FE-2367-4
Distribution Category UC-90d

EFFECTS OF SOLVENT CHARACTERISTICS ON WYODAK COAL LIQUEFACTION

Quarterly Technical Progress Report
for the Period November 1976-January 1977

H. F. Silver and R. J. Hurtubise

University of Wyoming
Laramie, Wyoming

Date Published - February 15, 1977

Prepared for

Energy Research and Development Administration
Fossil Energy
University Relations
Washington, D. C.

Under Contract No. E(49-18)-2367

EEFECTS OF SOLVENT CHARACTERISTICS

ON WYODAK COAL LIQUEFACTION

II. ABSTRACT

On May 1, 1976, a contract was awarded to the University of Wyoming for the investigation of the effects of solvent characteristics on Wyodak coal liquefaction. The principal invesigators on the program are Dr. Howard F. Silver, Department of Mineral Engineering, and Dr. Robert J. Hurtubise, Department of Chemistry.

During the third quarter of this project, exploratory runs were continued in an attempt to determine reaction conditions which would produce results representative of results obtained in a flow reactor at Wilsonville, Alabama. Since earlier results indicated a possible mass transfer limitation of hydrogen from the gas to the liquid phase, a larger impeller was installed in the batch reactor used in this work. This reactor modification has increased the extent of the coal liquefaction approximately 10 wt % at the same reaction conditions, and thus provides results within the range obtained at Wilsonville. Solvent balance remains a problem.

Work is proceeding satisfactorily toward developing procedures for analyzing nitrogen types in the liquefaction product. Progress has also been made in developing techniques for analyzing tetralin type and phenol type compounds in the solvents to be used.

III. OBJECTIVE AND SCOPE OF WORK

The objective of this proposed research is to investigate the effects of solvent characteristics on the extent of Wyodak coal liquefaction, asphaltene formation and nitrogen removal during the non-catalytic hydrogenation of Wyodak coal.

The research is divided into three major areas as follows:

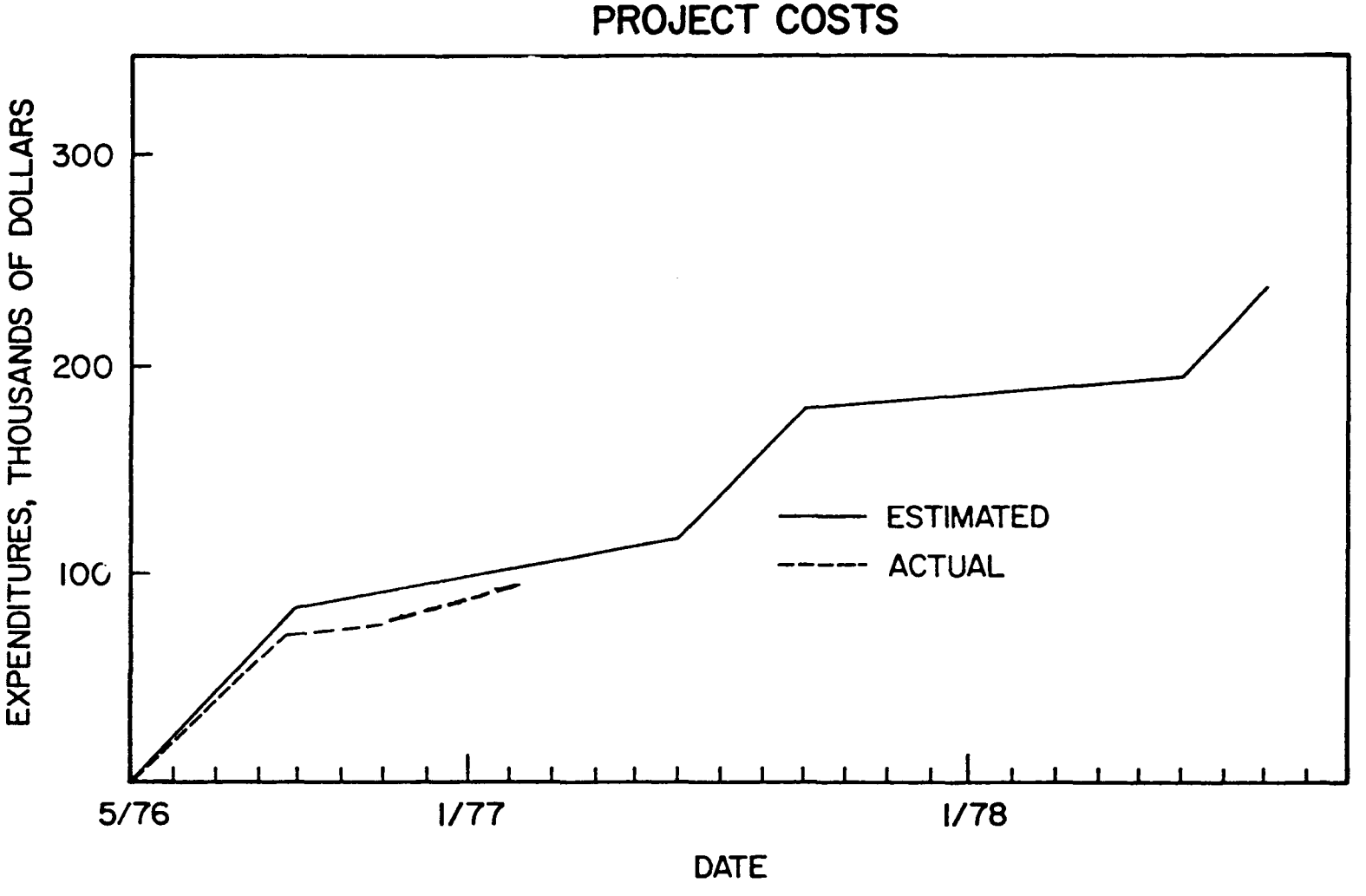
1. Reactor Experiments
   Processing Wyodak coal in a series of solvents to include solvent refined coal (SRC) process recycle oils, coal tar distillates and other solvents, both as received and modified, for example by prehydrogenation or blending, under reaction conditions representative of SRC processes.

2. Chemical Analyses
   a. Standard Chemical Analyses
      Use of accepted analytical procedures to evaluate both chemical and physical properties of both the reactants and products from the reactor.

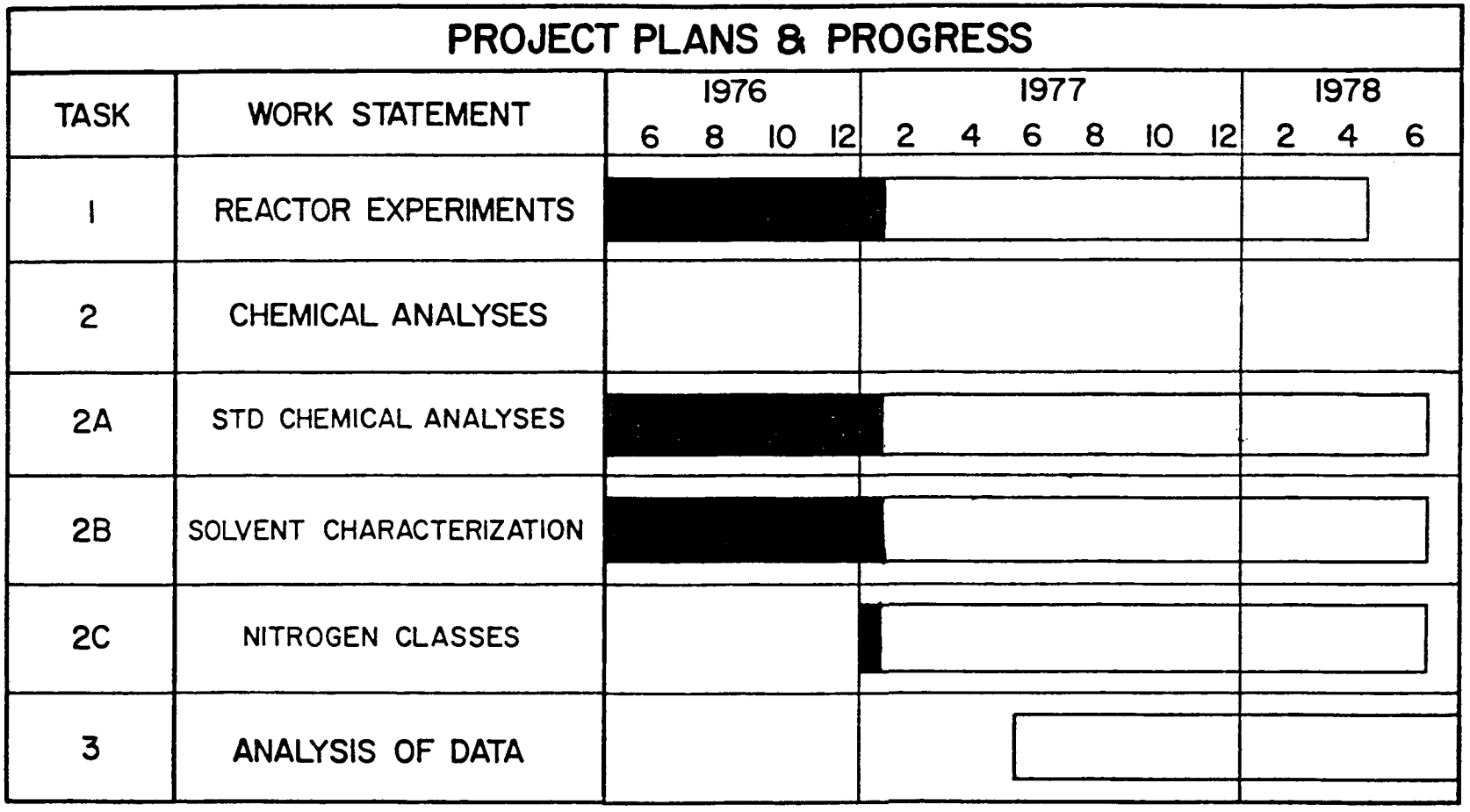
   b. Measurement of changes in the chemical characteristics of the solvents and the relative concentrations of aromatic, hydroaromatic and aliphatic hydrocarbons in the solvents.

c. Nitrogen Classes
Estimation of the concentration of nitrogen classes (quinoline, indole, aryl-amine, alkyl-amine and amide) using non-aqueous potentiometric titration and infrared spectroscopy.

3. Analysis of Data
Evaluation of the precision of the reaction data and correlation of the variables studied.


PROJECT COSTS
EXPENDITURES, THOUSANDS OF DOLLARS
300
200
100
ESTIMATED
ACTUAL
5/76
1/77
1/78
DATE

IV. SUMMARY OF PROGRESS TO DATE



V. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

This section of the progress report contains a discussion of the major tasks comprising thes program.

Reactor Experiments

In the last quarterly report, it was pointed out that hydrogen mass transfer from the gas phase to the liquid phase appeared to be limiting the extent of the coal liquefaction reaction. Results obtained in the batch reactor were low when compared to results obtained at Wilsonville and HRI under similar conditions. In order to minimize this problem, a larger diameter reactor agitator which should double the rate of hydrogen mass transfer was received from Autoclave Engineers Inc. and was installed during the past quarter. Three coal hydrogenation runs were completed using the new agitator.

As shown in Table I, preliminary evaluation of these three runs indicate that the use of the new impeller has increased the unadjusted extent of the coal liquefaction reaction based on benzene solubility by 10%, all other reaction conditions remaining the same. For comparison purposes, results adjusted to account for a mineral matter balance and to account for the benzene insoluble portion of liquid remaining adhered to the unreacted solids, following procedures developed by HRI, are also presented in Table I as "Adjusted Conversion". These results appear to confirm the hypothesis of Dr. C. Y. Wen of the University of West Virginia that mass transfer in a coal liquefaction reactor is a very important variable.

Although the extent of coal liquefaction reaction had been increased to levels comparable to those obtained at Wilsonville and HRI, liquid yields have not been comparable. In an attempt to increase solvent boiling material recovery, the initial hydrogen pressure in the reactor has been increased and the time at reactor temperature has been decreased. As shown in Table I, the extent of the coal liquefaction reaction does not seem to be a strong function of time in our reactor. This suggests that most of the liquefaction reaction which will occur has taken place during the period of time the reactor is being heated from about 600°F to reaction temperature. Further, at reaction temperature, the main reaction taking place seems to be the decomposition of solvent boiling range liquid to light oils and gases. On the basis of these observations, future runs will be made using an initial hydrogen pressure of 2000 psig and 0 minutes. Tests will be made to determine whether or not liquid yields can be increased by lowering reactor temperatures.

Chemical Analyses

Standard Chemical Analyses

Although H_2S was found in the gaseous products from earlier runs made using the original reactor agitator impeller, neither H_2S or NH_3 has been

detected in the gas phase products from recent runs. Work is proceeding in an attempt to improve N_2 and S balances around the reactor.

Nitrogen Classes

A method previously used in this laboratory for analyzing nitrogen types in shale oil appears to be applicable to coal liquids. Three coal-derived solvents have been analyzed--a recycle solvent received from Wilsonville, Alabama and designated F-1; F-1 solvent hydrogenated over Co-Mo catalyst at 700°F and 2000 psig initial pressure for 1 hour and designated F-2; and F-1 solvent hydrogenated over Co-Mo catalyst at 800°F and 3000 psig initial pressure for 1 hour and designated F-3. Results of this work are presented in Table II. Efforts are now underway to determine whether or not these procedures will be applicable to the higher boiling benzene soluble portion of the 800°F+ coal hydrogenation product.

Solvent Characterization

Further work on the silica gel open-column and high-performance liquid chromatographic (HPLC) separation of tetralin and naphthalene in F-1 revealed that a component in F-1 eluted at the same time as tetralin from the Waters' C_{18} column. Fluorescence spectroscopy indicated that the component was acenaphthene. Because of this it was decided to use aluminum oxide (activity II-III) in the initial open-column separation step. This adsorbent proved to give very good separation of tetralin, naphthalene, and acenaphthene when used in combination with the Waters' C_{18} column. A few refinements were made in the HPLC step. One C_{18} column is now used instead of two, which reduces the time of HPLC separation by half. Also, water-methanol (35:36) is now used as an eluent.

In addition to acenaphthene, fluorescence spectroscopy has been used to "identify" naphthalene, indan, and tetralin in F-1. Pure samples of these compounds are needed to compare their fluorescent properties with the fluorescent properties of "unknown" components, but all results so far indicate that the above have been separated and "identified". Future work on this aspect will involve purifying the present reference samples and determining their fluorescent properties.

Work continues on the quantitative method for tetralin and naphthalene in F-1, F-2, and F-3. Two problems with the HPLC equipment slowed progress in this area. The C_{18} column lost efficiency. Dimethylsulfoxide, methanol, tetrahydrofuran, and iso-octane all proved useless in reactivating the column. However, benzene reactivated the column.

Also, nonreproducible chromatographic peak heights were obtained. Solvent was being siphoned from the Waters' UK 6 sample injector vent tube during sample injection. This occurred because a liquid seal formed between the loosely placed teflon vent tube and the vent output tube. The net result was nonreproducible peak heights. The problem was rectified by removing the teflon tube.

Reference samples of phenols are being recrystallized and initial thin-layer chromatographic information on the purified samples is being obtained.

Analysis of Data

Insufficient results are available at this time to indicate the precision of the reactor experiments.

VI. CONCLUSIONS

Substantial progress has been made in determining the reactor operating conditions and in developing the experimental procedures which will be used in this program. However, more work in this area will be required before solvent studies are initiated.

TABLE I

PRELIMINARY WYODAK COAL LIQUEFACTION RESULTS

RUN	HRI 177-115-4	Wilsonville 24-25 Nov.	21	26[1]	22	25[1]	27[1]
TEMP (°F)	850	855	850	850	850	850	850
SPACE TIME (min)	43	43					
TIME AT TEMP (min)			40	40	40	40	0
P_{H2} (psi)							
Initial	2510	1780	2890	2845	3495	3740	3540
Final	2170	1260	2202	2250	2447	3260	3540
SOLVENT/COAL (wt/wt)	2	4	2	2	2	2	2
YIELDS (wt% MF coal)							
H_2-Free Gas	17.8	14.9	27.3	26.3	18.2	23.3	15.7
H_2O (ℓ)	10.4	8.5	9.3	5.3	6.7	9.5	14.4
Oil Yields							
-350°F	5.2	3.3	11.6	36.8	12.1	24.3	11.4
350-500°F	5.6	6.7	4.9	(3.4)	12.5	6.1	(2.8)
500-650°F	7.0	3.5	(10.1)	(20.1)	0.2	(10.1)	(5.8)
650-800°F	9.2	1.5	(5.8)	(2.4)	(10.6)	(6.2)	2.3
800°F+ (SRC)	38.1	43.0	32.8	33.7	40.9	39.5	47.7
Solids	10.4	24.9	33.5	27.0	26.8	17.7	20.0
UNADJUSTED CONVERSION (wt%)		84.0[2]	71.9	79.0	79.1	90.8	87.9
ADJUSTED CONVERSION (wt%)	93.3		77.6	83.7	85.0	91.7	87.9

[1]New Impeller; [2]Cresol Insoluble Conversion

TABLE II

NITROGEN TYPES IN WYODAK COAL-DERIVED SOLVENTS

Solvent	F-1	F-2	F-3
Wt% of Solvent			
Quinoline	0.328	0.159	0.100
Indoles	0.081	0.082	0.079
Aryl Amines	0.036	0.078	0.177
1°, 2° Amines	0.044	0.089	0.018
Unidentified	0.001	0.042	(0.004)
Total Nitrogen	0.49	0.45	0.37

J.S. GOVERNMENT PRINTING OFFICE: 1977-740-094/121