FE-2307-2
Distribution Category UC-90d

# RESEARCH AND DEVELOPMENT OF RAPID HYDROGENATION FOR COAL CONVERSION TO SYNTHETIC MOTOR FUELS

## (RISER CRACKING OF COAL)

Task Report: Task 1


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Project No. 8976


Date Published - May 1976

Prepared for the

UNITED STATES ENERGY RESEARCH
AND
DEVELOPMENT ADMINISTRATION

Under Contract No. E(49-18)-2307

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

# ABSTRACT

A bench-scale experimental reactor has been designed to define the important design parameters in the short residence-time hydrocracking of coal to synthetic motor fuels. The reactor is a 50 foot helical coil of 1/8-inch Incoloy tubing that will be heated electrically. Coal feed rates will be 5 - 10 lb/hr with residence times of 1 to 10 seconds. The reactor will operate up to 2000 psig at temperatures of 900 to 1500°F.

An experimental plan has been outlined for Task 2, Bench-Scale Unit Operations. Work in the first 15 months concentrates on important parameters that would affect the design of a PDU. In due course, carrier streams other than hydrogen will be explored, such as syngas and steam.

A detailed operating procedure for the bench-scale unit has been written, and is included in this report.

## A. INTRODUCTION

This document contains the details of our experimental plan and equipment designs for Task 2 of the program outlined in IGT's proposal entitled "Research and Development of Rapid Hydrogenation for Coal Conversion to Synthetic Motor Fuels". This program will be referred to hereafter as "Riser Cracking of Coal."

The scope of Task 2 of this program is to build and operate a bench-scale experimental unit. The work plan and details presented here fulfil the requirements of Task 1, which is the planning phase for Task 2.

The experimental plan is divided into two sections. The first section of 15 months leads up to the design of the Process Development Unit (PDU), and concentrates on information expedient to that design. The second section covers the continuation of the bench-scale experimental work, and explores particular areas in depth, and in general, takes a broader look at the variables involved in this short residence time, high-pressure pyrolysis process.

The design of the bench-scale unit is presented in a series of diagrams and descriptive material. The development of a coal-feeding system is nearing completion, but, otherwise, we have completed the design to our own satisfaction, ready for procurement. An operating procedure is included as part of the design information.

The Overall Program Plan and Manpower Schedule is included for reference as Appendix A.

## B. EXPERIMENTAL PLAN

### First 15 Months

A program schedule for the first 15 months of work is shown in Figure 1. The areas of particular interest are: the completion of Task 1 (Planning), the beginning of Task 2 (Construction and Operation of a Bench-Scale Unit), and the beginning of Task 3 (Design of a Process Development Unit). Six months are allowed for the construction of the bench-scale unit, leaving about six months to perform experimental work relating to the design of the process development unit, or PDU. Because of the shortness of time, the initial experimental work will cover as much ground as possible, at the sacrifice of detail, which will be filled in later in the program.

While the bench-scale unit is being built, trials will be made to assess the operability of the equipment. In these trials, air, or nitrogen, will be used as the feed gas, and coke, or coal char, as the solid phase. The capability of making a good material balance will be demonstrated in these trials.

The principal variables to be investigated will include coil outlet pressure, coil outlet temperature, residence time, temperature profile, or time-temperature history, particle size, coal type and feed gas composition. An array showing blocks of experiments of these variables is shown in Figure 2. To complete such an array in a methodical manner would be time consuming. In order to develop as much information as possible to guide the design of the PDU, the number of experiments will be reduced in an ordered manner to confine experimental work to those regions where the expected liquid yields will be of sufficient quantity to be of interest. The path of experiments through arrays of pressure, temperature, residence time, particle size and temperature profile is shown in Figure 3, and is also summarized in Table 1.

In the initial experiments, coil outlet temperature, coil outlet pressure, and residence time will be varied. The time-temperature history, or temperature profile, will be similar to the profile "B" shown in Figure 4. This profile provides rapid initial heating of the gas-solids stream; for this particular example, the temperature at time t is given by —

$$T = T_o + (T_f - T_o)\sqrt[3]{\frac{t}{\tau}} \qquad (1)$$

and the distance x from the coil entrance corresponding to time t is given by —

$$x = \frac{G_o R}{PA}(T_o + 460)t + \frac{G_o R \Delta T}{PA\sqrt[3]{\tau}}\, t^{4/3} \qquad (2)$$

subject to —

$$G_o = \frac{PAL}{R}\left[\frac{1}{(T_f + 460)\tau}\right] \qquad (3)$$

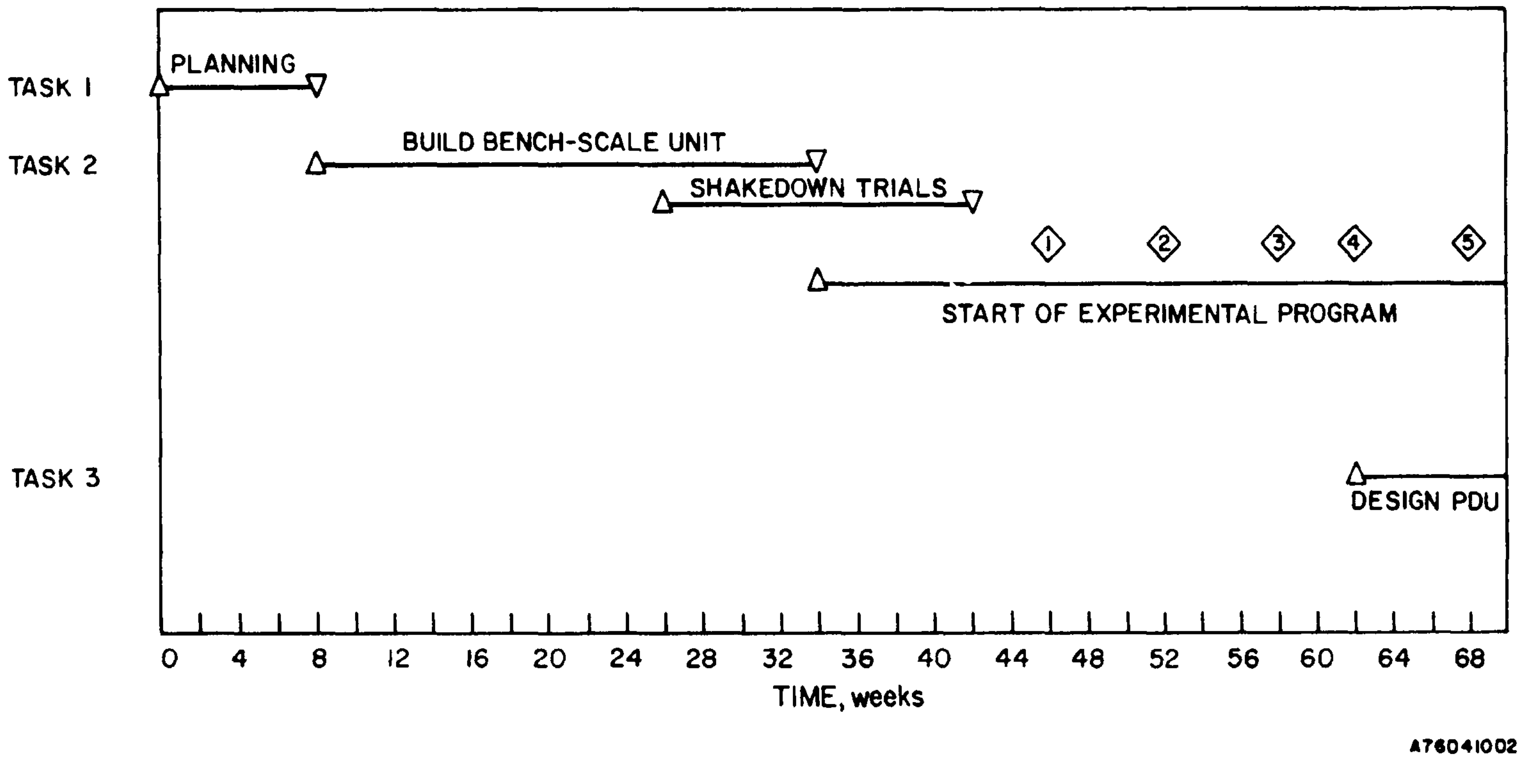



Figure 1. DECISION POINTS AND MILESTONES DURING 1ST YEAR OF EXPERIMENTAL WORK

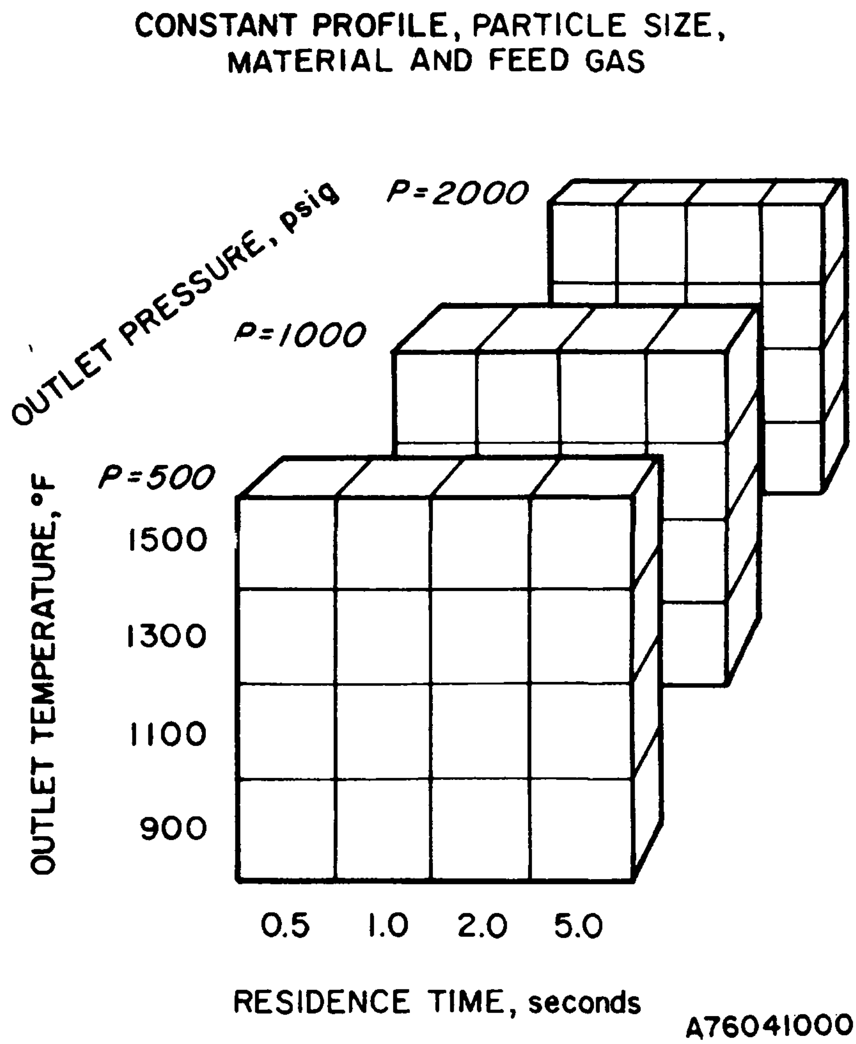



Figure 2. TYPICAL 4x4x3 ARRAY OF ORDERED EXPERIMENTS

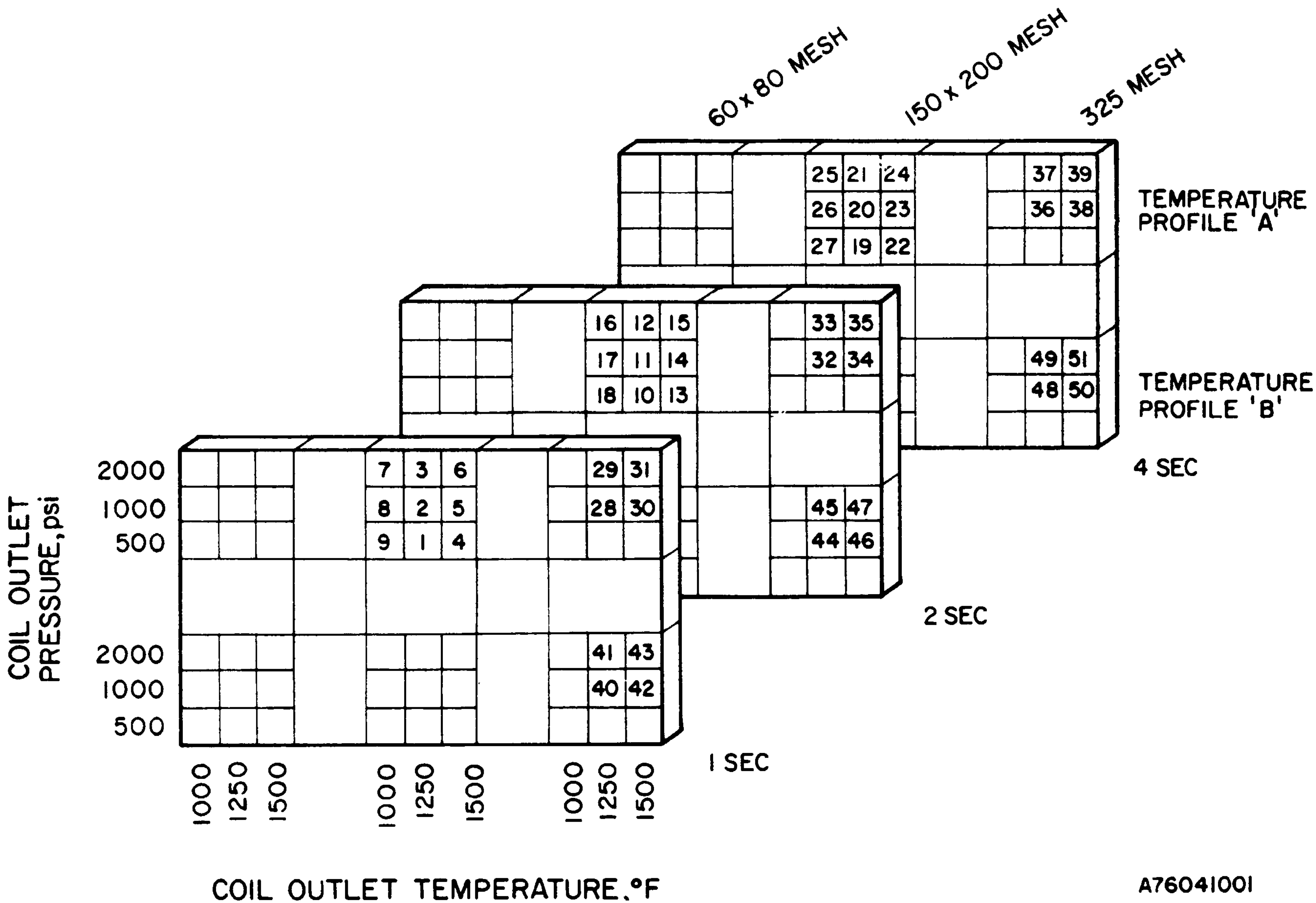



Figure 3. ORDERED PATH OF EXPERIMENTAL RUNS THROUGH PRESSURE-TEMPERATURE-RESIDENCE TIME - PARTICLE SIZE PROFILE ARRAYS

## Table 1. RUNS FOR THE FIRST 15 MONTHS

| Runs* | Purpose |
|---|---|
| 1-27 | To evaluate the effects of coil outlet temperature, coil outlet pressure and residence-time, holding the time-temperature history, feed-gas composition, and particle-size consist constant. In these runs, North Dakota lignite will be run with hydrogen. |
| | MILESTONE NO. 1: From analysis of the data reduce the levels of operating pressure from three to two, and determine the desirability of longer or shorter residence times. |
| 28-39 | Evaluate the effects of the increase in surface and reduction in particle radius obtained by using smaller particles. |
| | MILESTONE NO. 2: From analysis of the data determine if particle size reduction is beneficial. |
| 40-51 | Evaluate a second temperature profile at 1, 2, and 4 seconds residence time. |
| | MILESTONE NO. 3: From analysis of the data determine if yields and distribution of products between gases, liquids and solids can be markedly manipulated by change in temperature profile. |
| 52-64 | Make caking-coal trials; if initial runs are not successful, make trials in which coal ash is added to act as an adsorbent, or anti-blocking agent. |
| | MILESTONE NO. 4: From analysis of the data determine what conditions, if any, will allow caking coals to be processed. Summarize and evaluate all data for PDU design. |
| 65-70 | Make trials using steam and hydrogen, carbon monoxide and hydrogen and a mixture of steam, carbon monoxide and hydrogen. |
| | MILESTONE NO. 5: From analysis of the data assess the desirability of using syngas-like materials as feed gases. |
| 70-75 | If time permits, evaluate the use of catalytic materials added to the feed coal. The catalysis should be inexpensive. |

*The operating conditions for the first 51 runs are shown in Figure 3.

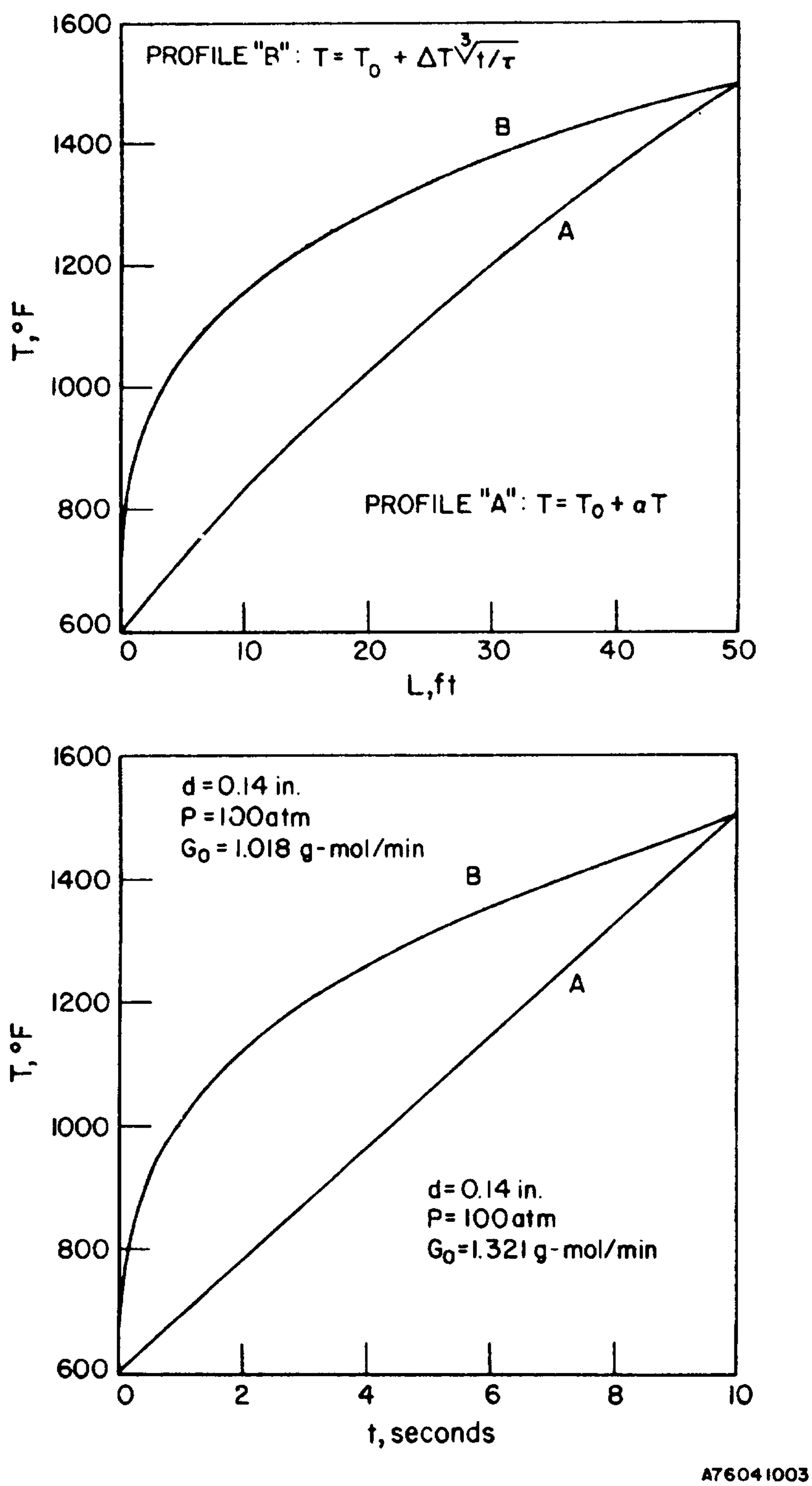



Figure 4. COMPARISON OF LINEAR AND NONLINEAR HEATING PROFILES

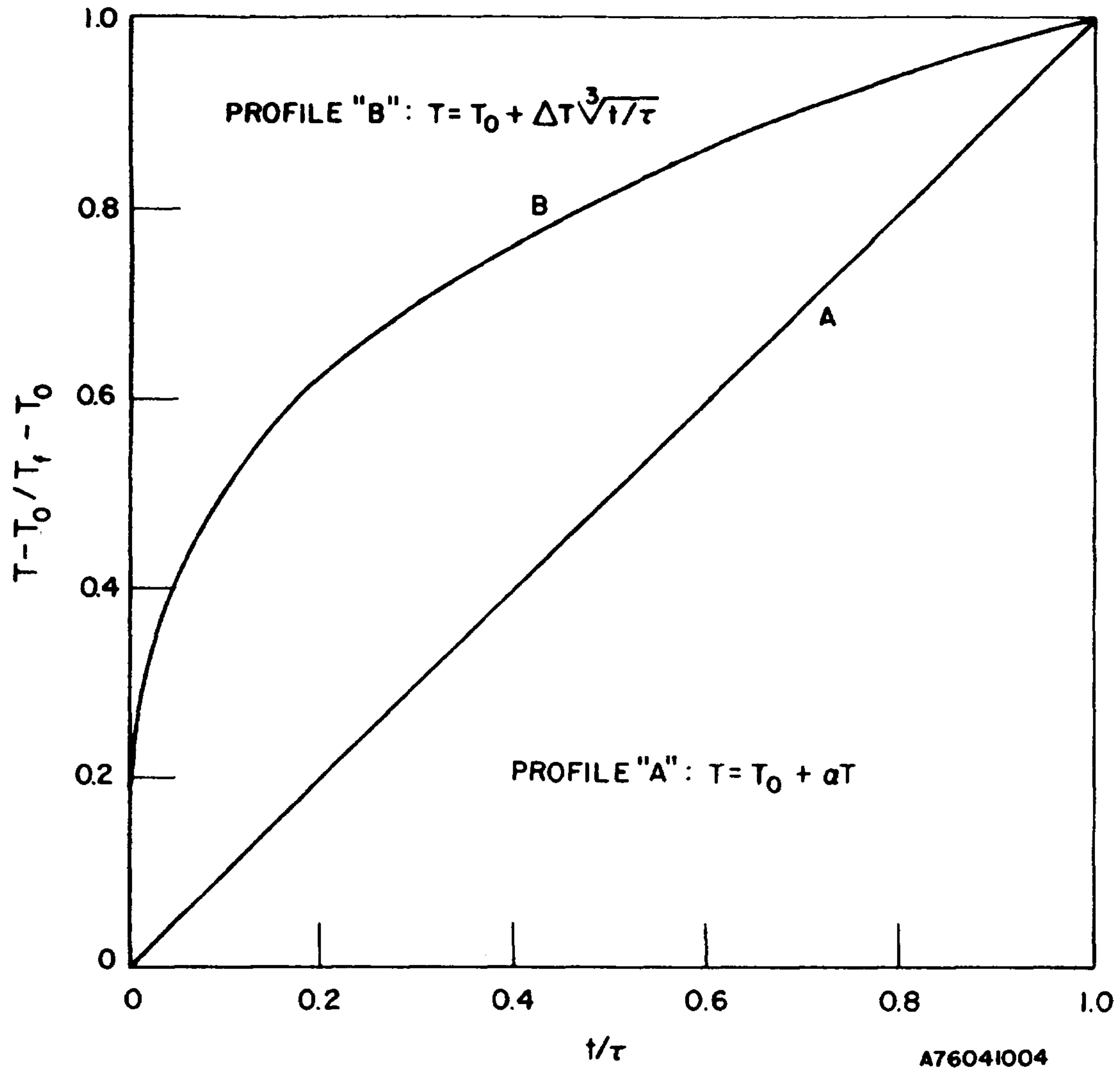



Figure 4a. COMPARISON OF NONLINEAR HEATING RATE WITH LINEAR HEATING RATE

where:

- $A$ is cross sectional area in $ft^2$,
- $G_o$ is mass flow rate, lb-moles per second,
- $P$ is pressure in atmospheres,
- $R$ is ideal gas law constant, 0.729 $ft^3$ - atm/$^oR$ - lb mole,
- $T$ is temperature, $^oF$,
- $T_f$ is coil outlet temperature, $^oF$,
- $T_o$ is coil inlet temperature, $^oF$
- $\Delta T$ is $T_f - T_o$,
- $t$ is time in seconds, and
- $\tau$ is total residence time in seconds.

These equations do not account for the increase in gas velocity due to devolatilization and gasification of the coal; these effects would have to be accounted for in an empirical manner. The shape of the profile, however, can be described mathematically, and altered by relatively simple mathematics.

The number of each experimental run is shown as the number within a box in an array starting with the number "1". The order has been arranged to favor ease of operation in the first runs, and then the direction of expected decline in gas and liquid yields. Thus, the planned list of experiments might be shortened further as yields are found to be too low to justify completion of a series. At the end of the first phase of planned experiments (Milestone No. 1, Figure 1), the data will be examined, and the effects of change in residence time evaluated. If possible, the number of operating pressures will be reduced to two.

In the next series of experiments, the effects of particle size will be explored. By reducing the particle size range from −150+200 to −325, the particle surface area per unit mass will approximately double, and the average particle diameter will be reduced by approximately half. Thus, mass transport across the gas film separating the particles from the bulk gas phase would be approximately doubled, and the length of diffusion paths within particles greatly shortened. Superficially, particle heating would take place more quickly, leading to the more rapid release of volatile matter.

Pyrolysis reactions can be very roughly described as first order with respect to the amount of feedstock present, while hydrogenation reactions would be expected to be a function of the product of the amount of feedstock present and the hydrogen partial pressure. Changes in mass transport across the gas films surrounding the particles, and changes in the heating rate of the particles, may have some effect on the course of the pyrolysis and hydrogenation reactions. Examination of the distribution of products between gases, liquids and solids should provide a basis for determining if change in particle size is an important effect, and if there are potential benefits in using small particles.

The results of these runs would be examined (Milestone No. 2, Figure 1) and an assessment of particle size made. A change in residence time might also be considered at this time; to realize residence times of more than 5 seconds under all conditions will require a coil 100 ft in length or more.

After choosing a particle size for further work on the basis of the preceding experiments, the impact of changes in temperature profile on yield and product distribution will be explored. Upon completion of these experiments, three additional feed gases would be tested to explore the technical feasibility of using:

a. A mixture of 50 mole-percent hydrogen in steam,

b. A mixture of 50 mole-percent carbon monoxide in hydrogen, and

c. A mixture of 50 mole-percent steam, 25 mole-percent carbon monoxide and 25 mole-percent hydrogen.

The results of these runs will be assessed at Milestone No. 5. In addition, trials will be made using caking coal, with and without an adsorbent, or antiblocking agent, derived from coal ash, or other appropriate material (coal char, for example). The results of these trials will be evaluated at Milestone No. 4. In the final runs of the preliminary series, prior to the design of the PDU, some trials of catalysts will be made, if time permits.

## Design of PDU

After approximately 12 to 15 months, the bench-scale unit will hopefully have been operated over a wide range of test conditions. The operating experience obtained in the early runs will be used to guide the choice of equipment for the PDU, particularly with respect to potential processing problems such as the collection of tar aerosols, uniform solids feeding, and the isolation of the products into solid, liquid and gaseous fractions.

## Continuing Studies in the Bench-Scale Unit

The continuing studies portion of the operation of the bench-scale unit will begin after the start of the PDU. The basic areas of investigation (Figure 5) will involve further investigations of the use of hydrogen, hydrogen/steam mixtures, synthesis gas and synthesis gas/steam mixtures as feed gases, and also the investigation of such variables as coal type, particle size, operating pressure and the time-temperature history of the particles.

This portion of the experimental program would be reviewed periodically, as shown in Table 2, to assess the significance of results obtained. Further experiments would also be designed in these reviews. The basic experimental plans (Figure 2) would involve proceeding in an orderly manner through arrays of experiments in which pressure, temperature and residence time would be the principal variables, holding coal type, particle size, feed-gas composition and temperature-profile constant.

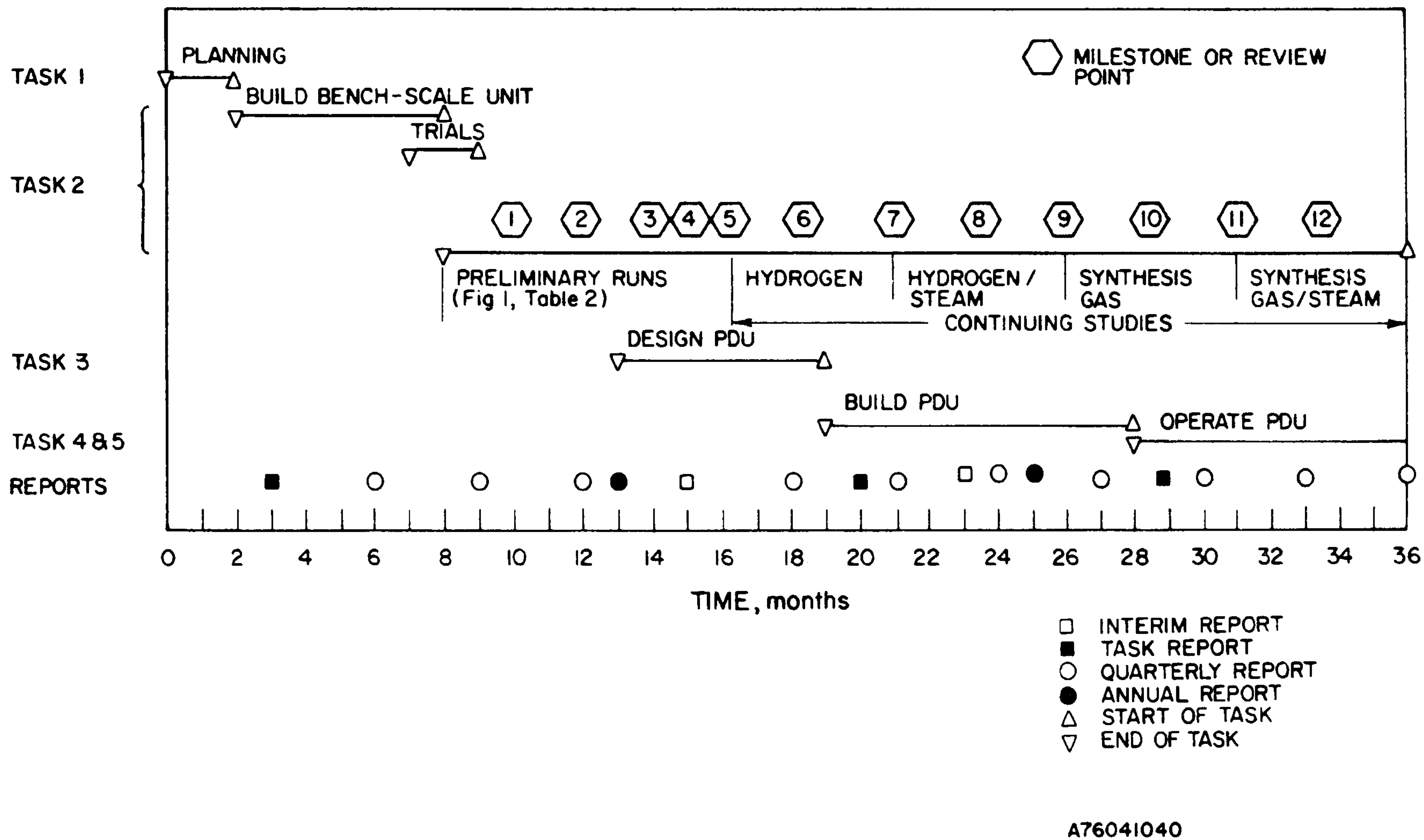



Figure 5. WORK PLAN FOR TASK 3

Table 2. MILESTONES OR POINTS OF REVIEW FOR CONTINUING STUDIES IN BENCH-SCALE UNIT

| Milestone or point of Review | |
|---|---|
| 6 | Review work with hydrogen and design experiments to complete work with hydrogen. |
| 7 | Review work with hydrogen and design experiments with mixtures of hydrogen and steam. |
| 8 | Review work with hydrogen/steam mixtures and design experiments to complete work with hydrogen and steam. |
| 9 | Review work with hydrogen/steam mixtures and design experiments with synthesis gas. |
| 10 | Review work with synthesis gas and design experiments to complete work with synthesis gas. |
| 11 | Review work with synthesis gas and design experiments with mixtures of synthesis gas and steam. |
| 12 | Review work with synthesis gas/steam mixtures and design experiments to complete work with synthesis gas and steam. |

For a given set of conditions, the liquids yield can be plotted in a three-dimensional space; by changing the variables forming the space, a surface can be generated, something like that shown in Figure 6. There are more than two variables, so that the notion of a surface representing all values of a dependent variable would more correctly be considered to exist in n+1 dimensional space, where n is the number of independent variables. For the reaction system being considered here, such a surface representing liquid yields can be given as –

$$\text{Liquid yields} = f\,(\text{coal type, operating pressure, particle time-temperature history, particle size, treatment gas composition}); \quad (4)$$

specific forms of such an equation are, of course, unknown.

The design of experiments would be concerned with the study of the change in liquids yield with changes in the independent variables using the concept of a "yield surface", and the manner in which it varies with change in the independent variables as a guide. The location of maxima, if they exist, on such surfaces would be of importance; a knowledge of the variation in yield with change in the independent variables would be essential in later optimization and technical feasibility assessment studies.

Basic Data

In operating the equipment, the following data would be taken for each run:

a. The amount of coal processed during the run, the proximate and ultimate analyses of the coal used in the run, and the particle size range.

b. The quantities of gas used to process the coal during the run, in the start-up and operation of the equipment. Transient conditions will be of short duration so that this information will convert to flow rates in a simple manner.

c. The quantity, composition and specific gravity of the gases produced.

d. The weight and composition of any liquids produced; a minimum of a carbon-hydrogen analysis would be made, with identification of the species present being made when a more elaborate analysis seems justified. Any water will be separated from the liquids collected by appropriate means and reported as a part of the analysis of the liquids.

e. The quantity and composition of the solids residue; a minimum of a carbon-hydrogen analysis will be made. Where justified, both a proximate and ultimate analysis will be made.

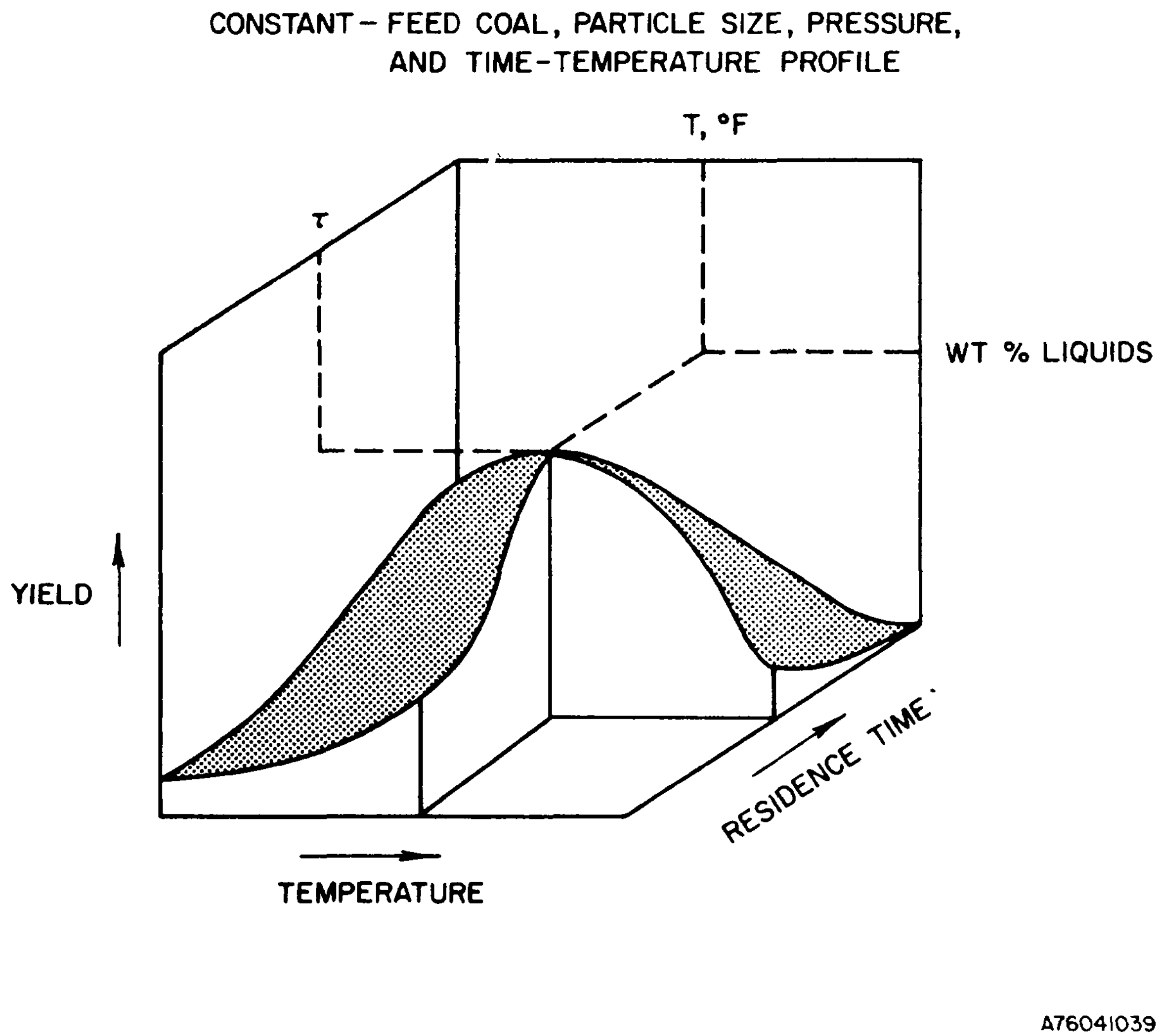



Figure 6. VARIATION OF CONCEPTUAL LIQUID YIELD WITH TEMPERATURE AND RESIDENCE TIME

Basic material balances will be made using this information, as well as elemental balances, particularly to explore the degree to which hydrogen is added to the products of the reactions.

In addition, operating information will be recorded, particularly the coil outlet pressure and temperature, and the variation in temperature over the length of the reactor tube, together with the control settings and observed values of all critical operating variables. This information will be used where possible to test mathematical models to explore the modeling of the conversions obtained.

In general, to be deemed a successful run, the equipment will have to have been operated over a sufficient length of time to bring the operation to a steady state; also, the shutdown must be voluntary, that is, much longer operating times must be technically possible. The quantities of feed materials must also be large enough that serious error due to uncertainty of measurement will not result. In the turn-around processing, the equipment will be examined for evidence of coking, or any other condition which might affect the operability of the equipment. Where deposition of tar on the interior surfaces of tubing downstream from the reactor is severe, it may be necessary to recover these materials by dissolving them in solvent and evaporating away the solvent to recover the material so deposited. This would be reported as a separate item in the material balance information.

## C. BENCH-SCALE UNIT DESIGN

The objective of the design of the bench-scale cracker is to simulate the flowing conditions of riser cracking of coal. This design parallels that employed in pyrolysis systems to allow accurate measurement of cracking temperature,as well as control and variation of residence time in the cracking furnace coil. Thus, in the initial stages of the experimental work, it will be possible to explore residence time, temperature and pressure with precise measurements of these variables.

Conditions for which the bench unit has been designed are as follows:

Coal Feed Rate: up to 10 lbs/coal per hour.

Carrier Hydrogen Rate: from 15 FPS (12 wt-% Hydrogen) to 70 FPS.

Alternate Carrier Streams:
1 - Hydrogen 100%
2 - Hydrogen and Steam
3 - Hydrogen and Carbon Monoxide (Syngas)
4 - Syngas and Steam

Pressures: 500 psig up to 2000 psig.

Temperature: 900°F up to 1500°F.

The design of individual components of the system is discussed under their appropriate headings below. A flow diagram (Figure 7) shows the assembly of the individual components.

As a guide in the design of the various components of the system, a design operating pressure of 2000 psig was set as a minimum for the entire system. Of the various components, only the reactor furnace coil will approach the design allowable stress at 1500°F operating temperature. At the severe conditions of 2000 psig and 1500°F, Incoloy 800 furnace coil-life will be limited to 1000 hours. At 1500 psig and 1500°F, coil life would be 10,000 hours.

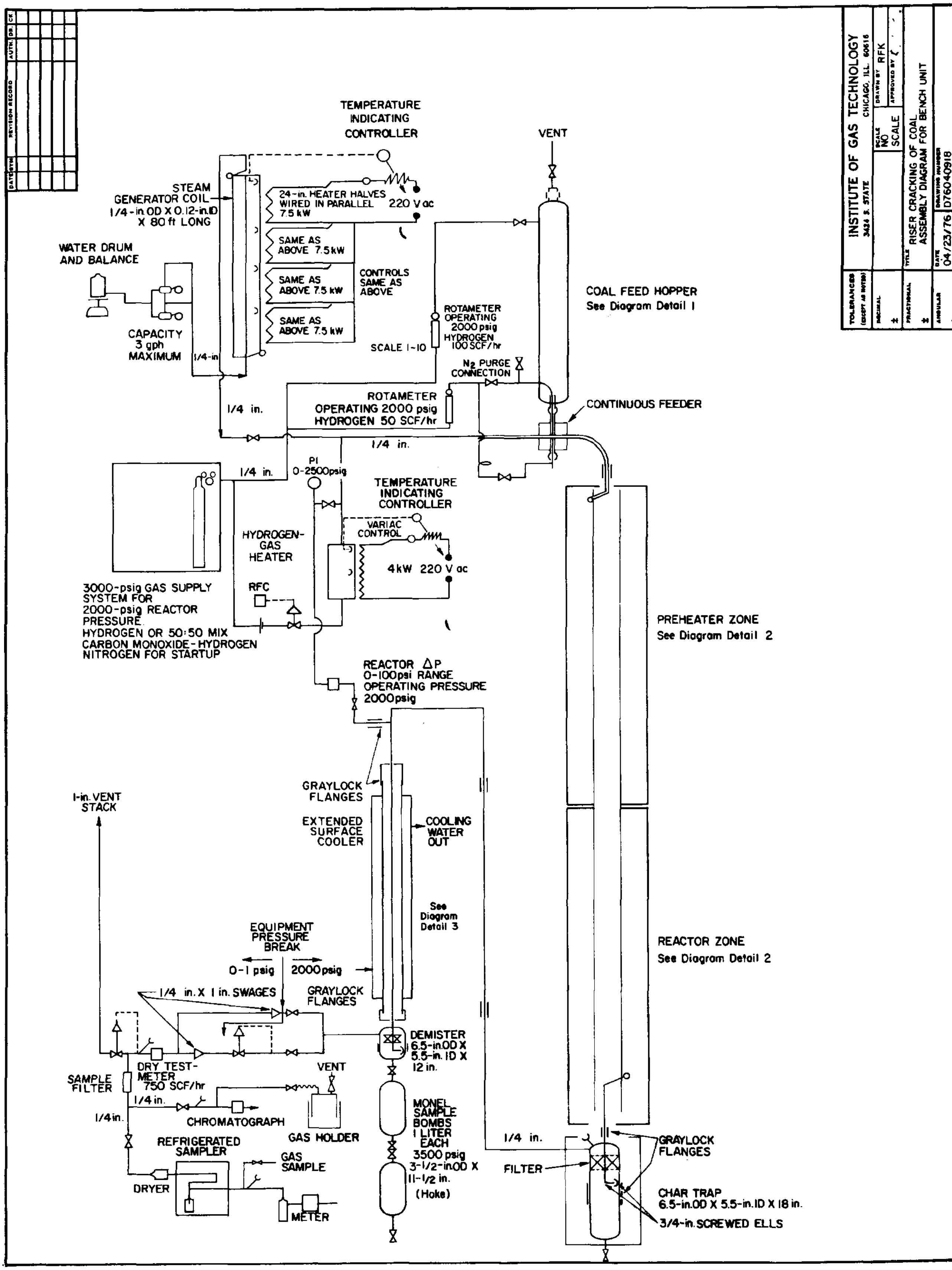



Figure 7. BENCH-SCALE UNIT FOR RISER CRACKING OF COAL

## Coal Feed Hopper and Feeder

Coal will be ground, classified, and segregated in batches, which will be kept dry until ready for transfer to the feed hopper.

The feed hopper is a two-thirds cubic foot vessel designed for pressurizing to 2100 psig for charging into the bench unit. It has a capacity of 20 lbs of coal, assuming 30 lb/cu. ft. density in the hopper. A connection has been provided for nitrogen purging of the loaded hopper prior to start of charging.

The feed hopper is designed for gravity feeding of the coal as uniformly as possible, and at a continuous rate of feeding.

Figure 8, following, shows the design details for the feed hopper.

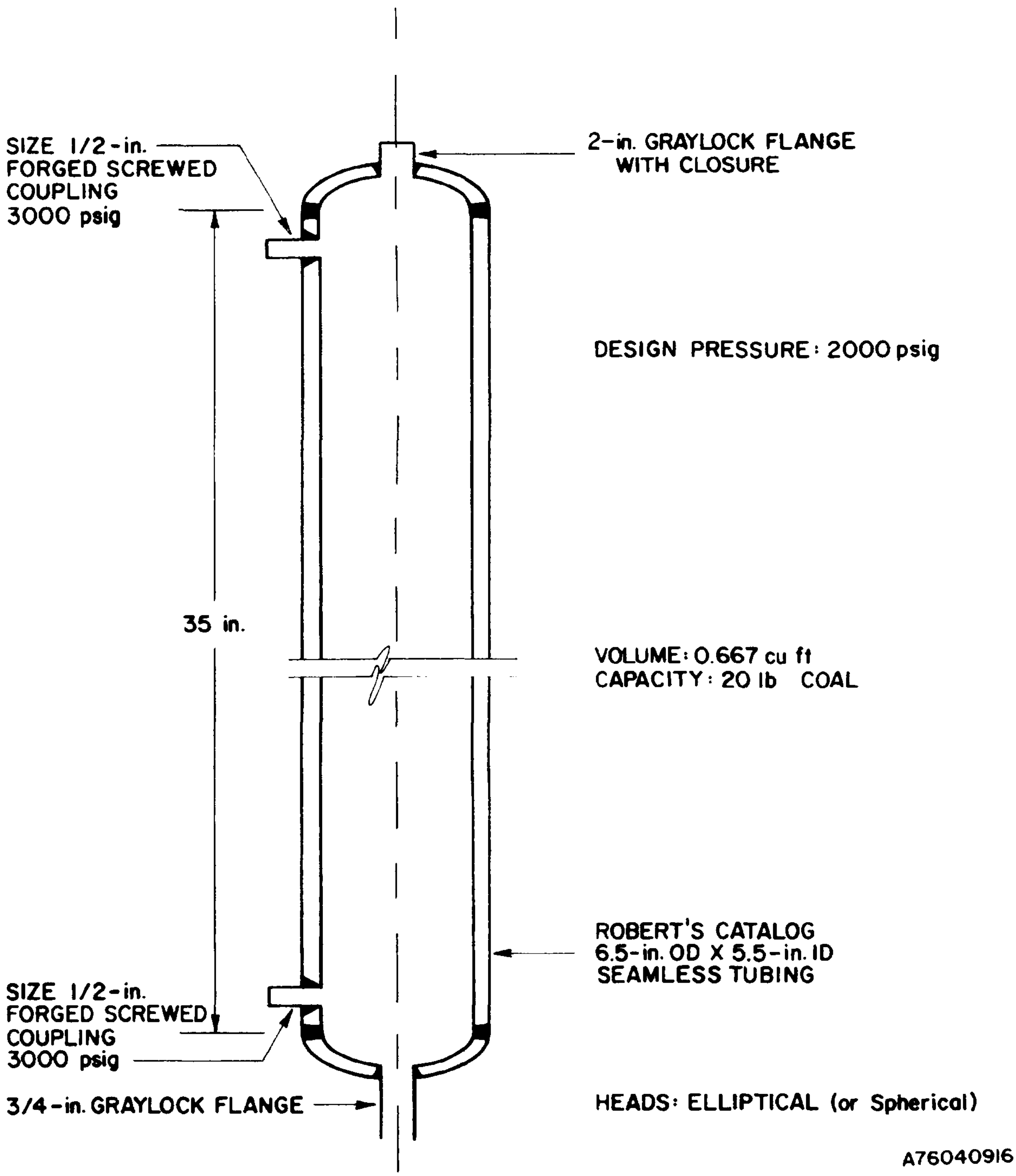



Figure 8. (Diagram Detail 1) FEED HOPPER FOR BENCH-SCALE UNIT – RISER CRACKING OF COAL

## Carrier Gas Supply

Carrier gas will be supplied once-through by means of a 3000 psi storage system. Prior to a run it will be pressured up with hydrogen,or a suitable mixture of hydrogen and carbon monoxide.

For the runs employing steam, a water tank and scale have been provided. An adjustable rate proportioning pump will measure the water and raise its pressure,prior to vaporizing in a steam boiler which is an 80 foot coil of pipe inside a stand of four 2-ft-high resistance heating furnaces. The steam supply system has been shown on the flow diagram, and is not detailed further. The carrier gas system is provided with rotameters to measure a controlled flow of pressurizing gas to the feed hopper, and aeration gas to the coal feeder. The source of these gases is the carrier gas system.

A small heater has been provided on the carrier gas stream mainly to keep this system warm and dry.

The details above are shown on the flow diagram, Figure 7.

## Reactor Preheater

The main source of heat to the combined coal and carrier gas stream is a preheater coil located above the reactor coil and integrally enclosed in the reactor furnace. This preheater coil has been provided to assure that the entire reactor coil heating system is available for temperature control of the 50-foot reactor coil. Details of the preheater furnace and coil construction are shown in the next section which describes the reactor coil and furnace.

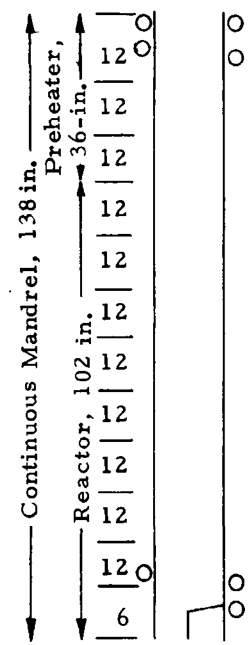
## Reactor Coil and Furnace

The reactor coil is designed to provide the range of flowing velocity of the carrier medium which would be obtained in a riser reactor. This range, 15 FPS to 70 FPS, may be obtained at a given pressure by varying the amount of carrier gas which accompanies the coal. Coal rate may also be varied to maintain a constant coal-to-gas ratio where desired. Variation of coal rates and carrier rates for the fixed coil length and diameter provides a choice of residence time. Major variations of the flowing velocity may be obtained by variation of the reactor pressure, thus varying the residence time. Of course, reactor pressure is an independent variable, just as is residence time.

The 50-foot-long reactor coil will be made of Incoloy 800 tubing, 0.25-inch outside diameter by 0.12-inch inside diameter. Heat will be applied at many zones along the coil to permit changing the heating-rate curve. Thermocouples along the coil will monitor the temperature, employing installation techniques that have been successful in other high-temperature bench-scale work.

The coil is wound on a mandrel which serves to support the coil as well as the thermocouples. Table 3 and Figure 9 show the orientation of the coils and thermocouples in the furnace and depict the number of coils, and length of coil, in each of the various heating zones. It will be noted that each heating zone is independently monitored, and the monitored temperature is controlled. The information included on the figure together with the gas velocity provides the data required for developing the residence time in the reactor coil. Essential dimensions and data have been supplied to permit the construction of the combined preheater and reactor from standard-size resistance heating units. The electrical wiring hookup is illustrated and the controls have been specified. Designation numbers for thermocouples are shown, together with notations, to show which thermocouples are indicated temperatures for the controller, and which temperatures are to be included on the temperature recorder.

Table 3. (Diagram Detail 2) COIL ORIENTATION AND MANDREL DETAILS FOR BENCH-SCALE UNIT FURNACE




| Heater Zone Height, in. | Number of Coils in Zone | Feet of Coil in Zone | Accumulated Feet of Coil From Inlet | Temperature Element No. | Heater Bottom Elevation From Bottom of Mandrel, in. | Heater Number for Temperature-Indicating Recorder and Temperature Recorder |
|---|---|---|---|---|---|---|
| | | | | 14* | | |
| 12 | 7.5 | 7.9 | 7.9 | 1 | 126 | 1 |
| 12 | 7.5 | 7.9 | 15.8 | 2 | 114 | 2 |
| 12 | 7.5 | 7.9 | 23.7 | 3 | 102 | 3 |
| 12 | 5.47 | 5.8 | 29.5 | 4 | 90 | 4 |
| 12 | 5.47 | 5.8 | 35.3 | 5 | 78 | 5 |
| 12 | 5.47 | 5.9 | 41.2 | 6 | 66 | 6 |
| 12 | 5.47 | 5.8 | 47.0 | 7 | 54 | 7 |
| 12 | 5.47 | 5.8 | 52.8 | 8 | 42 | 8 |
| 12 | 5.47 | 5.9 | 58.7 | 9 | 30 | 9 |
| 12 | 5.47 | 5.8 | 64.5 | 10 | 18 | 10 |
| 12 | 5.47 | 5.8 | 70.3 | 11, 13† | 6 | 11 |
| 6 | Straight | 0.5 | 70.8 | 12 | 0 | 12 (Outlet Temperature) |

Mandrel Data:

3-3/4-in. OD x 3.5-in. ID x 11-1/2 ft Long. Material: 304SS

Coil Data:

| | Preheater (in.) | Reactor (in.) | Total (in.) |
|---|---|---|---|
| Height of Wound Coil | 36 | 96 | 132 |
| Height of Straight Coil | 0 | 6 | 6 |
| Pitch (Distance Between Centerline of Adjacent Coils) | 1.6 | 2.2 | -- |

Tubing: 1/4-in. OD x 0.12-in ID x 71 ft Long. Material: Incoloy 800

*Temperature recording only.
†Temperature recording only; 4 in. above outlet.



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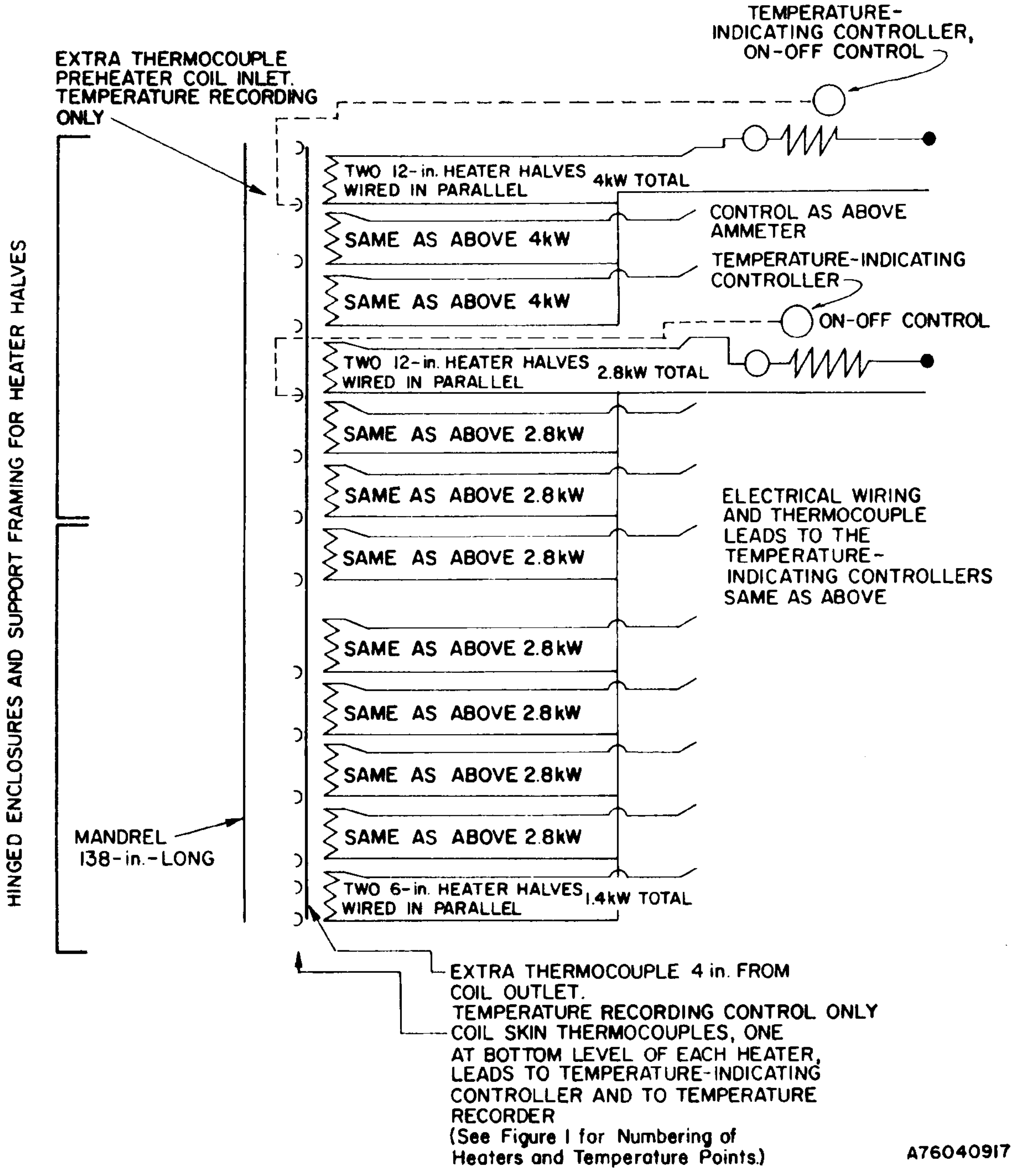



Figure 9. (Diagram Detail 2) ELECTRICAL AND INSTRUMENTATION PLANS FOR BENCH-SCALE UNIT FURNACE

Reactor Effluent Cooling System (See Figure 10)

The effluent of products, excess carrier-gas and unreacted char from the reactor coil will enter a char filter pot located immediately below the reactor. Effluent will be directed into the bottom section of the pot tangentially to the inside of the cylinder to effect separation of most of the char. The effluent, all vapor at this point, will then proceed upward through a filter for removal of remaining char fines. The upper part of the filter pot will be provided with a source of heat, so that natural heat loss will not result in tar condensation in this pot.

The filtered effluent will then proceed upward through an air cooler at such velocity as to preclude backflow of any condensate. This cooler will consist of a 12 foot length of 1/2 inch OD extended surface condenser tube.

The partially-cooled effluent will then proceed downflow through a counter-flow water-cooled double-pipe exchanger. The inside tube through which the effluent flows is a 12 foot length of 1/2-inch OD extended surface exchanger tube identical with the air-cooled tube. Each tube provides 3.2 square feet of cooling surface with the water cooler being greatly more effective. The effluent is brought to a temperature of 300°F with the condensation of tar, oil and water in this cooler.

As shown on the flow diagram, Figure 7, the cooler drains downward into a gas liquid separator located immediately below the cooler. The upper portion of this separator is identical, in construction, to the top of the char pot except that no heat is provided. The gases leave the top of the separator after passing through a vapor demister pad. The liquid from the bottom of the gas-liquid separator flows into a pair of one liter sample bombs which serve the dual purpose of accumulators, as well as containers for transporting the water-hydrocarbon sample to the laboratory for analyses.

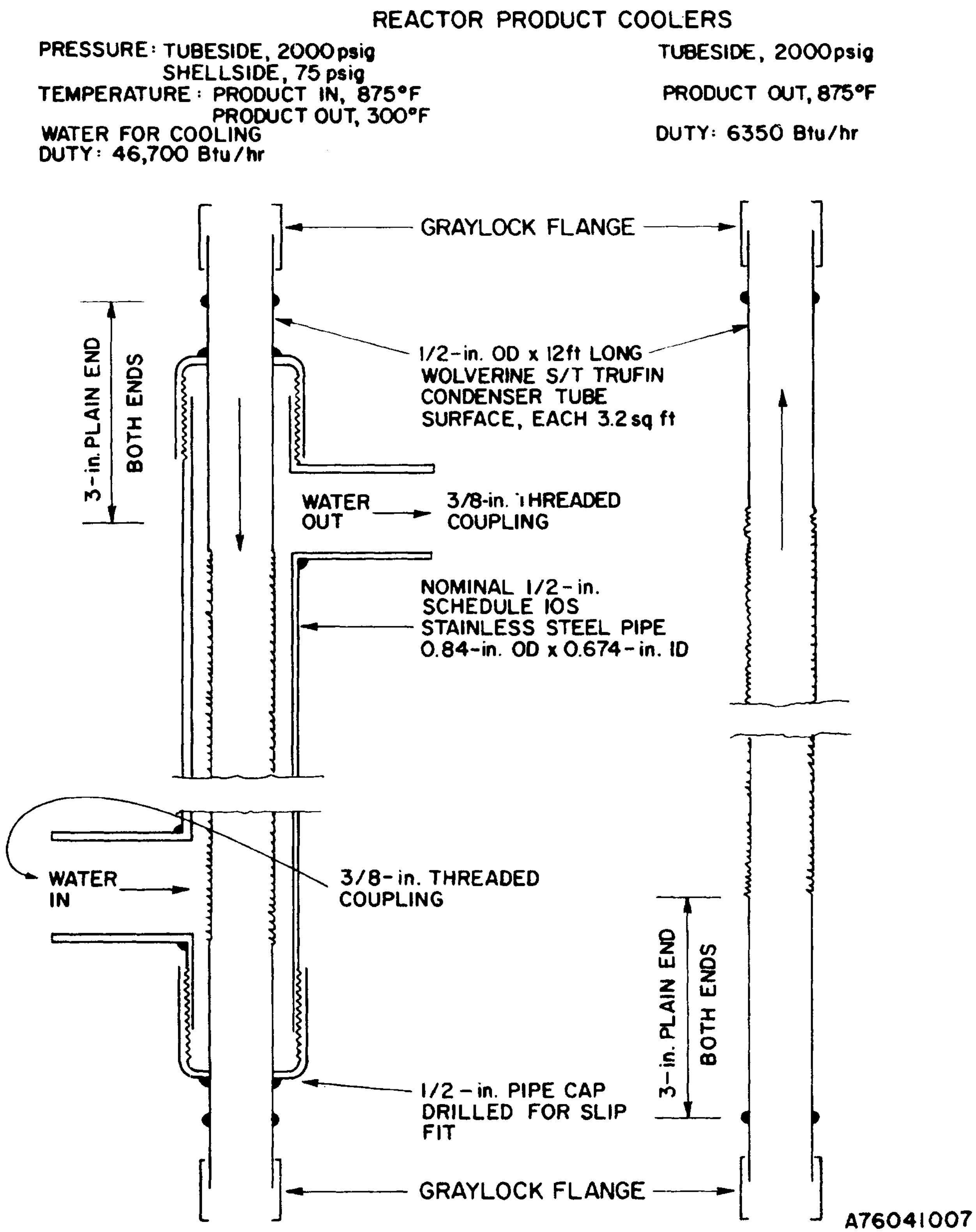



Figure 10. (Diagram Detail 3) COOLERS FOR BENCH-SCALE UNIT

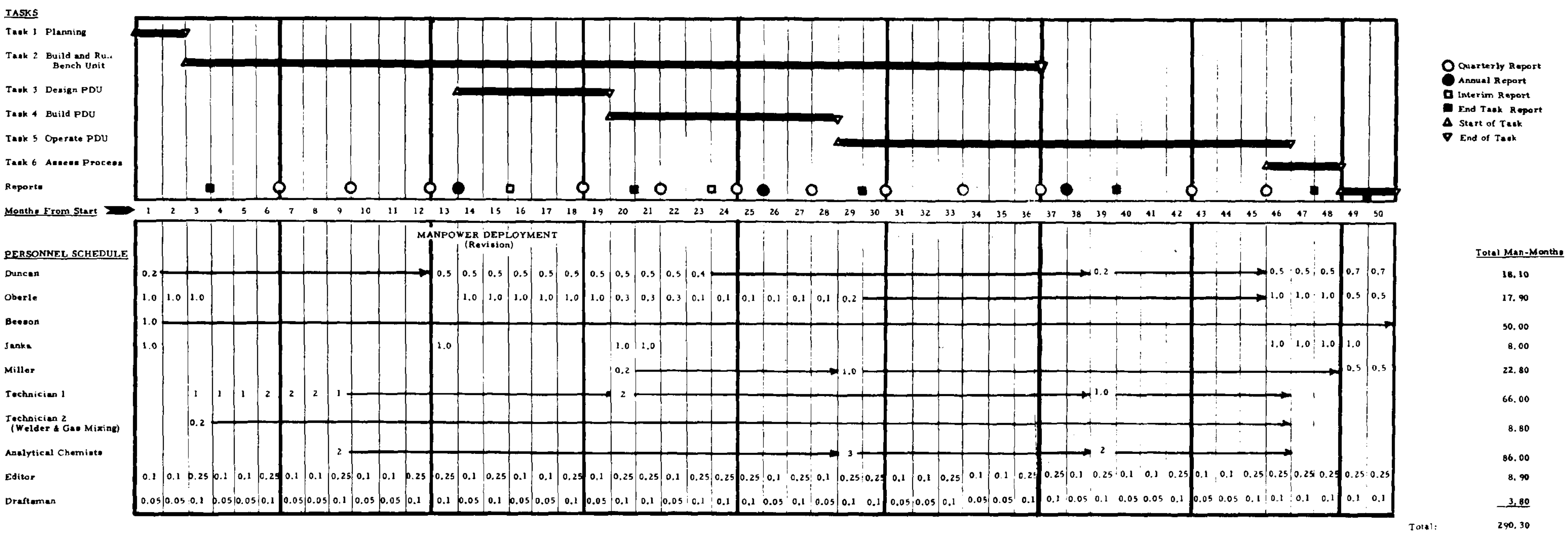
## Metering and Sampling System

The gas proceeds through a back-pressure regulator that holds the entire system pressure, is metered at approximately atmospheric pressure in a dry test meter, and is released to a vent stack. Small portions of the gas are filtered, and routed through a continuous gravitometer to a gas holder for composite sampling. Another small portion of the gas from the meter proceeds through a dryer and to a refrigerated sampler. The gas portion from the refrigerated sampler is metered and sampled for analysis. The liquid condensed in the refrigerator sampler is measured and analyzed. The analysis of the refrigerated gas and liquid are combined in their observed ratio of production to provide an accurate composition of the main gas effluent stream.

The layout of the sampling system is depicted in the flow diagram of Figure 7.

APPENDIX A

Overall Program Plan and
Manpower Schedule




PROGRAM PLAN AND MANPOWER SCHEDULE

A-1