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EFFECTS OF SOLVENT CHARACTERISTICS ON WYODAK COAL LIQUEFACTION

Quarterly Technical Progress Report
for the Period May - July 1976

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EFFECTS OF SOLVENT CHARACTERISTICS
ON WYODAK COAL LIQUEFACTION

II. ABSTRACT

On May, 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 investigators on the program are Dr. Howard F. Silver, Department of Mineral Engineering, and Dr. Robert J. Hurtubise, Department of Chemistry.

During the first quarter of the program, efforts were directed toward developing experimental procedures. A Wyodak coal-derived recycle solvent was received from the Wilsonville SRC plant. Samples of this solvent were hydrogenated over a catalyst. Initial Wyodak coal liquefaction runs indicate the need for more effort in the development of laboratory procedures.

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.

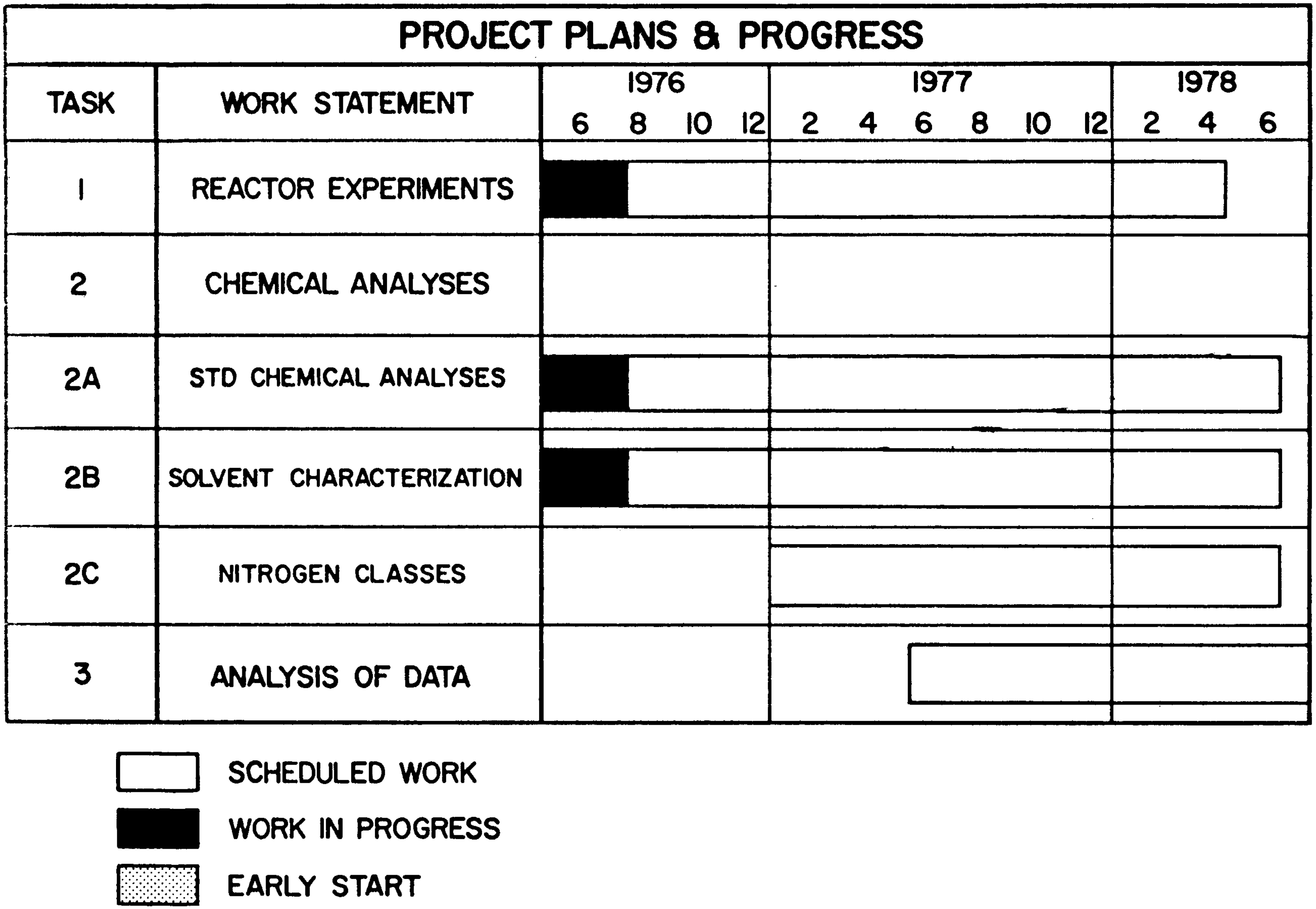
2. Chemical Analyses
   a. *Standard Chemical Analyses*
      Use of accepted analytical procedures to evaluate both chemical and physical properties of both the reactants and products from the reactor.

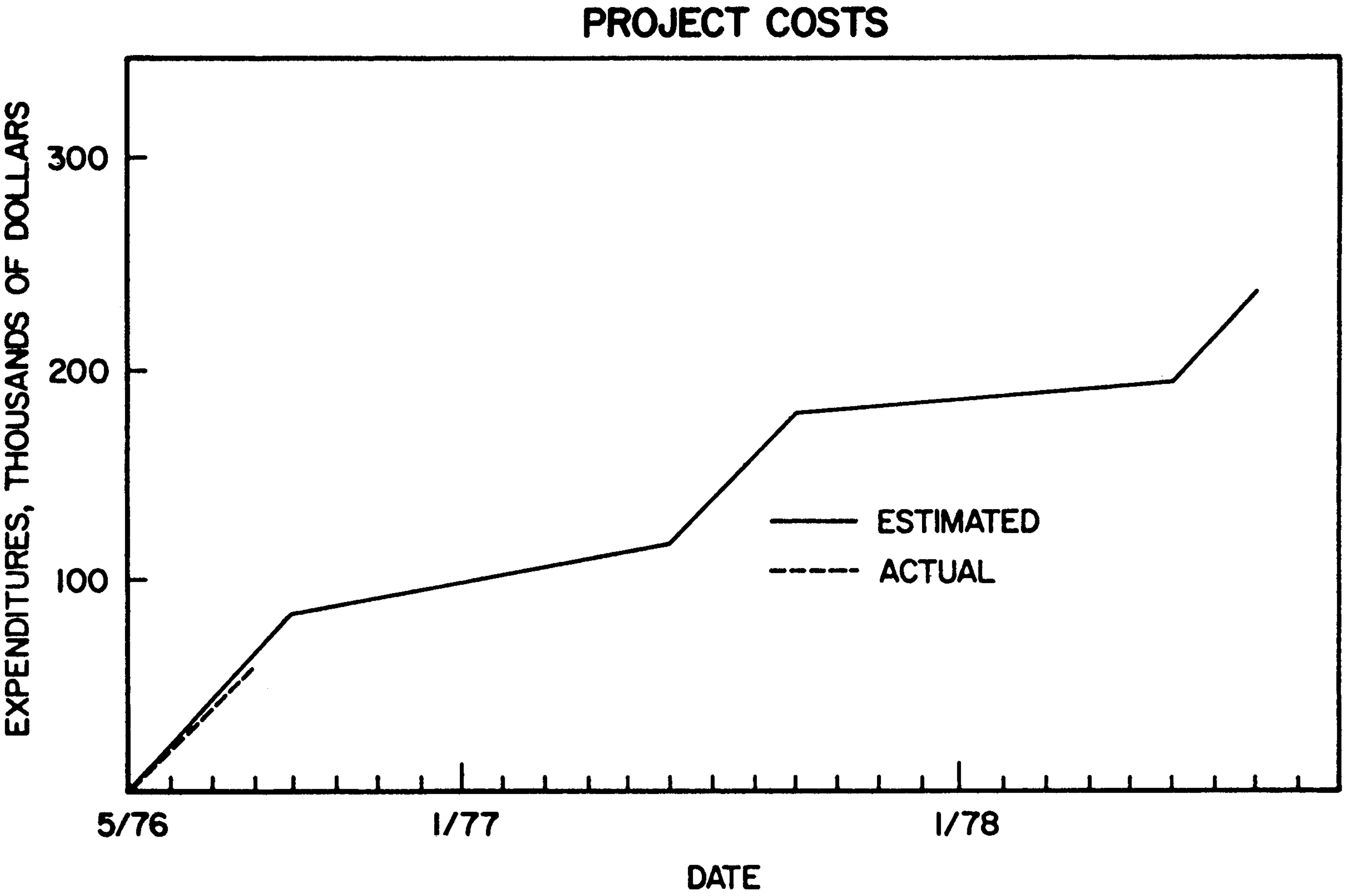
   b. Measurement of changes in the chemical characteristics of the solvents and the relative concentrations of aromatic, hydroaromatic and aliphatic hydrocarbons in the solvents.

   c. Nitrogen Classes
      Estimation of the concentration of nitrogen classes (quinoline, indole, aryl-amine, allkyl-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.

IV SUMMARY OF PROGRESS TO DATE


PROJECT PLANS & PROGRESS


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

V. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

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

Reactor Experiments

Because of the delay in the delivery to July 20, 1976 and installation of a Hewlett-Packard 5840 A gas chromatograph required for the analysis of gaseous products from the reactor, the initial reactor runs were directed toward experiments in which an accurate gas analysis was not essential. The first 12 runs were directed toward the preparation of hydrogenated Wyodak coal-derived recycle oil solvent. A summary of the properties of the Wyodak recycle oil solvent received from the Wilsonville SRC plant, F-1, and the hydrogenated solvents, F-2 and F-3, is presented in Table 1.

Despite the fact that the Hewlett-Packard gas chromatograph has not yet been installed, preliminary Wyodak coal liquefaction experiments have been initiated. The objective of these runs is to determine reactor operating conditions and procedures that will produce results substantially the same as those from a flow reactor. Since Hydrocarbon Research Incorporated (HRI) performed more highly controlled flow experiments with Wyodak coal than Wilsonville, efforts have been directed toward reproducing the HRI results.

Initial results based on the analysis of small samples of reactor product showed wide variations. Considerable effort has been expended in checking the analytical procedures used. It now appears that the problem is due to the inhomogeneity of the liquid and solid phases, leading to difficulties in obtaining representative samples. Efforts are being made to modify operating procedures to reduce this problem.

Chemical Analyses

Standard Chemical Analyses

Currently, gaseous products from the reactor are being analyzed on an Orsat. However, as soon as the Hewlett-Packard gas chromatograph is installed and checked out by a service representative, a major effort will be undertaken to calibrate this instrument. This chromatograph shall provide more rapid and accurate gas composition results than are currently being obtained from the Orsat.

Several different procedures for the elemental analyses of liquid and solid materials have been compared. As a result of this effort, a decision was made to use the procedures recommended by the Colorado School of Mines for sulfur analyses of liquids and solids. The procedure for nitrogen anlayses recommended by the Pittsburg and Midway Coal Mining Co. Solvent-Refined Coal Laboratory has been modified by replacing mercuric oxide with mercury. Duplicate analyses of the elements in the liquids and solids are reproducible within ASTM specifications.

TABLE I

Solvent Properties

Solvent	F-1	F-2	F-3
Description	As received from Wilsonville	F-1 Hydrogenated @ 700°F, 2000 psig and 1 hr over Co-Mo	F-1 Hydrogenated @ 800°F, 3000 psig and 1 hr over Co-Mo
Specific Gravity (60/60)	1.023	1.015	0.922
Distillation, °F (1,2)			
Vol % Distilled			
0/5	290/450	225/375	255/375
10/30	460/495	445/485	425/465
50	545	540	520
70/90	615/740	600/715	575/680
95/100	795/	780/	750/
E.P. (Vol %)	97	97	99
T (°F) @ E.P.	825	825	825
Wt % Distilled			
350°F -	0.9	4.0	4.2
350°-500°F	32.1	32.0	32.8
500°-650°F	42.0	41.0	44.0
650°-800°F	19.0	17.5	15.0
800°F +	6.0	5.5	4.0
Ultimate Analysis			
C	87.06	86.81	85.83
H	7.93	8.54	9.99
N	0.49	0.45	0.34
S	0.13	0.12	0.04
O (by diff.)	4.30	4.08	3.80
Ash	.09	0	0

Notes:

[1] Atmospheric distillation to 350°F, vacuum distillation @ 5 mm to E.P.

[2] Front end of F-3 partially removed by atmospheric distillation.

Nitrogen Classes

Work on the determination of nitrogen classes in the reactor product is not scheduled to begin until 1977. However, the Precision-Scientific Co. Recordomatic Titrometer, to be used for non-aqueous potentiometric titration, has been serviced and calibrated electronically.

Solvent Characterization

The Waters Associates liquid chromatograph has been received and installed by a company service representative. Thin layer chromatography, column chromatography and high performance chromatography using the Waters Associate liquid chromatograph have been used to separate classes of compounds in the solvent received from Wilsonville, F-1. Preliminary results indicate that tetraline, naphthalene, anthracene and fluoranthene can be separated readily.

Infrared spectra were obtained on the recycle solvent received from Wilsonville, F-1, and one of the hydrogenated solvents, F-2. Both spectra appeared the same except for the relative heights of some of the peaks. The following groups were indicated by the infrared spectra: O-H, N-H, C-O, Ar-O. Also, several alkyl and aromatic skeletal vibrations were indicated.

Proton NMR spectra were also obtained from samples of F-1 and F-2. The relative amounts of non-aromatic and aromatic protons were determined in these solvents by a semi-quantitative method. F-1 contains 44.4% aromatic protons and 55.6% non-aromatic protons. F-2 contains 42.7% aromatic protons and 57.3% non-aromatic protons.

Several fluorescence spectra were obtained from 0.05% solutions of F-1 solvent in benzene and chloroform. The spectra indicated several fluorescent components were present.

For the next quarter, work will center on isolation of classes of compounds with emphasis on hydroaromatic compounds and polycyclic aromatic compounds. Also, proton NMR, IR, fluorescence and mass spectrometry will be used to identify specific components.

Analysis of Data

Insufficient results are available at this time to indicate the precision of the reactor experiments. Data correlation is not scheduled to begin until 1977.

VI. CONCLUSIONS

Substantial progress has been made determining 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.