of preasphaltenes are formed possibly due to relatively low processing temperatures.

Coal Conversions

Coal conversions were obtained from the weight of the remaining residual filter cake which had undergone successive washes in hexane, toluene, and THF. The conversions were based on the fraction of carbonaceous material on a moisture and ash free basis that had been reacted. The liquefaction runs with no surfactant addition had a conversion of about 25 percent, whereas, the runs with 2 wt % surfactant had a conversion of about 28.5 percent. The relatively low conversions in this set of runs are apparently due to rather low processing temperatures.

V. SUMMARY

In summary, the experimental runs and the analysis described here for the Pittsburgh #8 coal constitute a rather narrow range of operating conditions. However, this small subset of operating conditions provides some comparison of the surfactant effect in liquefaction of this coal. A significant increase in the yield of the clear filtrate and an upgrading of the liquid product quality (in terms of an increase in lighter boiling fractions) are seen for this coal due to surfactant addition. These effects are consistent with a moderate increase in coal conversion due to the surfactant addition observed even at these low temperatures.

During the next reporting quarter, we plan to conduct runs using Illinois #6 coal that will constitute a subset of our test matrix, but will be designed to recommend test conditions for a possible bench scale test at the Pittsburgh Energy Technology Center (PETC). Specifically, these runs will be conducted at 300, 325, and 350°C and 1800 psig pressure for a processing time of 1 hr. The surfactant concentration will vary from 0 to 2.0 wt %.

VI. REFERENCES

1. *Coal Liquefaction Products*, Vol. 1, edited by H. D. Schultz, John Wiley, New York (1983).

2. Whitehurst, D. D., Mitchell, T. O., and Farcasiu, M., *Coal Liquefaction*, Academic Press, New York (1980).

3. Hsu, G. C., *Surfactant Studies for Coal Liquefaction*, Final Internal Report to U.S. Department of Energy, Pittsburgh Energy Technology Center, Contract No. DE-AI22-89PC89882, by Jet Propulsion Laboratory, Pasadena, California (December 1990).

4. *Standard Test Method for Distillation of Creosote and Creosote-Coal Tar Solutions*, ASTM D-246-89, American Society for Testing and Materials, Philadelphia, Pennsylvania (1989).