FE-2694-1
Distribution Category UC-90b

FUEL EXTENSION BY DISPERSION OF "CLEAN" COAL IN OIL

FIRST QUARTERLY REPORT

OCTOBER 1977 thru JANUARY 1978

Lester E. Burgess

GULF + WESTERN
ADVANCED DEVELOPMENT AND ENGINEERING CENTER
101 Chester Road
Swarthmore, PA 19081

MASTER

PREPARED FOR
THE DEPARTMENT OF ENERGY
POWER AND COMBUSTION BRANCH
FOSSIL ENERGY (MER)
UNDER CONTRACT EF-77-C-01-2694

TABLE OF CONTENTS

LIST OF FIGURES

I. DESCRIPTION OF CONTRACTUAL PROGRAM

1. Project Objective

The objective of this contract, "Fuel Extension by Dispersion of Clean Coal in Oil", is to demonstrate on a laboratory scale the feasibility for developing a process which, beginning at the mine, cleans the coal, simultaneously molecular grafts onto it a water-repellent, oil-compatible polymer coating, and finally disperses it in oil to produce a temperature-stable liquid fuel.

GULF + WESTERN's laboratory work to date leads to the conclusion that the unique molecular graft process will overcome the problem of settling during transportation and storage, which has characterized previous attempts to suspend pulverized coal in oil with the aid of surfactants. In comparison with conventional methods of coal preparation, the new process should result in a coal product which is freer from ash, sulfur, and water.

The new fuel may contain up to 60% coal extender, but exhibit few or none of the disadvantages associated with the solid fuel. The dispersed coal should be cleaner and drier than coal obtainable by other commercially feasible preparation methods, because the molecular grafting (MG) technique permits finer grinding to release more impurities. At the same time, the accompanying disadvantage of increased water retention is eliminated, because the coating allows substantial water removal by physical means.

Processing could be carried out at the mine, allowing pipeline transmission of the finished product. Because the chemical add-on imparts a permament surfactant effect to the coal particles, settling due to gravity or temperature effects should be minimized. The resulting fuel should be compatible with standard pumping and burner equipment, with few of the clogging or nonuniform feed problems encountered in other coal slurrying tests.

2. Project Description

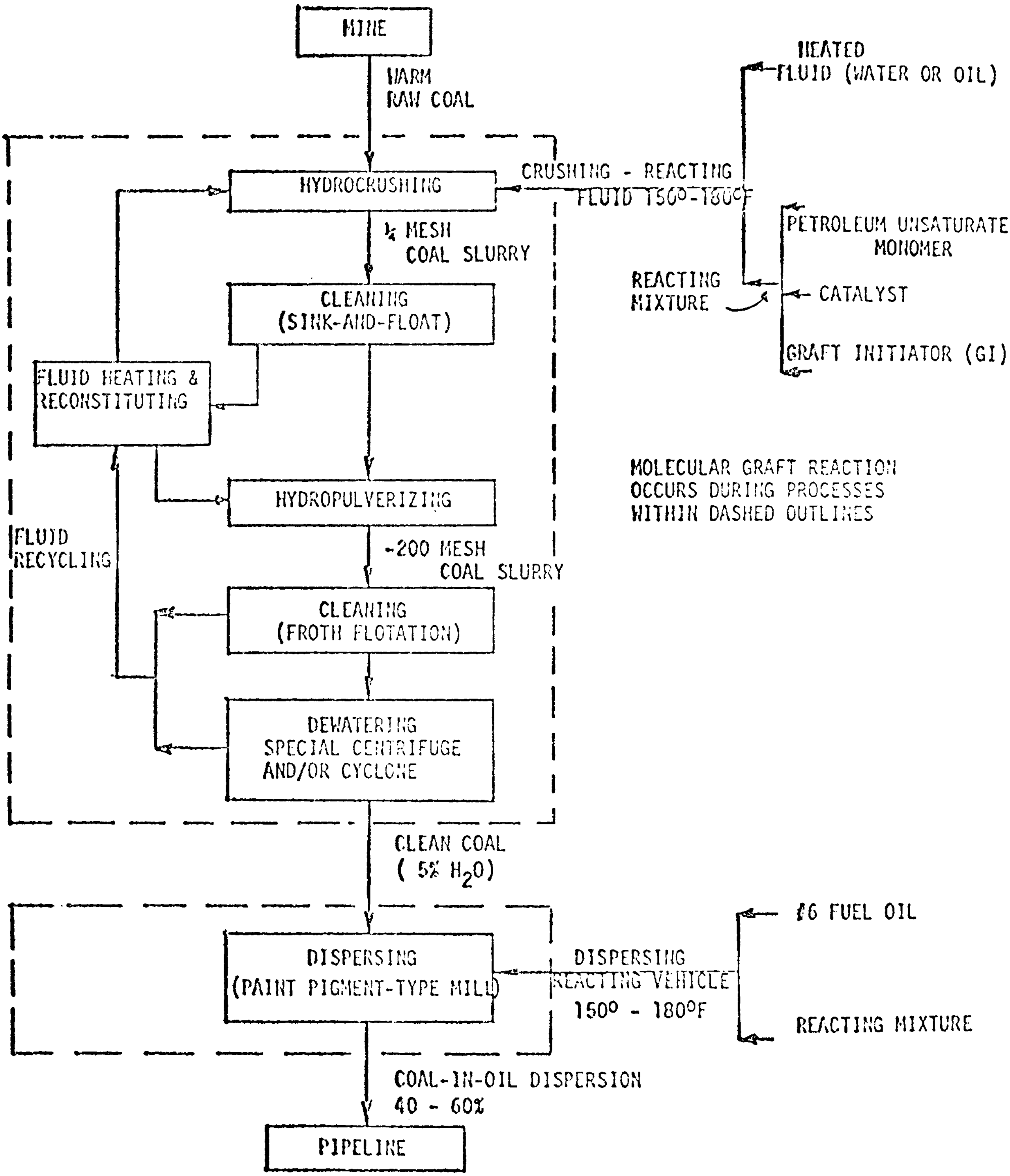
Figure 1 is a simplified flow chart of the G+W system concept which uses the proven molecular grafting (MG) process to clean coal and prepare a stable dispersion of coal in oil. The figure shows, within the dashed boxes, the areas in which the grafting reaction proceeds.

The novel aspect of this process is the use of a low cost monomer which reacts selectively with coal, but not ash, to form a hydrophobic coating. MG reacting is integrated into those steps where coal is crushed to a fine mesh size, physically separated from its impurities, dewatered, and finally dispersed in No. 6 fuel oil.

The grafted coating is developed by adding a monomer to the vehicle carrying the coal particles through all the grinding and cleaning processes, along with a grafting initiator (GI) and a catalyst to promote polymerization. The reacting mixture and crushing fluid are constantly recycled and maintained at 150°-180°F to produce the polymer coating. Increasingly clean coal is separated in several stages from heavier impurities and mechanically dewatered prior to dispersion.

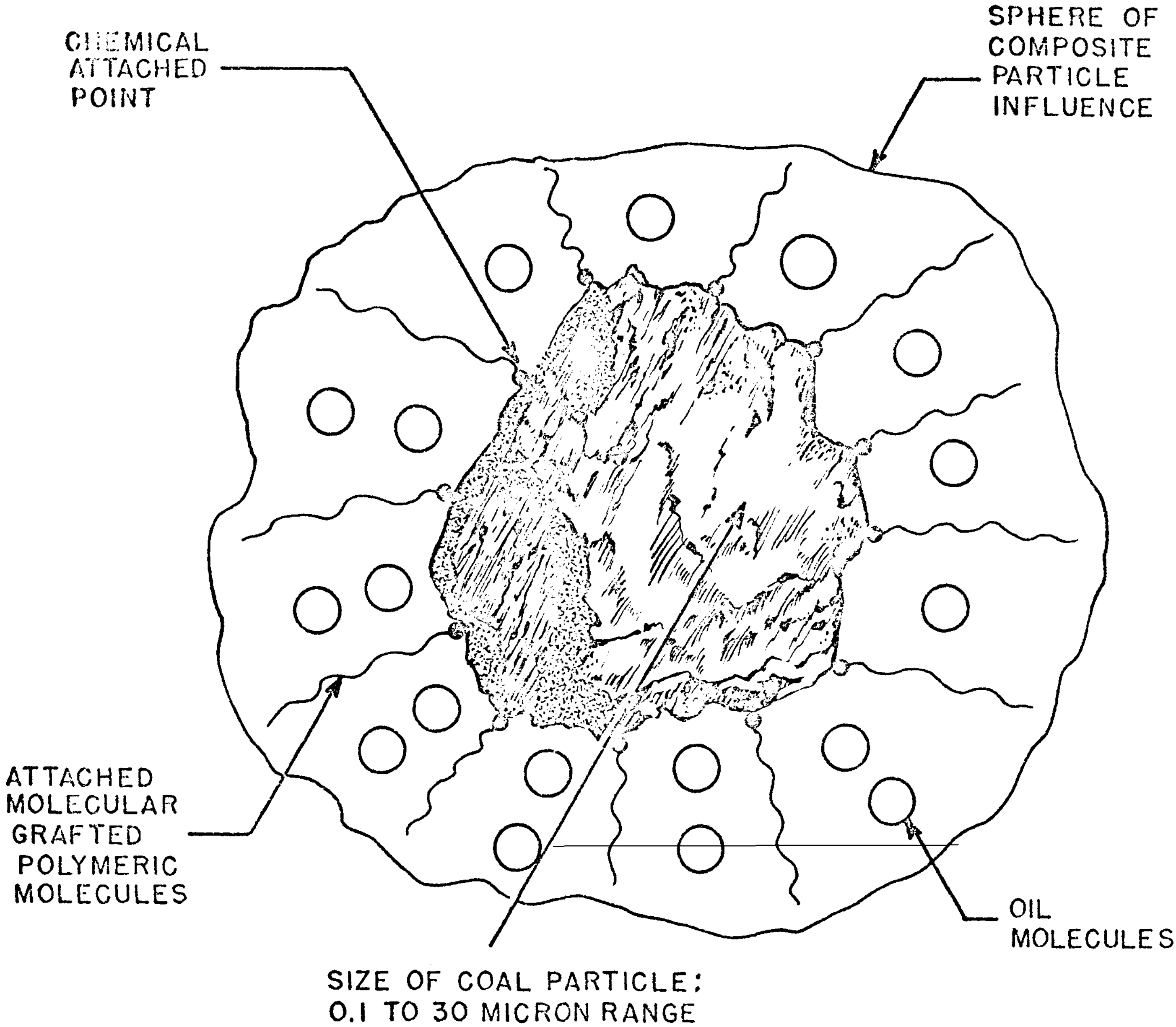
Sink-and-float, froth flotation, and other methods of physical cleaning should be improved, so that finer coal particle size may be achieved without sacrificing thermal efficiency due to retained water. The grafted organic add-on would impart water repellency, thus permitting effective surface dewatering, plus moisture displacement from pores.

The finely crushed, dried (5% water) coal powder is dispersed in heated fuel oil by utilizing the type of equipment designed for paint pigment dispersion. Additional reacting mixture is introduced during this step to graft polymer chains onto the newly-exposed coal surfaces. Figure 2 shows a particle with its attached oleophilic polymer chain "whiskers". The grafted molecules further



SIMPLIFIED FLOW CHART
G+W MOLECULAR GRAFT COAL-IN-OIL PROCESS

FIGURE 1



MOLECULAR GRAFTING TO THE
PULVERIZED CLEAN COAL PARTICLE

FIGURE 2

displace absorbed water and, by their micelle-like character, introduce a viscosity controlling character to the dispersion. It is anticipated that the composite density of the particle will be slightly reduced, more closely matching that of the oil vehicle.

Serving as a permanent surfactant, the grafted add-on should provide coal-oil compatibility, and result in a temperature-stable dispersion which is highly resistant to settling.

Figure 3 illustrates a concept for production of a clean half coal-half oil liquid fuel by use of the G+W molecular graft process.

Although water would be the most conventional candidate for the crushing and cleaning fluid, other vehicles will be considered.

3. Technical Goals

The ultimate objective of the program is to develop a complete system to physically clean, dewater, and disperse finely ground coal in oil to prepare a superior low cost fuel. The key to the process is the development of a molecular graft reacting and dispersing system which will impart to the coal particles the desired characteristics. This treatment produces coal with less moisture than that obtainable from normal coal preparation processes.

This work requires the following phased approach:

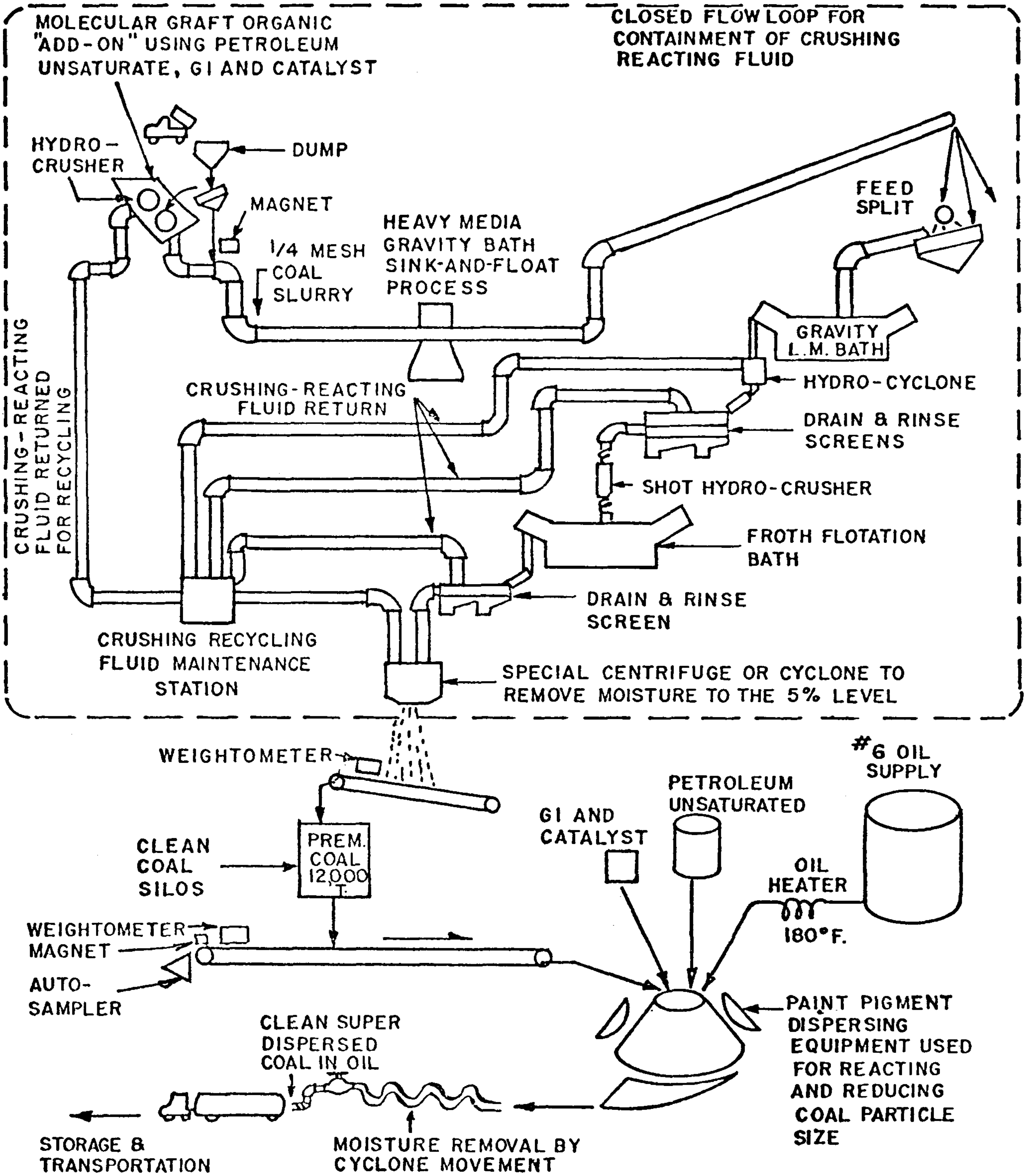
I. Laboratory Feasibility Study

II. Subscale Pilot Plant Development

III. Prototype System Development

IV. Production System Development

This contract involves only Phase I, the Laboratory Feasibility Study. The goal is a laboratory demonstration to prove the feasibility of both improved coal cleaning and coal-in-oil dispersion stability through molecular grafting.



MOLECULAR GRAFT TREATED COAL FOR CLEANING AND DISPERSING PROCESS

FIGURE 3

II. TECHNICAL APPROACH

1. Scope of Work

GULF + WESTERN AD&E Center shall provide the personnel, facilities, equipment, materials, services, and other items necessary for the performance of a 13-month laboratory research program to prove the feasibility of both improved coal cleaning and coal-in-oil dispersion stability through molecular grafting. The program shall include, but not necessarily be limited to, the tasks and subtasks described in the following section.

2. Tasks Description

Task I - Designing Preliminary Laboratory Process to Disperse Clean Coal

The first task shall analyze the current state-of-the-art and then design a complete laboratory process to crush, molecular graft react, clean, dewater, and grind dispersed coal in No. 6 fuel oil. The following process variables shall be investigated:

Hydrocrushing
Sink-and-Float Cleaning
Hydropulverizing
Froth Flotation Cleaning
Dewatering
Dispersing
Size Reduction Techniques

Task 2 - Grafting and Dispersing Experiments

Using information obtained from Task 1, experiments on a laboratory scale shall be carried out on molecular grafting coal particles, cleaning and dispersing them in No. 6 fuel oil.

This task should result in the selection of a stable hydrocrushing and reacting mixture which produces a low-cost hydrophobic particulate film. Choice of petroleum monomer reactant will be based on cost, availability, and consistency of quality.

Considerable emphasis shall be placed on utilizing a low-cost grafting initiator and catalyst. In addition, surfactant cationic-type monomers may be chosen for use at each level, singly or in combination.

Another objective of this task shall be to investigate the possibility of reducing reaction time and/or lowering reaction temperature to 120-125^{o}F. This task also shall provide a basis for study of fluid maintenance, solution makeup, treated particle dewatering characteristics, MG organophilic and hydrophobic characteristics, viscosity control, shelf and pot life, and low and high temperature stability. A minimum of 50 candidate molecular grafting formulas shall be investigated.

Task 2 shall be carried out in the laboratory, initially using 100 gram samples of clean coal for dispersion tests and 500 gram samples of dirty chunk coal for cleaning tests. Experiment results shall determine the most effective vehicles for grafting, crushing, cleaning, and finally dispersing coal in No. 6 fuel oil.

Task 3 - Testing of Dispersion Stability and Viscosity

Dispersion stabilizing ability of candidate grafting and dispersing system shall be determined.

a. Test Program

The dispersion stability and viscosity of various candidate grafting and dispersion systems will be tested.

b. Test Parameters and Methodology

Dispersion stabilizing ability of candidate grafting and dispersing systems shall be determined by subjecting the final mixture to an acceleration of 200 g's for 2 hours and observing settling characteristics.

The following ASTM tests shall be modified for use in this work:

(D869)27 Settling Properties of Traffic Paints

(D1309)29 Settling Properties of Traffic Paints During Storage

(D2698)28 Determination of Pigment Content of Solvent Type Paints by High Speed Centrifuging

(D1010)27 Asphalt Emulsions for Use as Protective Coatings for Metal Testing

Viscosity tests shall be carried out using such equipment as a Brookfield viscometer, an Interchemical rotational viscometer, and an extrusion rheometer to determine the most advantageous rheological parameter for the preferred non-Newtonian oil-coal luquid.

Task 4 - Hydrocrushing, Cleaning, Grafting, and Drying Equipment

Each step of the process discussed in Task 1 shall be analyzed for its effect upon the finished product. The reaction efficiency of molecular grafting at various stages of hydrocrushing shall be examined, and grafted particles shall be checked for their hydrophobic character.

Both reacted and untreated coal shall be compared for sink-and-float and froth separation efficiency to determine optimum particle size, floating agent requirements, and level of cleaning.

Drying efficiency is of paramount importance in achieving proper dispersion quality. Using centrifugal, cyclone, and ultrasonic centrifuge dryers, measurements shall be made with several particle sizes for both surface and absorbed moisture.

Simultaneous reactive grinding tests shall be conducted using different types of equipment to determine the best grinding tool for optimum rates and effects. Two-step grinding, followed by grafting and dispersion, also shall be investigated.

Task 4 shall be carried out in the laboratory with simulated hardware. At least three different approaches shall be studied for each process step to segregate the most eligible candidate processes.

End product dispersion quality shall be the determining factor in this task. Test results will lead to selection of optimum process variables for each element which will be integrated into a complete system.

Task 5 - Integration of Process into a Laboratory Model

This task shall involve design of a laboratory model of the process selected by Task 4. This bench operation shall be capable of producing sufficient coal-in-oil mixture for laboratory testing. The outcome of Task 5 shall be a system demonstration apparatus with a laboratory scale production capability.

Task 6 - Testing Clean Coal-in-Oil Dispersion

Clean coal-in-oil dispersions will be tested for physical and chemical properties required for an efficient fuel.

Coal, cleaned and dried using the most promising procedure, will be tested for the following:

Coal-oil loading level and dispersion stability
Rheological properties
Approximate analysis
Burning characteristics
Combustion residues and gases
Pumping and filtering characteristics

Simplified burner tests will be carried out to observe heating and burning efficiencies.

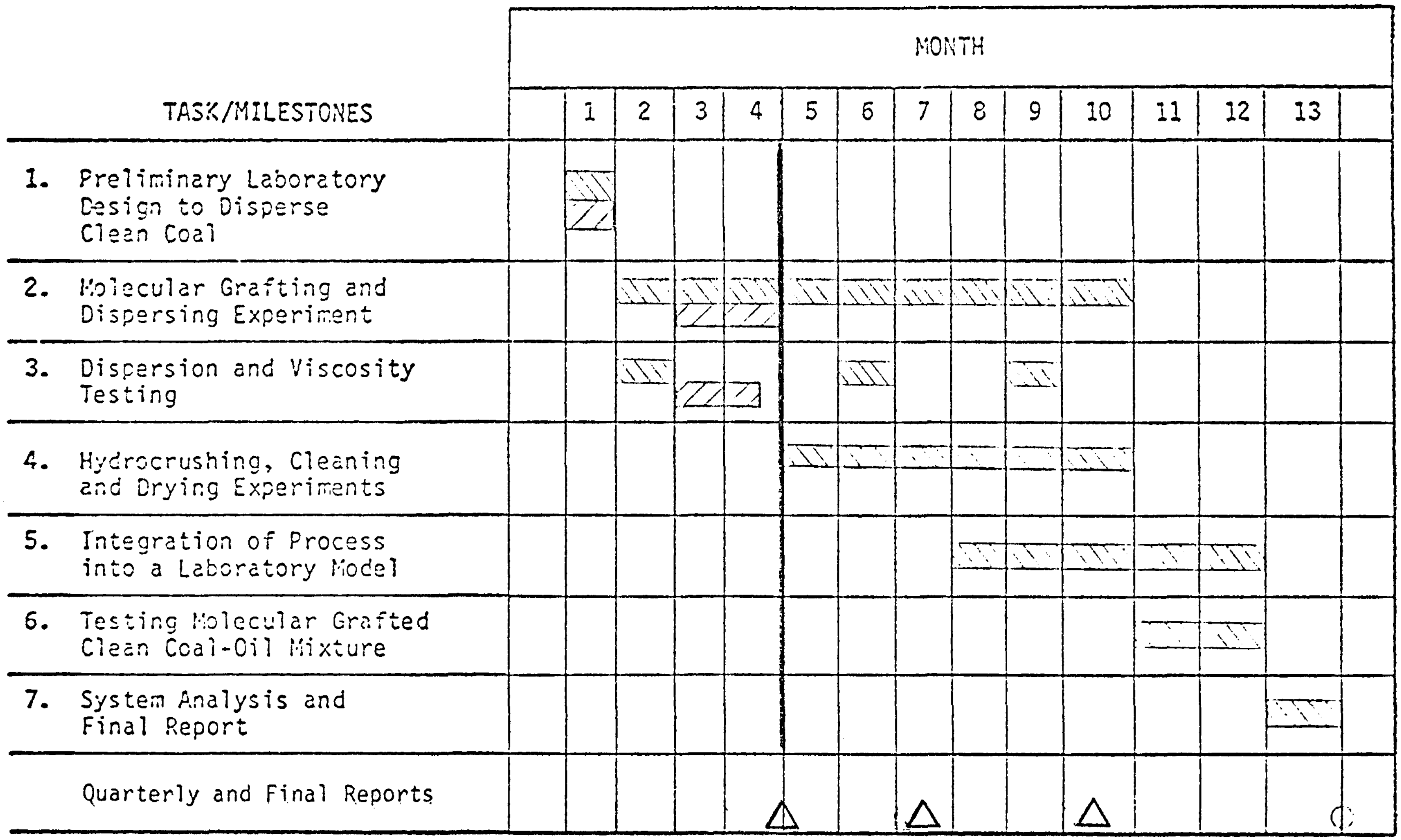
Task 7 - System Analysis

The test data shall be reviewed to provide an analysis of the proposed production.

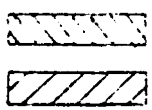
3. Schedule

Figure 4 shows the original schedule, as well as the actual time used to complete work for the first quarter.

SCHEDULE FOR PHASE I



Legend:



Proposed

Actual

TASK SCHEDULE

FIGURE 4

III. WORK DISCUSSION FOR TASKS OF THE FIRST QUARTER

1. Strategy

The work of the first period involves establishing the specific strategy leading to the selection of the reaction solution and processing procedures, preparing the laboratory set-up, and selecting candidate reaction materials. These are Tasks 1, 2, and 3 described in Section II.

The strategy of the initial research is to select monomers, grafting initiators, and catalysts by the use of established procedures. The laboratory procedures used for these tests provide a method to screen the different candidate materials.

The first objective is the selection of an aqueous chemical grafting solution, needed for the beneficiation experiments. Initial grafting experiments are to yield a first generation reaction solution to serve as the beneficiation fluid. This solution is to be delivered to the mineral dressing personnel of the G+W Natural Resources Group for subsequent cleaning activities.

Following initial experiments, the fuel chemical grafting system is to be developed. The coal is to be treated to improve its dispersion stability and assist in dewatering it prior to its dispersion in oil. Then, coal beneficiation research is to be undertaken to refine the process concept while improving the chemical grafting agents.

In order to accomplish the objectives, the following specific tasks were to be undertaken:

a. Provide laboratory set-up through the use of available laboratory equipment modified to suit the concept.

b. Review the petroleum-coal industry to select the most suitable low cost monomers available for chemical grafting.

c. Review the mineral dressing industry to locate current equipment available for complete coal beneficiation.

d. Conduct experiments to identify monomers which provide a stable slurry.

e. Determine grafting reaction system with suitable monomers, grafting initiators, catalysts, and reaction parameters.

f. Develop procedures to test for quick settling.

g. Complete chemical grafting beneficiation experiments.

h. Complete dewatering experiments.

i. Complete chemical grafting (CG) dispersion in oil experiments.

2. Tasks Completed

a. Laboratory Mineral Dressing

Laboratory mineral dressing equipment is being modified to simulate the coal cleaning process concept of Figure 3. This equipment is tabulated in Appendix 1.

b. Review of Available Monomers

A review was completed of the petroleum-coal industry for the availability of monomers in the price range of $.04 to $.10/lb.

Appendix 2 lists monomers investigated and their sources. It appears that low value materials such as still bottoms and "sludge" in oil refineries are used as fuels directly or mixed into No. 6 Industrial Grade Fuel Oil. Monomeric type materials are put into gasoline to improve its octane rating. Coal tar materials may be available, but not in the large quantities needed for the G+W process. Reports and articles on this subject have been requested and received from technical libraries and other sources.

The materials which were requested to carry out experimental work included: (1) C_6-C_8 olefinic distillates from catalytic cracker refining;

(2) coker gasoline (3) #6 fuel oil. Vendor sources and material received to date are listed in Appendix 2.

c. Laboratory Chemical Grafting Experiments

Seventeen chemical grafting experiments have been completed, and are described in this section, with backup data in Appendix 3. These experiments are grouped into five categories, as follows.

(1) Coal Characterization

Vendor data on the coal used is given in Appendix 4. One experiment was performed on coal characterization:

Exp. #1 - Benezene Extraction of Pittsburgh Coal

In terms of coalation aging, the Pittsburgh seam coal appears to be relatively young. It is believed that considerable cross linking of the coal theoretically characteristic of young coal molecules, is responsible for the very low benzene extraction.

(2) Reactions in a Slurry without GI

Initial experiments were carried out to show that a slurry mixture of monomers without grafting initiator offers some dispersion stability. These simplified experiments were used to screen out candidate monomers. In this reaction method, the monomers were slurried with the coal and the mixture treated with a quick heat exposure to react and develop the desired dispersing properties. The best procedure followed was to mix the reacted coal with various settling liquids, placing it in settling tubes and observing the settling line movement with time.

Exp. #2 - Monomer Reacted Coal Slurry in #2 Fuel Oil

Exp. #3 - Monomer Reacted Coal Slurry in Naphtha

Exp. #4 - Monomer Reacted Coal-Slurry in Mineral Oil

Exp. #5 - Monomer Reacted Coal Slurry in #6 Fuel Oil

Exp. #6 - Use of Cracker Gasoline as a Reaction Monomer

Exp. #7 - Cracker Gasoline Used as Both Solvent and Reactant for a Stable Coal-Oil Slurry

Exp. #8 - Cracker Gasoline Reacted Coal Tested in Mineral Oil

It appears that the above slurry reactions show very little improvement in the dispersion stability of coal. These reactions were carried out without the proprietary GI and showed that this important reaction ingredient is required. This reaction technique may also be inferior.

(3) Reflux Reactions without GI

The slurry reactions did not appear to be discriminating as a candidate material selection method in showing the difference in monomer surfactant effects. As a result, reflux reactions with similar reactants were carried out.

Exp. #9 - Reflux Cracker Gasoline Reaction Using Benzene as a Reaction Solvent

Exp. #10 - Cracker Gasoline Reflux Reaction with Increased Reaction Time without GI

(4) Comparison of Illinois #6 Coal with Pittsburgh Coal in Chemical Grafting Reaction

Because the Pittsburgh Seam Coal showed virtually no extractive solubility, and the monomer surfactant reaction results were so poor, experiments were carried out to show the relative reactivity of this coal compared to Illinois #6.

Exp. #11 - Illinois #6 Coal Slurry Reaction

(5) Reflux Reactions Using GI

Previous reactions showed that the monomers (unsaturated molecules) offer some stability improvement through surfactant effects. The following experiments were intended to show that the use of grafting initiation is necessary to improve dispersion stability. Experiments carried out prior to this contract using styrene monomer showed improved dispersion stability. To show the difference in reactivity between Illinois #6 and Pittsburgh seam coal, this reaction method was repeated with both coals.

Exp. #12 - Reflux Styrene Reaction with Illinois #6 Coal

Exp. #13 - Reacted Coal from Treatment of Experiment #12 with Diethyl Aminethyl Methacrzlate

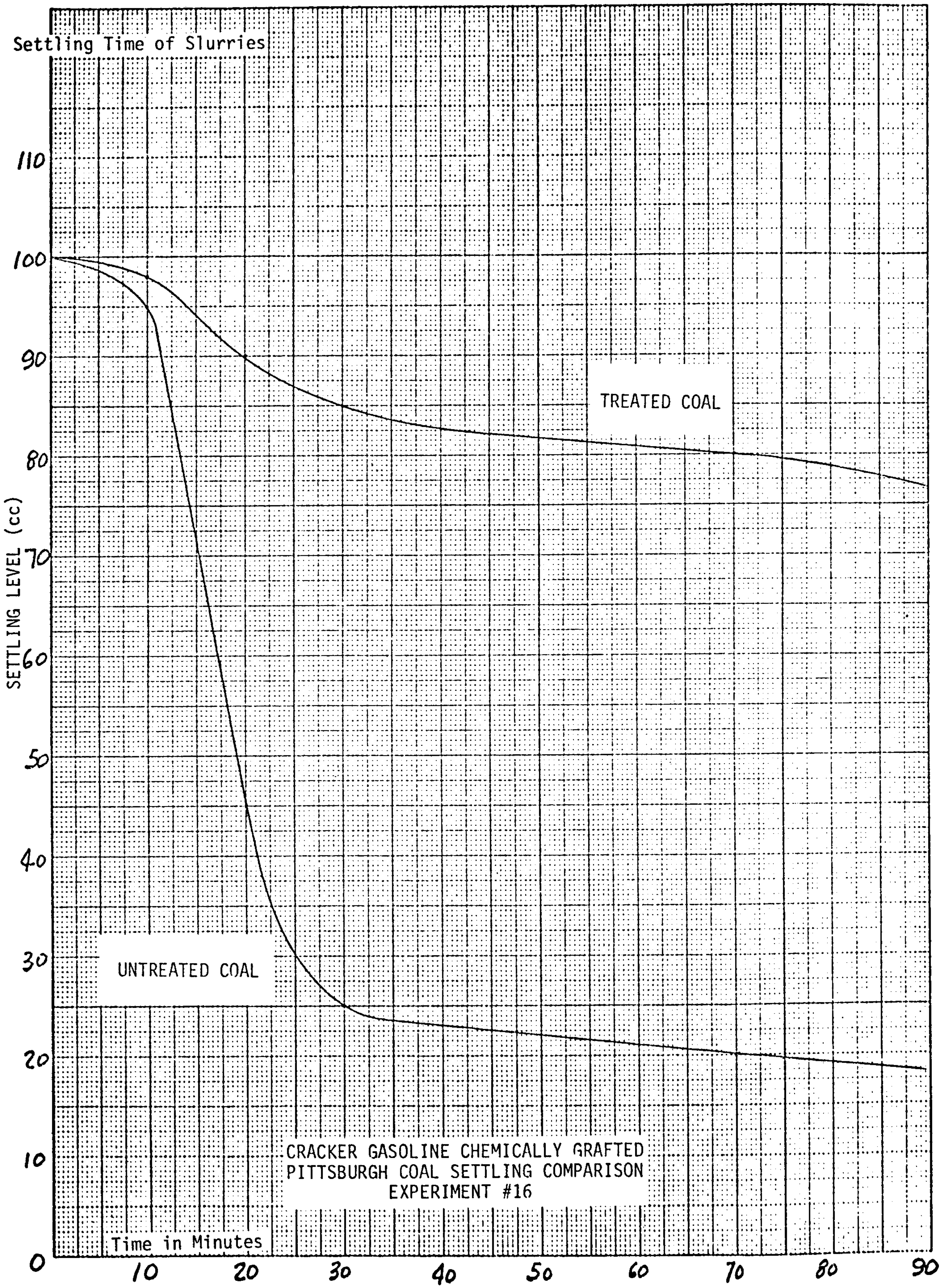
Exp. #14 - Reflux Styrene Reactions Using GI for Both Pittsburgh and Illinois #6 Coal

Exp. #15 - Coal Reflux Reaction with Dicyclopendiene Monomer and GI

These experiments show that Illinois #6 coal is more reactive than Pittsburgh seam coal in a chemical grafting reaction. Also, these monomer materials are shown to be less effective in promoting dispersion stability than anticipated. The settling rates for the styrene reaction and the dicyclopendiene are similar.

Exp. #16 - Reaction on Pittsburgh Coal with Cracker Gasoline and GI

The curve of Figure 5 clearly shows the improvement in oil dispersion stability of Pittsburgh seam coal when reacted with cracker gasoline. The reaction results compared to Exp. #10 also show that GI is required to achieve the reaction effects.



Settling Time of Slurries
110
100
90
80
70
60
50
40
30
20
10
0
SETTLING LEVEL (cc)
TREATED COAL
UNTREATED COAL
CRACKER GASOLINE CHEMICALLY GRAFTED
PITTSBURGH COAL SETTLING COMPARISON
EXPERIMENT #16
Time in Minutes
10
20
30
40
50
60
70
80
90

FIGURE 5

IV. OPEN ITEMS AND RECOMMENDATIONS

The following recommendations for continuing the project are consistent with the limited data achieved in these early experiments:

1. Complete experiments developing a hydrous reaction solution.
2. Initiate beneficiation reaction work.
3. Continue the study to select low cost monomers.
4. Determine the function of the individual reactants.
5. Use a lower cost grafting initiator.
6. Improve the reaction through the use of a small quantity of low cost cationic or anionic surfactant type monomers.
7. Complete the vendor offering review for beneficiation equipment to assist the work of process design.
8. Repeat the encouraging cracker gasoline experiment to establish the validity of the results.
9. Conform to original schedule.

Delays in DOE approval of G+W purchase orders to subcontractor caused some slippage in the schedule, as shown in Figure 4. This time will be made up during the second quarter, and it is believed that such delays can be avoided in the future.

V. SUMMARY OF STATUS, ASSESSMENT AND FORECAST

The work of the first quarter, which also included preparing the management plan and issuing subcontracts, is described in this report. The technical survey work included a determination of laboratory beneficiation equipment available, considerations for its modification, and an investigation of vendors of low cost monomers for use in chemical grafting to improve the dispersion stability of coal in oil.

Initial experimental work was performed in order to select candidate materials. Hydrous chemical grafting beneficiation will start after the selection of an aqueous molecular grafting solution. Early experimental results show that there is substantial improvement in oil-coal dispersion stability from a chemical grafting reaction of Pittsburgh seam coal with cracker gasoline monomers. This experiment must be confirmed by repeating with the same batch of cracker gasoline and another similar material.

The conclusions that can be drawn at this point in the program are as follows:

1. The equipment for the laboratory set-up is available and can be modified to determine the reaction feasibility of the process concept.
2. Monomers for the coal chemical grafting reaction are available in sufficient quantity at the price of $.05-.08 per pound.
3. Slurry reactions of coal without GI show limited improvement in dispersion stability due to surfactant effects.
4. Reflux reactions without GI show limited improvement in dispersion stability of coal due to surfactant effects.
5. The reflux reaction shows superior stabilization effects because of the more severe reaction conditions on the surface of the coal.

6. Reflux reactions with GI, using styrene monomer, show considerable improvement over reactions without GI on dispersion stability.

7. Reflux reactions on Pittsburgh coal using cracker gasoline show substantial improvements in dispersion stability.

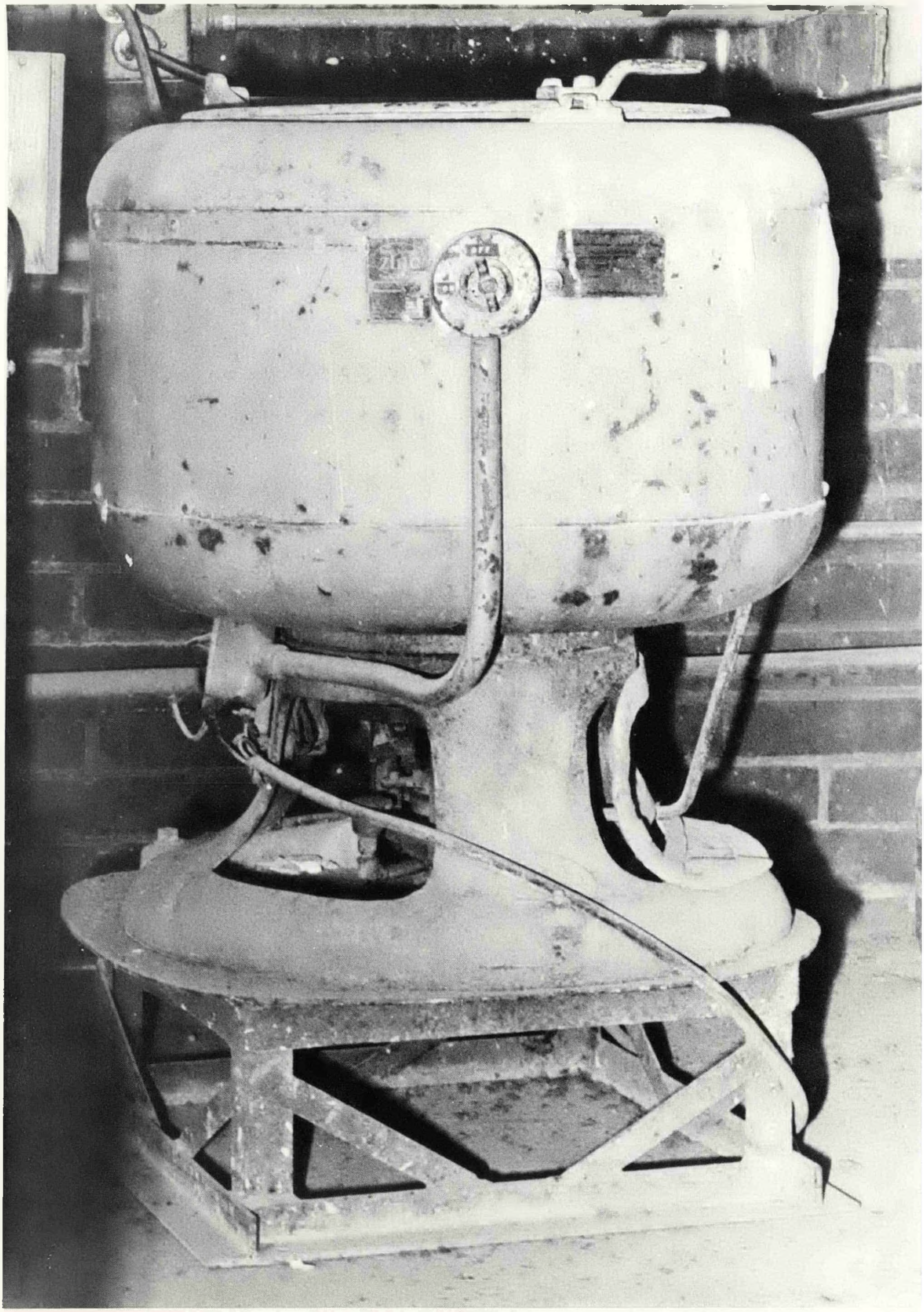
8. The Illinois #6 coal is somewhat more reactive than Pittsburgh seam coal.

From this initial work, there is evidence that chemical grafting may be used to improve the oil dispersion stability of coal. Much more work is required to confirm this observation.

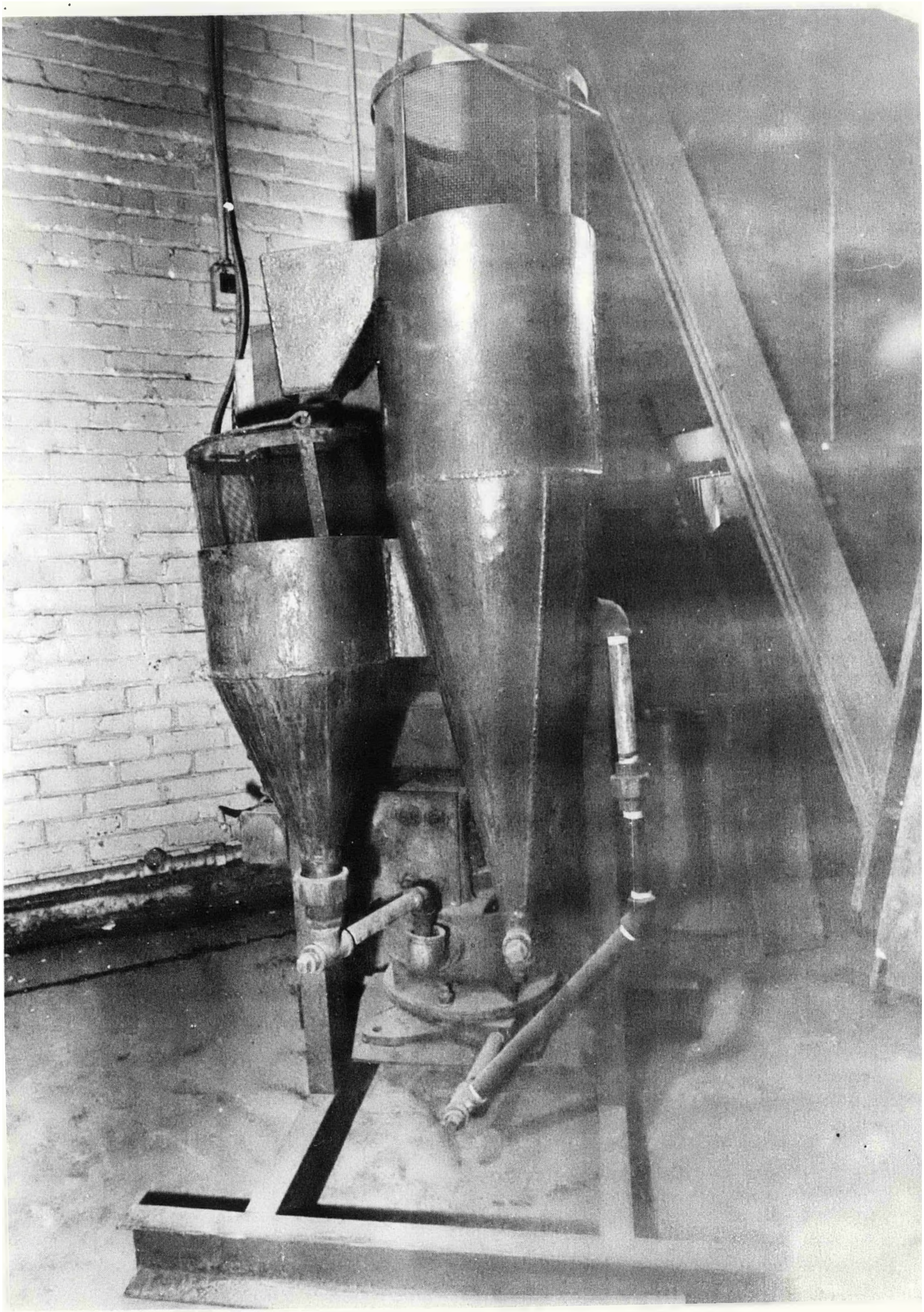
The work during the second quarter will extend the understanding of using chemical grafting to improve the coal-oil dispersion stability. Experiments of coal beneficiation with grafting will be undertaken, and the effects of this processing approach determined. Dewatering effects will be observed.

APPENDIX 1

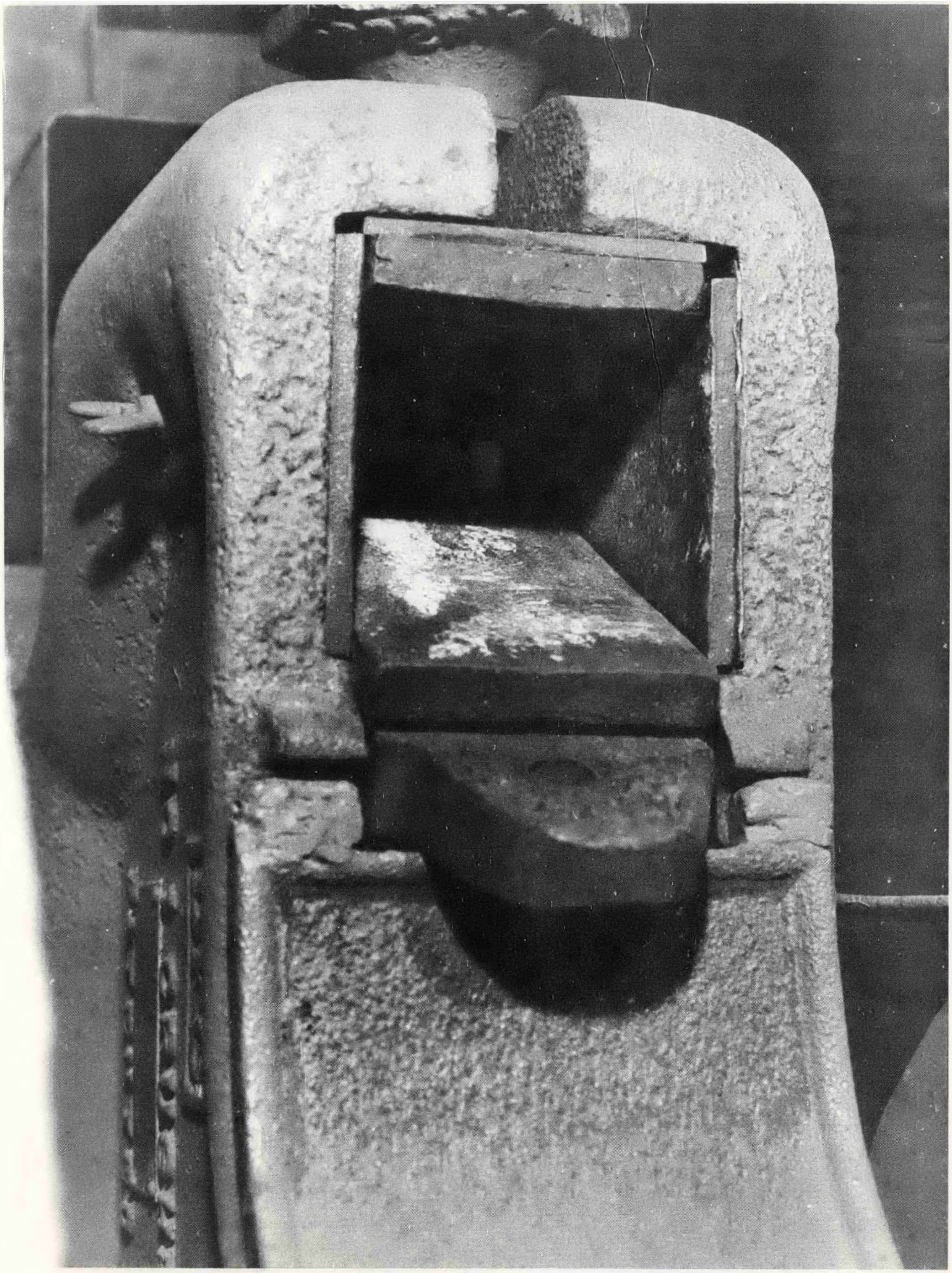
PHOTOGRAPHS OF LABORATORY MINERAL DRESSING EQUIPMENT UNDER MODIFICATION



CENTRIFUGE FOR COAL DRYING



HEAVY MEDIA LABORATORY SEPARATOR



TOP VIEW OF JAW CRUSHER FOR HYDRO-CRUSHING

LABORATORY FROTH FLOTATION APPARATUS

JAW CRUSHER FOR HYDRO-CRUSHING

APPENDIX 2

VENDOR CONTACTS FOR MONOMERS

Vendor Contacts for Monomers

The table on the following page lists monomers investigated and their sources.

The following is a list of vendor contacts and some monomer and price data:

a. Amoco Oil: Jeff Smith, (312) 420-4934
   (1) Olefin stream (100% olefinic), 56¢/gal (7¢/lb)
   (2) Coker gasoline (10% olefinic), 56¢/gal (7¢/lb)

b. Gulf Oil (Phila.): Doug Ayer (Lab Director), (215) 339-7000, Ext. 7238
   (1) Olefin stream (100% olefinic), price from marketing later
   (2) #6 Fuel (no olefins), 4-8¢/lb

c. Sun Oil (Marcus Hook Refinery): Jim Lusch, (215) 972-2421
   (1) Olefin stream (data to be supplied later)
   (2) Coker gasoline from Western refinery (data to be supplied later)
   (3) #6 Fuel, 4-8¢/lb

d. Reilly Tar & Chemical: William Roder, (317) 247-8141
   (1) Heavy (coal tar) oil and anthracene bearing salts
   (2) Polycyclic Aromatic Hydrocarbons (trace of olefins, some phenols)

e. U.S. Steel Chemicals: John Weinert, (412) 433-7865
   Still bottom: (1) heavy hydrocarbons (2) Phthalics

Monomers received to date are as follows:

a. Amoco Oil Co., Polymer Gasoline, C_3-C_4 Olefin (@50% olefinic), 4 gal received 1/25/78.

b. ARCO Chemical, C_5 Olefin: Cyclopentene, etc. (@ 53% olefinic), 1 gal received 1/24/78.

c. Exxon Chemical, Isoprene Diolefin (@ 99% olefinic), 1 gal received 1/15/78

d. Reilly Tar & Chemical Co., (1) Heavy Oil (most aromatic) (2) Anthracene Bearing Salts; 5 gal each received 1/6/78.

Type of Monomer	Source	Availability	Price	Composition	Impurities
Coker Naphtha	AMOCO	TO BE DETERMINED	Est. 56¢/gal	Carbon 85.4% Hydrogen 14.03% Nitrogen 140 ppm C_6 94.9	Sulfur 0.27%
Polymer Gasoline	AMOCO	TO BE DETERMINED	Est. 56¢/gal	C_4 - C_s Olefin @50%	
G_s Stream (Dicyclopentadienes)	ARCO		Est. 10¢/lb	C_s Olefin 53.2% C_s Dienes 8.4% DCPD 5.1%	Parafin over 20%
Isoprene	EXXON	Bulk, Tank case 30,000 gal	34¢/lb	Dialefin 99% Cyclopentedine 0.6%	Sulfur 10ppm
Coal Tar Heavy Oil	REILLY	5,000,000 gal/yr	39¢/gal	Naphthalene Biphemyl, etc. 60-80%	Polynuclear Aromatic Hydrocarbons
Coal Tar Anthracon Oil	REILLY	99MM gal/yr	45¢/gal	Anthracene Phenathrene Carbazole	Polynuclear Aromatic Hydrocarbons
Light Catalytic Cracked Gasoline	GULF OIL	5,000,000 bll/day	Est. 45¢/gal	Olefin 34.7%	
#6 Fuel Oil	GULF OIL	1.6MM bll/day	\$12.85 to \$13.50/bll (4-8¢/lb)		Sulfur 0.47% Water, etc. 0.2%

APPENDIX 3

COAL DATA

Letter from Donald C. Jones of Conoco Coal Development Company
Dated August 15, 1975

Letter from Carl J. Alessandro from The Smith Facing And Supply Co.
Dated November 28, 1977

CONOCO

Conoco Coal Development Company
Research Division
Library, Pennsylvania 15129
(412) 288-8700

August 15, 1975

Mr. Les Bergius
Palmer Research Company of America
2186 Mill Avenue
Brooklyn, New York 11234

Dear Mr. Bergius:

As requested by Mr. Edward Schmetz of Energy Research & Development Administration, 40 lb of -100 mesh Burning Star coal was shipped via UPS on August 15, 1975.

Typical proximate and ultimate analyses are shown in the attached Table.

Respectfully yours,

Donald C. Jones
bs
Attachment:
Table

Typical Analyses of Burning Star (Illinois No. 6) Coal
(Moisture-Free Basis)

Proximate Analysis	
Volatile Matter	41.4
Fixed Carbon	48.4
Ash Oxidized	10.2
Ultimate Analysis	
Hydrogen	4.71
Carbon	70.79
Nitrogen	1.27
Oxygen (diff.)	10.14
Total Sulfur	2.93
Organic Sulfur	2.15
Pyritic Sulfur	0.54
Sulfate Sulfur	0.24

DCJ:bs
Project No. 197.01
8/15/75

The Smith Facing and Supply Co.
CUSTOM SERVICES. BLENDING PACKAGING PULVERIZING
SPECIALTY FOUNDRY AND STEEL MILL PRODUCTS
1857 Carlor Road • Cleveland, Ohio 44113 • 216/661-6040

November 28, 1977

Doctor Cherry
Germantown Laboratories, Inc.
4150 Henry Avenue
Philadelphia, Pennsylvania 19144

Dear Doctor Cherry:

I want to apologize for the delay in sending the information you requested to you. Our -200 Mesh Seacoal or Ground Bituminous Coal has a sieve analysis of 70-80% thru the 200 mesh screen. The -325 mesh analysis is as follows:

-200 Mesh, 85 - 90%
-325 Mesh, 70% Minimum

The previous information that you had received was not correct as to the screen analysis.

The costs of the two grades in bulk at our maximum capacity is as follows:

-200 Mesh Grade -- $95.00 Per Ton
-325 Mesh Grade - $145.00 Per Ton

F.O.B. Cleveland, Ohio
Terms are Net - 30 Days

The typical chemical analysis is:

Carbon	58.0%
Volatile	38.0%
Ash	4.0%
Sulphur	1.0%

If you are in need of any further chemical data on this material, you will have to have further tests run. We do not have this information available at this time.

If I can be of further service, feel free to contact me.

Very truly yours,

Carl J. Alessandro,
Technical Service & Sales Manager

CJA/pls

APPENDIX 4

EXPERIMENTAL DATA

This appendix contains technical data for each of the system experiments conducted in the first quarter of the contract.

EXPERIMENT #1

TITLE: Benzene Extraction of Pittsburgh Coal

OBJECTIVE: To determine the amount of benzene extract in Pittsburgh seam coal.

PROCEDURE: Materials: Pittsburgh seam coal (as received) 50 gm

Benzene 100 gm

Conditions: Extraction charged in soxhlet apparatus and refluxed with 100 gm benzene for three hours. Refluxed coal was filtered through filter paper and solvent was evaporated to dryness. Weight of extracted residue was determined. Proximate analysis of Pittsburgh seam coal was carried out

RESULT: Weight of Extracted Residue = 0.100 gm

% Extracted = 0.2

Proximate Analysis if Pittsburgh Coal

	PRCA	Analysis Supplied by Vendor
Moisture	4.05%	-
Volatile	38.5 %	38.0%
Ash	4.1 %	4 %
Sulfur	1.1 %	1 %
Carbon	bal.	

COMMENT: A similar extraction was performed for Illinois #6 coal, which give a coal extraction level of 4.5-5%. Pittsburgh coal is younger and may be less reactive than Illinois #6 coal. The carbon content of Illinois #6 coal is significantly higher (70.8% mf. basis), as is the sulfur content (2.15%) compared with the Pittsburgh coal.

EXPERIMENT # 2

TITLE: Monomer Reacted Coal Slurry in #2 Fuel Oil

OBJECTIVE: To evaluate the dispersion stability of monomer-reacted coal-slurry in #2 fuel oil.

PROCEDURE: The following reaction mixture was prepared:

Fuel oil	25	gm
Lauryl methacrylate	20	gm
Ethylene glycol dimethacrylate	2.5	gm
Diethylaminoethyl methacrylate	2.5	gm
Benzoyl peroxide	0.25	gm
DMT (5% DMT solution in oil)	0.25	gm

The coal was mixed with the reaction mixture in 10:1 and heated at 150°F for 20 minutes. This reacted coal slurry was mixed with #2 fuel oil in 1:1 proportions and further treated at 150°F for 30 minutes.

Settling tests were carried out in #2 fuel oil.

RESULT: The coal settled to the bottom of the container in a three hour period. A similar experiment using untreated coal was run for comparison. This coal also settled to the bottom in three hours.

COMMENT: The monomer reaction solution used without grafting initiator offers no surfactant effect and hence no dispersion stability.

EXPERIMENT #3

TITLE: Monomer Reacted Coal Slurry in Naphtha

OBJECTIVE: To study the settling stability of monomer reacted coal in naphtha for comparison to #2 fuel oil.

PROCEDURE: The procedure was same as followed in Experiment #3, only naphtha solvent was used as the settling media.

RESULT: The coal-slurry settled within a three hour period. This result was comparable to that of Experiment #2.

COMMENT: A change in settling medium without significant change in viscosity showed no marked improvement in the settling stability of the slurry. Low level surfactant effects of the settling medium itself provide little influence.

EXPERIMENT #4

TITLE: Monomer Reacted Coal Slurry in Mineral Oil

OBJECTIVE: To determine the effect of viscosity of the settling medium on the stability of the slurry.

PROCEDURE: Same as in Experiment #3, except #2 fuel oil was replaced by the higher viscosity Diamond mineral oil.

RESULT: The coal-slurry required 5 hours to settle. In Experiments #2 and #3 settling occurred within 3 hours.

COMMENT: The increase in voscosity produced a substantial increase in settling time. This is consistent with Stokes law.

EXPERIMENT #5

TITLE: Monomer Reacted Coal Slurry in #6 Fuel Oil

OBJECTIVE: To compare the settling rate of coal slurry in #6 fuel oil with mineral oil.

PROCEDURE: The formulation was similar to that of Experiment #3. Three settling test samples were prepared:

1. Untreated coal in mineral oil.
2. Treated coal in mineral oil.
3. Treated coal in #6 fuel oil at 50°C.

RESULT: Both the treated and untreated coal settled in 5 hours in mineral oil. The coal slurry required 6 to 7 hours to settle in #6 fuel oil.

COMMENT: This settling rate in #6 fuel oil was slower in this higher viscosity settling media, as expected. No marked improvement was attributed to monomer surfactant effects.

EXPERIMENT #6

TITLE: Use of Cracker Gasoline as a Reaction Monomer

OBJECTIVE: To determine the effect of cracker gasoline on a coal-slurry settling rate.

PROCEDURE: 10 mg coal was mixed with 1 gm cracker gasoline and 1 gm benzene containing 0.1 gm benzoyl peroxide and 0.05 gm DMT. The slurry was heated at 60-65^{o}C for 20 minutes. The reacted coal was mixed with 10 gm mineral oil and observed at 65^{o}C for 30 minutes. Coal settling tests were carried out using the treated coal in #2 fuel oil.

RESULT: Coal settled in one hour.

COMMENT: Cracker gasoline reacted with coal in a slurry and did not display any surfactant effects.

EXPERIMENT #7

TITLE: Cracker Gasoline Used as Both Solvent and Reactant for a Stable Coal-Oil Slurry

OBJECTIVE: To study the reactivity of cracker gasoline used both as reactant and reaction solvent.

PROCEDURE: 10 gm coal was mixed with 10 gm cracker gasoline and 0.1 gm benzoyl peroxide. Three samples were prepared, as in Experiment #6. Tests were carried out as in Experiment #6.

RESULT: Same as Experiment #6.

COMMENT: The reaction kinetics do not appear to be related to the concentration of reactant.

EXPERIMENT #8

TITLE: Cracker Gasoline Reacted Coal Tested in Mineral Oil

OBJECTIVE: To determine if a higher viscosity settling media displayed improved settling rate.

PROCEDURE: Experiment #7 was repeated, with the reacted coal tested as a slurry suspension in mineral oil.

RESULT: Coal settled as in Experiment #7.

COMMENT: This experiment showed that the surfactant contribution of cracker gasoline is negligible and not dependent on viscosity in various settling mediums.

EXPERIMENT #9

TITLE: Reflux Cracker Gasoline Reaction Using Benzene as a Reaction Solvent

OBJECTIVE: To determine the effect of using benzene in a reflux cracker gasoline coal reaction (not including a grafting initiator).

PROCEDURE: 10 mg coal was mixed with 5 gm cracker gasoline, 5 gm benzene, and 0.1 gm benzoyl peroxide. Mixture was refluxed for 20 minutes at 65°C. The reacted coal was mixed with 10 gm mineral oil kept at 65°C for 30 minutes.

RESULT: Coal settled as in Experiment #8.

COMMENT: The presence of benzene in the coal slurry reaction did not improve the effects of the reaction. It would appear that increasing the mean-free reaction path or swelling the coal through the use of benzene as a reaction solvent did not improve this reaction. GI appears to be required to increase the reaction conditions.

EXPERIMENT #10

TITLE: Cracker Gasoline Reflux Reaction with Increased Reaction Time Without GI

OBJECTIVE: To determine the effect of a reflux reaction using cracker gasoline without GI.

PROCEDURE: 10 gm coal was mixed with 10 gm cracker gasoline and 0.1 gm benzoyl peroxide. The solution was refluxed at 65^{o}C for 1 hour. The reactants were filtered off. The reacted coal was mixed in 10 gm oil at 65^{o}C for 30 minutes. The settling test was carried out in #2 fuel oil.

RESULT: Coal settled in one hour (similar to Experiment #9).

COMMENT: The reflux reaction without GI did not produce surfactant properties on the coal as demonstrated in a oil-slurry settling test.

EXPERIMENT #11

TITLE: Illinois #6 Coal Slurry Reaction

OBJECTIVE: To compare the coal-slurry stability of Illinois #6 coal with Pittsburgh coal.

PROCEDURE: Experiment #3 was repeated using #2 fuel oil for both the types of coals. Settling tests were carried out in #2 fuel oil.

RESULT: The settling rates for Illinois #6 coal and Pittsburgh coal were comparable. Illinois #6 coal displayed a dark colored uniform layer due to extractable materials. Pittsburgh coal showed distinct layers of coal and oil. In both cases there was some improvement in settling stability due to the reaction when compared to a control settling test of untreated coal. Illinois #6 coal appeared to have a slightly slower settling rate.

COMMENT: There appears to be a slight difference in the slurry reaction between Illinois #6 and Pittsburgh seam coal. This type of reaction displayed a small improvement in the surfactant reaction effect without GI of Illinois #6 coal compared to Pittsburgh seam coal.

EXPERIMENT #12

TITLE: Reflux Styrene Reaction with Illinois #6 Coal

OBJECTIVE: To compare the reactivity of Illinois #6 coal and Pittsburgh coal in a chemical grafting reaction.

PROCEDURE:

	Reaction I (Illinois #6)	Reaction II (Pittsburgh)
Coal	10 gm	10 gm
Styrene	10 gm	10 gm
GI	10 gm	10 gm
BPO	0.1 gm	0.1 gm

The slurries were heated at 60-65°C for 30 min. Settling tests were carried out in #2 fuel oil, with each of the above reaction products mixed with #2 fuel oil for a total volume of 100 cc.

RESULT:

1. Settling Rate

Time (min)	Illinois #6 Coal (cc)	Pittsburgh Coal (cc)
0	90	90
15	90	70
45	*	20

2. Solids

30 cc of supernatant liquid was removed and evaporated to dryness. The solid contents were determined by weighing.

Weight of solids in 30 cc of Illinois #6 coal slurry = 0.7 gm

Weight of solids in 30 cc of Pittsburgh coal slurry = 1.0 gm

(It is anticipated that the coal can be further dried and show less weight.)

3. Settled Coal

Coal observed as a hard layer at the bottom of the graduated

* Illinois #6 coal settling was difficult to observe.

cylinder after 2.75 hr was measured as:

Illinois #6 coal	15 cc
Pittsburgh coal	16 cc

CONCLUSION: The initial settling rate of the two coals is slightly different, but within three hours both slurries settle to the same level.

EXPERIMENT #13

TITLE: Reacted Coal from Treatment of Experiment #12 with Diethyl Aminethyl Methacrzlate

OBJECTIVE: To determine if a chemically grafted coal shows improved settling characteristics if reacted further with a surfactant type monomer.

PROCEDURE: Coal slurry mixed with 5 gm diethyl aminethyl methanylate, and heated at 65^{o}C for 30 min. Settling tests were carried out in #2 fuel oil.

	Settling Times (min)	
	Treated	Untreated
Pittsburgh	60	15
Illinois #6	75	25

Note: Because of the dark color of the solvent caused by the Illinois coal after about 60 minutes, a special observation technique was required. The slurry liquids were transferred to another container, and the solids left at the bottom of each container were compared.

COMMENTS: Both coals settled to the same level after 60 minutes; however, Illinois was better initially. Diethyl aminethyl methanylate monomer has some surfactant effects on chemical graft treated coals.

EXPERIMENT #14

TITLE: Reflux Styrene Reactions Using GI for Both Pittsburgh and Illinois #6

OBJECTIVE: To determine the chemical grafting reactivity of Pittsburgh and Illinois #6 coal for oil slurry stability.

PROCEDURE:

Materials	Pittsburgh and Illinois #6 coal
Coal	50 gm
Benzene	100 gm
Styrene	5 gm
BPO	1 gm
GI	10 gm

Conditions

Reaction Temp	70°C
Time	6 hours

Test

Reacted coal was compared for settling rate in #2 fuel oil.

REACTION PRODUCTS:

	Illinois #6	Pittsburgh
Extract	1.8 gm	0.1 gm
Coal Residue	48.3 gm	49.9 gm

RESULT: A. Pittsburgh Coal

Time	Settling Level of Untreated Coal	Settling Level of Treated Coa
0 min	100 cc	100 cc
10	97	98
20	43	53
30	29	40
40	22	29
60	20	20

EXPERIMENT #14 (continued)

B. Illinois #6 Coal

Time	Settling Level of Untreated Coal	Settling Level of Treated Coal
0 min	100 cc	100 cc
20	98	100

Note: Unable to accurately judge settling because of darkness caused by the soluble portion.

C. Modified Settling Test for Illinois #6 Coal

Diluted the slurry to 200 cc and then repeated test:

Time	Untreated	Treated
0 min	100 cc	100 cc
10	-	-
25	-	-

Because of inability to clearly distinguish the settling line, the bottom of the cylinder was touched with a glass rod. It was observed that the treated coal has settled more at the bottom than the untreated coal with this procedure.

COMMENTS: This experiment showed some improvement of chemical grafted Pittsburgh coal over the control. Settling observation of Illinois #6 provided a problem because of extraction darkness. It also showed that Illinois #6 coal is chemically more reactive than Pittsburgh seam coal in this kind of reaction.

EXPERIMENT #15

TITLE: Reflux Reaction with Dicyclopentadiene Monomer and GI

OBJECTIVE: To determine the chemical grafting reactivity of Pittsburgh seam coal using dicyclopentadiene monomer for coal-oil slurry dispersion stability.

PROCEDURE: Materials

Pittsburgh seam coal	30 gm
Dicyclopentadiene	30 gm
Naphtha solvent	30 gm
GI	10 gm
BPO	1 gm

Conditions

Temp.	70-75^{o}C
Time	3 hours

Test

Settling tests were carried out in #2 and #6 fuel oils.

Reacted coal was mixed in #6 fuel oil for oil-coal settling test.

10 gm coal plus 100 gm #2 fuel oil slurry.

RESULT: A. #2 Fuel Oil Settling Test

Comparison of the oil dispersion stability of the reacted coal.

Time	Treated Coal	Untreated Coal
0 min	100 cc	100 cc
10	99	98
20	95	50
30	25	28
40	20	22

EXPERIMENT #15 (continued)

B. #6 Fuel Oil Settling Test

Time	Treated Coal	Untreated Coal
0 min	100 cc	100 cc
15	95	90
30	70	70
45	45	43
60	27	27
75	20	20

COMMENTS: Dicyclopendiene monomer did not appear to improve the dispersion stability of Pittsburgh seam coal.

EXPERIMENT #16

TITLE: Reaction on Pittsburgh Seam Coal with Cracker Gasoline and GI

OBJECTIVE: To determine the chemical grafting reactivity of Pittsburgh seam coal with cracker gasoline monomer for oil slurry stability.

PROCEDURE: Material

Pittsburgh coal	30 gm
Cracker gasoline	30 gm
GI	10 gm
BPO	1 gm

Conditions

Reaction Temp.	65^oC
Reaction Time	6 hours

Test

The settling test was carried out using #2 fuel oil.

RESULT: A. The extractive yield was negligible.

B. Settling Rate Comparison

Time	Treated Coal	Untreated Coal
0 min	100 cc	100 cc
10	98	95
20	90	45
30	85	25
70	80	20
210	40	10

COMMENT: Using GI and cracker gasoline monomer, the Pittsburgh seam coal displayed a substantial improvement in oil dispersion stability over untreated coal. It is also superior to dicyclopentadiene monomer and styrene monomer. See Figure 5.

☆U.S. GOVERNMENT PRINTING OFFICE: 1978-740-2(