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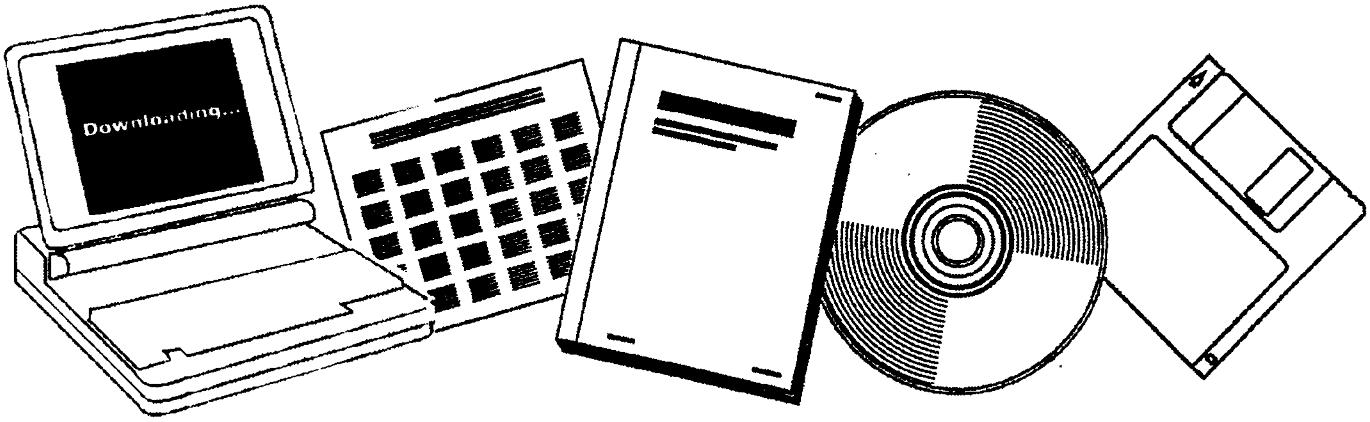
CATALYST AND REACTOR DEVELOPMENT FOR A LIQUID PHASE FISCHER-TROPSCH PROCESS. QUARTERLY TECHNICAL PROGRESS REPORT, 1 OCTOBER-31 DECEMBER 1980

AIR PRODUCTS AND CHEMICALS, INC.
ALLENTOWN, PA

JAN 1981



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DOE/PC/30021-T5
(DE81029117)
Distribution Category UC-90d

DE81-029117

Catalyst and Reactor Development for a Liquid Phase Fischer-Tropsch Process

Quarterly Technical Progress Report
for Period 1 October 1980-31 December 1980

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January 1981

Prepared for the United States Department of Energy
Under Contract No. DE-AC22-80PC 30021

REPRODUCED BY: NTIS
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National Technical Information Service
Springfield, Virginia 22161

ABSTRACT

Air Products, under contract to the DOE, has begun a three year porgram in "Catalyst and Reactor Development for a Liquid Phase Fischer-Tropsch Process." The program contains four major tasks: (1) Project Work Plan, (2) Slurry Catalyst Development, (3) Slurry Reactor Design Studies, and (4) Pilot Facility Design. During the first quarter, Task 1 has been completed with the preparation of a Project Work Plan describing in detail the methods and technical approach to be used. Task 2 has four sub-tasks. The first segment of the background studies deals with the effect of metal particle size on product selectivity and is included in this report. Based on these background studies, ten of twenty modified traditional Fischer-Tropsch catalysts to be prepared and slurry phase tested have been identified. Slurry reactor specifications have been finalized and a comprehensive product analysis scheme and data handling system has been established. Forty of the fifty supported metal cluster catalysts to be prepared and gas phase screened have been identified. Two metal cluster catalysts have been prepared. A detailed experimental plan for the first phase of Task 3 using a 5-inch diameter cold flow reactor simulator has been completed. No work on Task 4 is planned until March 1983.

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1.0 Introduction

The national need for an adequate domestic supply of distillate hydrocarbon liquids for transportation and heating fuels is becoming critical. Coal liquefaction can be an important source of liquid fuels in the future. Coal liquefaction can be accomplished by both the direct route (hydrogenation of coal in a donor solvent) or by indirect routes (gasification of coal followed by recombination reactions, e.g., Fischer-Tropsch).

Although there has been considerable research and pilot-scale effort on direct liquefaction processes in the U.S. in recent years, there has been relatively little domestic effort in indirect liquefaction; most of the indirect liquefaction technology has been developed abroad (Germany and South Africa). Indirect liquefaction via the Mobil-M process, with either methanol or Fischer-Tropsch olefins as intermediates, is a potentially attractive route to gasoline.

While both direct and indirect liquefaction should be practiced in the future, the indirect route has an advantage when highly paraffinic hydrocarbons (such as diesel fuel) are the desired products.

Many factors influence the viability of Fischer-Tropsch indirect liquefaction technology as a source of liquid fuels. Some of these factors, such as the price and availability of petroleum-based fuels, are nontechnical, virtually uncontrollable, and seemingly unpredictable. However, a major technical problem influencing the viability of the Fischer-Tropsch reaction is its poor selectivity for liquid fuels.

Product selectivity of the Fischer-Tropsch reaction has been the focus of extensive research for many years, yet still remains a prime target for technical innovation. Fischer-Tropsch technology, as it is currently practiced commercially for liquid fuels production, provides a broad range of hydrocarbon products which require costly downstream refining. Ideally, technology should be available for the selective production of gasoline and other transportation fuels.

The problem of product selectivity has received considerable attention (1-19 plus see Section 5.2.3). Selectivity can be influenced by variations in the catalyst composition and process conditions. Yet, in spite of the extensive effort devoted to this problem, a suitable catalyst has not been developed for producing a narrow range hydrocarbon product such as gasoline or diesel fuel without the coproduction of lighter and heavier undesirable products. Development of a highly selective catalyst certainly has the largest potential impact on the desired product distribution.

The Fischer-Tropsch reaction is highly exothermic, and improved heat transfer would also be expected to have a major beneficial effect on product selectivity. Higher selectivity through improved temperature control provided the impetus for research during the 1940's and 1950's to develop a liquid phase process. These efforts began in Germany in 1938 and continued until 1953, culminating with a demonstration plant in Rheinpreussen. Much of this work is summarized by Kolbel and Ackerman (20, 21, 22). During the period 1944 to 1955, the Bureau of Mines also evaluated liquid phase processes as part of their synthetic liquid fuels program and a summary of this work appears in a Bureau of Mines report (23). Finally Hall, Gall and Smith (24), working at the British fuel research station, Department of Scientific and Industrial Research, compared fixed-bed, liquid phase, and fluidized bed processes. Iron catalysts were used by all of these workers, and it does not appear that much effort was devoted to catalyst modification for improved activity and selectivity. The results and conclusions reported by these workers are generally but not always in agreement. Liquid phase operations always resulted in improved selectivity to liquid products, usually through lower methane production. However, considerable differences were reported in the space-time yield, catalyst life and ease of operation of liquid phase reactors.

In addition to improved product selectivity, liquid phase operation offers the advantages of ease of scale-up and the ability to directly utilize the carbon monoxide-rich synthesis gas produced by coal gasifiers.

The full potential of the liquid phase Fischer-Tropsch process has clearly not yet been realized, and its further development is an important part of our country's program to establish viable technology for converting coal to hydrocarbon fuels. Therefore, Air Products (APCI) under contract to the DOE has undertaken a program in catalyst and reactor development for a liquid phase Fischer-Tropsch process.

This contract spans 36 months and is divided into four major tasks. This report describes the work accomplished during the first quarter.

2.0 Objective

The overall objective of this program is to evaluate catalysts and slurry reactor systems for the selective conversion of synthesis gas into transportation fuels via a single stage, liquid phase process.

Task 1 - To establish a detailed Project Work Plan.

Task 2 - To evaluate and test catalysts for their potential to convert synthesis gas to gasoline, diesel fuel, or a mixture of transportation fuels suitable for domestic markets, and to quantify catalyst activity, selectivity, stability and aging with a target process concept involving a single stage, liquid phase reactor system.

Task 3 - To evaluate through the use of cold-flow reactor simulators the flow characteristics and behavior of slurry reactors for the production of hydrocarbons from synthesis gas. This includes (1) defining heat, mass and momentum transfer parameters which affect the design of slurry reactors, (2) establishing operating limits for slurry reactors with respect to system physical parameters, (3) developing or confirming correlations for predicting the flow characteristics and heat/mass transfer of slurry reactors, and (4) defining the necessary requirements for the design of larger scale reactors.

Task 4 - To develop a preliminary design for a pilot-scale slurry phase Fischer-Tropsch reactor.

3.0 Summary and Conclusions

3.1 Task 1 - Project Work Plan

This task has been completed by submission of the detailed Project Work Plan to the DOE Technical Project Manager. The major elements of this work plan are included in the Appendix.

3.2 Task 2 - Slurry Catalyst Development

3.2.1 Sub-Task 2a - Background Studies

An extensive survey of available information on the performance of catalysts for conventional and slurry phase Fischer-Tropsch processes has been carried out and will continue to be updated and expanded throughout the contract by periodic computer literature searches and personal contacts. Similarly, a broad data base on the operation of slurry reactors is being updated.

Ten of the twenty modified traditional Fischer-Tropsch catalysts to be prepared and tested under the contract have been identified from these studies.

3.2.2 Sub-Task 2b - Bench Scale Reactor Set-Up

Construction of a 300 mL slurry reactor is nearing completion. This reactor is being provided by the contractor for use until the two slurry reactors specified in the contract are constructed. All major items for these two reactors have been ordered.

A comprehensive product analytical scheme has been established. Computer programming to allow transfer of data from the gas chromatograph computing integrators to a Tektronix microcomputer and, thence, to the mainframe computer is nearly complete.

A Chem Data Systems gas phase screening reactor to be used to test supported cluster catalysts (Sub-Task 2d) has been installed and is now fully operational.

In addition, the following associated reactors have been provided by the contractor: (1) a 15 mL gas phase tubular reactor for screening the modified traditional catalysts, (2) a 150 mL gas phase tubular reactor for activating sufficient quantities of catalyst in the gas phase for testing in the slurry phase in order to compare activation procedures, and (3) a tubular, stirred, flow reactor for preparing coprecipitated catalysts under accurately controlled temperature and pH.

3.2.3 Sub-Task 2c - Catalyst Preparation and Slurry Reactor Testing

Ten of the twenty modified traditional Fischer-Tropsch catalysts to be prepared and tested under the contract have been identified. Preparation and testing of these catalysts will begin in the next quarter.

3.2.4 Sub-Task 2d - Metal Cluster Catalyst Preparation and Screening Tests

The remainder of this section contains potentially patentable data and has been issued under a supplementary report marked "Not For Publication."

3.3 Task 3 - Slurry Reactor Design Studies

An experimental plan has been established to evaluate flow characteristics and behavior of slurry reactors using a 5-inch diameter cold flow reactor simulator. This phase of Task 3 is intended to define design requirements for reactors without internal heat transfer surfaces. This program will investigate the effect of superficial gas and slurry velocities, solids concentration and characteristics, and liquid phase characteristics on gas holdup, mass transfer, phase dispersion and solids distribution.

3.4 Task 4 - Pilot Facility Design

No action is planned until March 1983.

4.0 Acknowledgements

The contributions to this program made by J. LaBar, L. Schaffer and E. Valagene are gratefully acknowledged.

5.0 Results and Discussion

5.1 Task 1 - Project Work Plan

The major portion of the Project Work Plan dealing with methods and technical approach, program schedule and key personnel/groups involved in this program is included in the Appendix. Not included in the Appendix are the portions of the work plan detailing project costs and man-hours.

5.2 Task 2 - Slurry Catalyst Development

5.2.1 Sub-Task 2a - Background Studies

The first segment of the background studies has dealt with the effect of metal particle size on product selectivity. This work has led to the identification of 10 of the 20 modified traditional catalysts that will be prepared and tested. This section of the background study is included in Section 5.2.3 - Sub-Task 2c - Catalyst Preparation and Slurry Reactor Testing. Additional background studies dealing with the operation of slurry reactors have provided much of the basis for the experimental plan for Task 3.

It is intended that when complete the entire background study will be provided as a separate document. Until then, various segments will be incorporated with the appropriate task to which they relate.

5.2.2 Sub-Task 2b - Bench Scale Reactor Set-Up

The following types of test reactors will be used in this program:

1. 15 mL tubular gas phase screening reactor

   Used for screening modified traditional catalysts prior to slurry testing.

2. 150 mL tubular gas phase reactor

   Used for gas phase activation of catalysts, both traditional types and supported clusters, when necessary, and for comparison with in-situ slurry phase activation.

3. 300 mL slurry reactor (provided by contractor)

   Used for slurry phase testing of catalysts until slurry reactors provided by contract are constructed.

4. 300 mL and 1000 mL slurry reactors

   Used for slurry phase testing.

5. Chem Data Systems catalyst screening reactor

   Used for gas phase screening of supported cluster catalysts.

A detailed specification and description of the slurry reactors and associated analytical system is included in the Experimental section, 6.2.2. Two sizes of reactors will be built, a 300 mL and 1000 mL; the layout of both systems will be identical and is illustrated in Figure 1. The reactors will be capable of 24 hour continuous operation and most of the monitored operating parameters will be recorded on a multipoint chart recorder. Operation is also possible with continuous slurry feed or recycle via a stirred reservoir, with the slurry level in the reactors being automatically controlled. Major items of equipment for these reactors have been ordered.

Construction of an identical 300 mL CSTR system provided by APCI is now nearly complete. Currently, the instrumentation and the C_5/C_6 product splitting column downstream of the reactor are being assembled. This reactor will be used initially for slurry phase catalyst testing to get the program underway, but will be returned to internal use when the two slurry reactors constructed for the contract are completed.

A detailed product analysis system has been set up and tested. The aim is to provide as complete as possible a total product profile so that, in combination with measured feed and product flow rates, an accurate mass balance can be obtained. The system utilizes a Carle SX-397B gas chromatograph to determine hydrocarbon isomers of C_1-C_5, CO, H_2, and CO_2 in gas phase samples taken from the top of a C_5/C_6 splitting column. Liquid products will be analyzed as two separate phases. Hydrocarbons in the range C_5-C_{25} will be routinely analyzed on a 1/8" SP2100 column in a Perkin-Elmer Sigma 1, and on a capillary, stainless steel OV-101 for greater isomer resolution. Oxygenates in aqueous phase samples will be determined using a 1/8" SP1200/1% H_3PO_4 column. In addition, representative samples will be analyzed for PONA by a fluorescent indicator column chromatography technique.

The operation of all the chromatographs is controlled by a Perkin-Elmer Sigma 10 computing integrator. Treated data together with input process parameters describing each sample will be assembled on a Tektronix 4052, which will also provide checks on consecutive sets of data, selectivity profiles and intermediate mass balances. The data and calculations will be transferred to a mainframe computer archive.

Programming to transfer data from the Sigma 10 to the Tektronix has been completed. Software for the mainframe archive is being provided by the Management Information Services Department.

The detailed description of the Chem Data Systems gas-phase screening reactor is also included in the Experimental section, 6.2.2. This system is now fully operational.

5.2.3 Sub-Task 2c - Catalyst Preparation and Slurry Reactor Testing

The evaluation of previously published conventional and slurry phase Fischer-Tropsch catalysts has not been completed. However, the study is sufficiently advanced to enable the following ten modified conventional catalysts to be recommended for slurry phase testing. The background justification for each catalyst is included and the selection is intended to be a representative cross-section of the final 20 proposed catalysts.

It is our intention to identify the remaining ten catalysts as continuing background studies and experimental results derived from the 20 day tests of the catalysts listed here provide additional data. In this way, it will be possible to include for testing any of the latest developments in an intensely studied field, as well as to optimize any that are shown experimentally to have potential.

The section included here is a brief discussion of the available literature relevant to the theory that the product distribution in the Fischer-Tropsch synthesis can be affected by the metal particle size of the catalyst as well as by shape selectivity.

Influence of Metal Particle Size on Product Selectivity

The detailed mechanism of the Fischer-Tropsch synthesis is still uncertain despite the many investigations that have been made. Recent work has tended to support the surface carbide route in which the initiation steps are the rapid dissociation of adsorbed CO and hydrogenation of the resulting carbide to give surface $-CH_x$ species (1, 25, 26, 41, 44);

$$\begin{tikzcd}
 & & CH_4 \\
CO_{ads} \arrow[r, "fast"] & (CH_x)_{ads} \arrow[ur] \arrow[dr, "slow"] & \\
 & & -(CH_2)_n-
\end{tikzcd}$$

Further hydrogenation leads to methane, while polymerization produces the higher hydrocarbon Fischer-Tropsch products. The growing chain can be terminated either by desorption from the polymerization site with or without hydrogenation, leading to alkanes or 1-alkenes, or by further reaction with adsorbed CO to give oxygenated species.

If the probability of incorporation of an additional surface $-CH_2$ into the growing chain is independent of the chain length, a conventional Schulz-Flory distribution of products occurs (6). The product selectivity implications of this distribution are severe, predicting a maximum gasoline fraction (C_5-C_{11}) of 47 wt.%, corresponding to a probability of chain growth (α) of 0.76, accompanied by a minimum of 34 wt.% C_1-C_4 and 18% diesel fraction (C_{12}-C_{25}), the remainder being heavy waxes.

With a few notable exceptions, the majority of iron and cobalt catalysts utilized in the past have synthesized product profiles largely conforming to the conventional Schulz-Flory distribution over the C_1-C_{14} range (27). Additives, promotors and supports appear to have served only to alter the value of α and, hence, the average carbon number of the product. At the low end of the range, deviations are typically found; for example, with cobalt catalysts an excess of C_1 and a deficiency of C_2-C_4 often occurs. One of the potential advantages of slurry phase operation is that the better temperature control and the ability to utilize higher CO/H_2 ratios, compared with fixed or fluidized bed reactors enables the methane yield to be minimized. However, if the conventional Schulz-Flory distribution were to completely define Fischer-Tropsch product profiles, slurry phase operation would only be able to reduce the methane formation to the value predicted by the distribution, e.g., 6 wt.% at the 47% maximum gasoline yield.

Some notable exceptions to this distribution have, however, appeared. For example, coprecipitated iron/manganese catalysts, with Fe/Mn = 1:9 and promoted with potassium, are capable of selectively producing high yields of C_2-C_4 with a high olefin content (20, 28, 29). Iron carbonyls supported on metal oxides have also been found to give high selectivities. For example, $HFe_3(CO)_{11}^-$ supported on Al_2O_3 initially produced a high yield of propylene that decreased with time as the small 2 nm particles initially produced on the surface agglomerated during the course of the reaction (30). Iron catalysts supported on zeolites also show a non-standard distribution, e.g., ZSM-5 as a support gives rise to a sharp cut-off around C_{11} (31-34).

Recently reported cobalt catalysts also show marked deviations from the conventional Schulz-Flory distribution. Using $Co_2(CO)_8$ to deposit 2% cobalt on Al_2O_3, the hydrocarbon distribution was shown to depend upon the pore size distribution of the support (8). An alumina of 90 m^2/g and mean pore radius of 30 nm gave a hydrocarbon distribution of mainly C_{10}-C_{20} peaking at C_{15}, while one of 325 m^2/g and 6.5 nm produced a high C_3-C_{10} fraction peaking at C_4.

A Co(0)/Cd(II)-A zeolite supported catalyst, obtained by reducing Co(II) exchanged A with Cd vapor, exhibited ~100% selectivity to propylene under very specific temperature and pressure conditions (35). The selectivity was lost permanently at higher temperature due, it was theorized, to sintering of the cobalt clusters to larger particles.

Similarly, ruthenium catalysts can also show sharp differences to the conventional Schulz-Flory distribution under specific preparative conditions. On γ-Al_2O_3, 1% Ru gave a hydrocarbon distribution peaking at C_{10}, with near zero C_1-C_4 (16). Ru(III) exchanged NaY and LaY zeolite gave distributions with sharp cut-offs at C_{11} and C_5 respectively (9, 37, 39), corresponding to Ru particle sizes of 4 and 1.5 nm respectively. The metal particle sizes were constrained to these dimensions by the zeolite matrix during the formation of the catalyst.

Evidence, therefore, exists to show that metal particle size influences Fischer-Tropsch product distribution. The effect of finite metal particle size can be accounted for by modifying the conventional Schulz-Flory distribution (38, 39). In the "extended Schulz-Flory" model (ESF), polymerization of the surface $-CH_2$ species occurs with a probability (α) that is independent of chain length up to a limit which is proportional to the number of metal atoms in the surface catalytic particle. This implies that the growing chain is stabilized by adsorption to the metal atom surface. The distribution of hydrocarbons in the Fischer-Tropsch product is then closely related to the metal particle size distribution of the catalyst, provided that the value of α is high. Assuming a skewed Gaussian distribution for non-zeolite supported catalysts, deviations from the conventional distribution can be reproduced by the ESF theory in terms of three parameters: α, the geometric mean of the particle size distribution $\bar{D}$, and its standard deviation σ. Results from zeolitic supported catalysts can be accounted for by an assymetric Gaussian with a cut-off at $\bar{D}$.

Conventional Fischer-Tropsch catalysts are characterized by a broad range of metal particle sizes and typically give traditional Schulz-Flory product distribution. Selectivity is produced by a narrow particle size range. For example, the results obtained with 1% Ru/Al_2O_3 (36) are reproduced by the ESF theory with $\alpha = 0.95$, $\bar{D} = 10$, $\sigma = 1.25$. Similarly, the 2% Co/Al_2O_3 results (8) are accounted for by a common value of $\alpha = 0.89$ but differing $\bar{D}$ and σ values of 4, 1.44 and 17, 2.10 for the small and large pore supports, respectively. However, even the ESF theory fails to account entirely for anomalously high yields of methane, emphasizing again the potential importance of successful slurry phase operation in minimizing this side reaction.

A major result of the ESF theory is that the limitations of the broad product profile, predicted by the conventional Schulz-Flory distribution, can be overcome. A narrow product range can by synthesized by the Fischer-Tropsch reaction if:

a. a narrow and stable metal particle size distribution can be obtained on the catalyst surface, whose size is adjusted to give the desired product range,

b. the polymerization probability α is sufficiently high to enable the influence of metal particle size to be exerted; otherwise a low molecular weight conventional Schulz-Flory distribution results.

The first condition (a) can be satisfied by:

c. the use of oxide supports of narrow pore size distribution,

d. the use of zeolite supports with the metal deposited and retained inside the structure and not on the external surface.

It can also be influenced by:

e. thermal pretreatment and activation of the catalyst (20),

f. the use of alloys, or bifunctional catalysts prepared by coprecipitation, in which separated surface crystallites of the catalytic metal or of the metal rich phase, are formed (26, 5, 41).

The second condition (b) requires:

g. the use of an active catalytic metal, e.g., Ru,

h. the use of promoters, e.g., potassium which may operate by increasing the electron density at the surface and facilitating CO dissociation (25, 40,),

i. optimum reaction conditions, e.g., high partial pressures of CO in the synthesis gas.

Proposed Catalysts for Slurry Phase Testing

The remainder of this section contains potentially patentable data and has been issued under a supplementary report marked "Not For Publication."

5.2.4 Sub-Task 2d - Metal Cluster Catalyst Preparation and Screening Tests

The remainder of this section contains potentially patentable data and has been issued under a supplementary report marked "Not For Publication."

5.3 Task 3 - Slurry Reactor Design Studies

The objectives of this task will be met by using both a 5-inch and a 12-inch diameter cold flow reactor simulator. The 5 inch simulator will be used to define design parameters for reactors using external heat transfer. The 12 inch simulator will be used to evaluate fluid flow in three phase systems in the presence of internal heat transfer surfaces. The 5 inch reactor simulator work will be undertaken first.

During this quarter a detailed experimental plan has been developed for the 5 inch reactor simulator. This plan is outlined here and described in detail in the Experimental section, 6.3. Also included in the Experimental section is a description of the apparatus.

Outline of 5-Inch Diameter Reactor Simulator Program

I. Experiments in Kerosene and Water
  A. Independent Variables
    1. Five gas superficial velocities: 0.05-0.5 ft/sec
    2. Three liquid superficial velocities: 0-0.1 ft/sec
    3. Two different solids: silica and iron oxide
    4. Four solids concentrations: 0, 10, 20, 30 wt.%
    5. Three solid sizes: 1-5 μm, 45-53 μm, 90-106 μm
  B. Dependent Variables
    1. Gas hold-up
    2. Solids dispersion
    3. Gas dispersion

II. Experiments in Water Only
  A. Independent Variables
    Same as in I.
  B. Dependent Variables
    1. Mass Transfer
    2. Liquid dispersion

In addition, selected liquid dispersion experiments will be performed in kerosene and a search will be made for an acceptable method of measuring mass transfer in kerosene under the cold-flow reactor conditions.

6.0 Experimental

6.1 Task 1 - Project Work Plan

No experimental.

6.2 Task 2 - Slurry Catalyst Development

6.2.1 Sub-Task 2a - Background Studies

No experimental.

6.2.2 Sub-Task 2b - Bench-Scale Reactor Set-Up

A. Slurry Reactors

Two sizes of slurry reactors will be built, one 300 mL and one 1000 mL; the layout of both systems will be identical and is illustrated in Figure 1. The availability of two reactor sizes will give flexibility to the catalyst testing program with the more active catalysts requiring high space velocities being tested in the smaller reactor.

For safety, the gas supply cylinders will be manifolded outside the laboratory building, and to prevent the build-up of toxic or flammable concentrations of CO and H_2, the reactors and all auxiliary equipment will be located inside ventilated reactor cells. The gas supplies to the reactors will be automatically shut off in the event of ventilation fan failure.

The reactors will be capable of 24 hour continuous operation, and most of the monitored operating parameters will be recorded on a multipoint chart recorder. Operation is also possible with continuous slurry feed or recycle via a stirred reservoir with the slurry level in the reactors being automatically controlled.

All necessary safety and shut-down devices will be employed. The pressurized part of the system will be protected by 1100 psig vent valves, and the minimum pressure rating of components under their conditions of use will be 1500 psig. All heaters will be fitted with upper limit temperature switches to prevent overheating if their primary controllers fail. Overheating of the reactor contents will give rise to automatic gas shut-off and maximum water flow through the reactor cooling coils. Pressure limit switches coupled to a transducer monitoring the reactor pressure will also automatically switch off the inlet gas supply, should the reactor overpressurize or a significant leak develop.

a. Gas Manifolds and Inlet Lines

The regulated pressure of the CO and H_2 supplies will be 1000 psig maximum, and both manifolds will be equipped with vent valves set at 1100 psig, with automatic magnetic excess flow shut-off valves to guard against major leaks. The gases will be piped into the reactor cells through 1/4" stainless steel tubing, and, after oxygen removal and drying stages, both lines will be split between the two reactors with further pressure letdown using piston regulators.

The inlet flow rates of CO and H_2 will be individually controlled by Brooks thermal mass flow meters and will be recorded and time integrated. After carbonyl removal from the CO stream, CO and H_2 will be mixed and input to the reactor via a preheater.

With this system, feed gas blends of CO and H_2 between 0.5 and 2.0 can be produced with an absolute accuracy of ±2.7% and maintained to within ±0.5%. Feed gas flow will be up to 150 STP l/h to give a GHSV range of 300-1000 h^{-1}.

b. Reactors

The reactors themselves will be Autoclave Engineers stainless steel autoclaves of 300 mL and 1000 mL sizes, equipped with Magnadrive II stirrers capable of delivering 16 in. lbs. of static torque and 0.63 HP @ 2500 rpm. They will contain a stainless steel cooling coil, thermocouple well and baffle assembly, and will be fitted with rupture discs. The gas inlet point will be beneath the 6-flat-bladed turbine impeller, which, because it is a hollow shaft Dispersimax type, will induce gas backmixing from the gas space above the slurry.

Exit gas will pass through an air cooled partial condenser with a controlled top temperature of 200°C to reflux slurry oil back to the reactor, and then through a heated line to a back pressure regulator to be letdown to 5 psig.

c. Reactor Temperature Control

The reactors will be heated under thermostatic proportional control, and typical temperatures will be 250-300°C with a maximum of 350°C. The heat produced by the exothermic Fischer-Tropsch reaction will be removed by evaporation of cooling water in the internal coil, and, for safety, the disappearance of inlet water pressure will shut off the reactor gas supply. The flow of water to the cooling coil will be controlled by a solenoid and regulating valve in series, activated by the reactor thermocouple. A high temperature alarm will open a bypass solenoid to the cooling coil and shut off the gas supply, as already described.

d. Slurry Recycle

A high temperature, differential pressure transducer, connected between the gas inlet and outlet lines, will be used to monitor the level of oil slurry in the reactor. When operating with continuous slurry feed and withdrawal, slurry will be pumped into the reactor at a constant rate of up to 3.3 vol/vol/h from a stirred glass reservoir by a Bran and Lubbe N-P31 piston metering pump constructed of 316 stainless and tungsten carbide. A rise in the differential pressure above a set point will open an electrically operated ball valve and allow slurry to transfer back to the glass reservoir via throttling valves. A high/low alarm on the differential pressure transducer will shut off the slurry pump if a malfunction of the transducer or an abnormal level of slurry should occur.

The glass reservoir will be protected by a 3/4" in-line relief valve, which is sized to allow a maximum pressure of 10 psig in the event of a malfunction of the slurry control system.

An inventory of the total slurry volume will be maintained. Slurry may be removed from the reservoir for reactivation or simply replaced with fresh material. If a net synthesis of high boiling hydrocarbons occurs, the excess oil may be filtered from the slurry in the reservoir via a sinter and vacuum line. Alternative treatments of the slurry are possible, e.g., vacuum distillation of the oil to recover products during recycle, and will be similarly carried out in glass apparatus.

e. Product Distillation

After pressure letdown to 5 psig, the reactor product will be passed to a glass C_5/C_6 splitting column, also protected by a 3/4" in-line relief valve in the event of back pressure regulator failure. The column will be fitted with a refrigerated top coil and temperature controlled reboiler.

Overhead from the column, containing unreacted CO and H_2, CO_2, water vapor and C_1-C_5 hydrocarbons, will pass through a calibrated wet test meter to a vent line.

Bottom products, composed mainly of hydrocarbons of C_6 and above plus water, will be collected for analysis and weighed or, during unattended operation, transferred via a syphon to a metal storage container fitted with a refrigerated vent.

B. 15 mL Gas Phase Tubular Reactor

A 15 mL gas phase tubular screening reactor is illustrated in Figure 2. This reactor will be used to rapidly screen modified conventional Fischer-Tropsch catalyst preparations so that limited optimization studies of such factors as metal loading, support pore size, thermal pretreatment and activation procedure can be made before subjecting a catalyst to a full 20 day slurry phase test program.

C. Analytical Procedures and Data Handling

The main analysis system consisting of five gas chromatographic schemes is illustrated in Figure 3. Permanent gases and light organic products are analyzed by a Carle 397B process gas chromatograph, which performs two discrete analyses simultaneously. The system consists of two sections:

1. a flame ionization detected (FID) gas chromatograph, and
2. a thermistor type thermal conductivity detected (TCD) gas chromatograph.

The FID system utilizes a helium carrier and contains two columns along with column switching valves for the analysis of C_5 and lower carbon number hydrocarbons (see Figure 4 FID). Any components above C_5 are eluted together as a C_{6+} backflush. The gas-liquid separation stage of the reactor will be optimized to produce little or no C_{6+} response.

The FID system fails to resolve ethylene/ethane; however, these components are resolved by a second analysis in the TCD section.

The TCD section utilizes a dual carrier gas system (helium/nitrogen) with two columns, column switching valves and a hydrogen transfer system. The analysis of all components except hydrogen is performed with a thermistor detector in a helium carrier. Analysis of hydrogen in helium is insensitive because of their similar thermal conductivities, and a hydrogen transfer system is used to circumvent this problem. The hydrogen component from the sample is diffused from the helium carrier through a heated palladium wall into a nitrogen carrier stream, where it can be efficiently detected utilizing a hot wire thermal conductivity detector. The outputs from the thermistor and hot wire detectors are multiplexed and appear as one chromatogram (see Figure 4 TCD).

By this means, all components in the gaseous product of the C_5/C_6 splitter are analyzed except water vapor. This will be determined by utilizing a Carle 111 gas chromatograph with a Porapak QS column/helium carrier and a thermistor detector. A signal multiplexer device was built which allows the water vapor analysis to be run concurrent with the Carle 397B gas analysis.

The combined output from the thermal conductivity detectors and the flame ionization detector is processed by a Sigma-10 computing integrator. This also controls all valve functions and multiplexer switching in the system (see Figures 5 and 6).

Liquid samples from the reactor will consist of an aqueous phase containing oxygenates and an organic phase containing C_6 and above. After separation, these phases are analyzed utilizing a Sigma 1 gas chromatograph which is equipped with dual flame ionization detectors and a Varian liquid auto sampler. Aqueous phase samples are analyzed with a 1/8" x 20' SP1200/1% H_3PO_4/ Supelcoport column (Figure 7). Organic phase samples are analyzed with a 1/8" x 10' SP2100/Supelcoport column (Figure 8). Sample vials are loaded into the Varian auto sampler and a basic program described under the program section of this report which is resident within the Sigma-10 computing integrator controls sampling and column switching between aqueous and organic phase samples. The Sigma-10 used for liquid samples is the same unit used for gas analysis; the unit can simultaneously handle both analyses.

A second Sigma-10 is used in conjunction with a Sigma-3 chromatograph which is fitted with an OV-101WC 150 meter x 0.010" capillary column. This column is used for isomer separations in the organic phase samples (Figure 9). This analysis will not be run routinely but will be used to analyze specific samples within a run to determine the branched isomer compositions present. Routine analyses with the Sigma 1, above, will produce branched vs. straight chain ratios but will not identify individual isomers.

A column chromatographic group separation method (ASTM D1319-77 PONA) will also routinely be applied to the organic liquid phase. ASTM D1319 is a standard method for the determination of saturated, non-aromatic olefinic and aromatic concentrations in liquid samples by a fluorescent indicator absorption method. All apparatus and reagents for this method have been ordered.

ASTM D-2159-64 is a standard method for the determination of naphthenes in saturated fractions by a refractive index intercept method. ASTM D1319 does not distinguish between non-cyclic paraffins and naphthenes. ASTM D2159 will be applied to the paraffin containing cut from the ASTM D1319 test to effectively determine the naphthene content.

Several methods for slurry oil analysis have been investigated. GC methods attempted thus far have not been satisfactory. The low volatility of the vacuum oil intended for use as the slurry base and the high number of components present, remain as principal problems in any GC analysis, giving rise to a broad overall response with minimal resolution of individual peaks. This method could only be used, therefore, to detect changes in the composition by comparison of ranges rather than discrete peaks.

An HLPC method is, therefore, currently under consideration. It is anticipated that HPLC will allow a better discrete analysis since it is not affected by the low volatility of high boiling components. An HPLC apparatus is currently being assembled and delivery of the solvent (1,1,2-trichloro-trifluoroethane) is awaited.

Computer Interfacing

Because of the large amount of data which will be generated during this project, it is necessary to utilize a computer for data processing. A Tektronix 4052 graphics computer will ultimately be used to collect, correlate and concentrate data from the analysis system and from operator manual entries. After concentration, this data will be transmitted via a telephone line to the mainframe computer for archiving and manipulation. A second copy of the data will be maintained at the laboratory for rapid access and experimental control. As the 4052 system is not yet installed, a Tektronix 4051 system is currently being utilized to demonstrate the feasibility of linkage to the analysis system.

Programming Section

Several programs for the Tektronix and Sigma-10 systems have been written. These programs fall into either the analytical aid or data transmission areas. Programs which aid in the analysis sytem have principally been written for the Sigma-10 computing integrator. GAS is a program which allows the operator to schedule gas analyses for up to two separate reactors. Gas samples are automatically taken at prescribed times from designated reactor streams. The program allows 24 hour unattended analysis. The gas chromatograph is hardware limited to serving only two reactors. If only one reactor is being used, automatic recalibration at specified times is also possible.

LIQUID is a program which allows the operator to schedule overnight analyses of both aqueous and organic phase liquid samples. Organic phase samples are first loaded into the Varian auto sampler followed by the aqueous samples. The program monitors the sampling and switches columns and analysis methods before initiating aqueous phase samples. This program will allow overnight automated analyses of liquid samples.

BAR is a program which performs post-analysis calculations on hydrocarbon capillary analyses. This program constructs a profile of the straight-chain vs. branched areas for each carbon number range.

Figure 9 shows a capillary separation of #2 heating oil. Figure 10 shows a representative output from BAR which greatly simplifies the capillary analysis and makes direct visual comparisons possible.

Two programs have been written during this quarter to facilitate the transfer of data from the Sigma-10 integrator to the Tektronix computer. TRANS-1 is a Sigma-10 resident program which interacts with the second program, TRANS-2, which is Tektronix resident. The Tektronix unit was designated as a second terminal device for the Sigma-10 system. This allows a master/slave relationship between the Tektronix and Sigma systems. Because of its enhanced capability, the Tektronix system is designated as the master and is in complete control of the Sigma system. The Tektronix system initiates communications with the Sigma on a command level and establishes the protocol used under program level communications. The Tektronix then commands the execution of TRANS-1, the transfer program which is Sigma resident. TRANS-2 sync. is fully protected and performs sync and data integrity checks. The program also contains routines for retrieving data from the Tektronix tape unit and for directorizing the data tape. On delivery of the 4052 system, TRANS-2 will be modified for tape-to-disc operation.

D. Gas Phase Reactor and Analytical Test Unit For Metal Cluster Catalyst Screening

The gas phase screening reactor is a fully integrated reactor-chromatogrpahy system built by Chem Data Systems. The basic unit is a CSD model 803CF-HP Continuous Flow Reaction System with reactor bypass/purge and outlet sampling valve for operation to 1500 psig and 700°C. In addition to the basic unit, the following modifications have been provided:

- Provision for 4 reactant gas inlets or 2 liquid and 2 gas inlets with electronic mass flow controllers - one pre-calibrated for carbon monoxide and one calibrated for hydrogen. Also includes diverter valves in flow module (1500 psi).

- Provision for one set of six gas sampling loops in matched pairs - 1 mL, 2 mL and 4 mL.

- Provision for 2 pressure gauges - S.S. with S.S. diaphragm seals provided at top and bottom of reactor with purge valves and pressure relief valves and auxiliary pressure gauge and purging system for 1500 psi operation.

- One back pressure regulator for operation at 1500 psi on reactor outlet, S.S. with all fittings.

- CDS 0101-5542 Second Catalytic Reactor Module, with reactor tubes 9" x 3/8" O.D., 1/4" I.D.

- Gas/Liquid Separator for each reactor.

- Provision for inserting movable thermocouple probes in reactor bed - (Thermowell) - Type K Thermocouple CDS 0101-5570.

- Extra set of reactor core, tube and cap for 9" x 3/4" O.D., 1/4" I.D.

- Provision for a possible third reactor module. (This module would be a completely separate module).

- CDS 0810-1070 Model 450 Failsafe - Automatic shutdown of feed and power in case of temperature control failure.

- Model 5060 Automatic Programmable Oven Module with Model 210 Temperature Programmer with automatic door open control.

- CDS 0101-5560-3 Dual Flame Ionization Detector Module, including electronics.

- CDS 0800-5540 Thermal Conductivity Detector Module, including detector heater control and bridge circuitry, factory installed in CDS 803CF System.

- CDS 0210-574-2 Cryogenic Option for Control to 0°C.

- Column Switching Valve for use with GC column selection.

- Column Backflush Valve - automatically operated.

- Automation - with GC - includes Model 400 Programmable Timer with battery protection, Model 400-001 Function Selector for Manual/Auto Setup of Valve Drivers, and 5 Valve Drivers.

- Spectra Physics SP4100 Computing Integrator for data acquisition and manipulation.

This unit is designed for automatic unattended operation.

The analytical system consists of dual columns with dual FID and TCD. Sub-ambient temperature programming capability is available. Column selection has not yet been finalized but will likely follow closely the types used with the slurry phase testing program.

6.2.3 Sub-Task 2c - Catalyst Preparation and Slurry Reactor Testing

None of the modified traditional Fischer-Tropsch catalysts have been prepared yet. To obtain consistent results with catalysts prepared by coprecipitation techniques, it has been reported that close pH and temperature control must be effective during precipitation with rapid washing and filtering of the product immediately afterwards (32, 33).

A stirred tubular flow reactor has been built for this purpose and is illustrated in Figures 11 and 12. Reactant solutions, e.g., a solution of mixed metal nitrates and an ammonia solution, are separately and tangentially fed in at the bottom at rates controlled by feedback from a pH probe situated near the outlet. Residence times are typically 20 seconds. By this means, the pH of precipitation can be controlled to ±0.1 pH units.

The reactor has been tested with weak acid/base titrations and will shortly be used for catalyst preparation.

6.2.4 Sub-Task 2d - Metal Cluster Catalyst Preparation and Screening Tests

The remainder of this section contains potentially patentable data and has been issued under a supplementary report marked "Not For Publication."

6.3 Task 3 - Slurry Reactor Design Studies

There are two complimentary parts to the experimental program in this task. From January through December 1981, a 5-inch diameter column will be used to simulate the operation of slurry reactors without internal heat transfer surfaces. Operation with internal heat transfer will be studied using a 12-inch diameter column from December 1981 through January 1983. It is not proposed to detail the 12 inch testing program at this stage since it will likely be dependent in part on results obtained with the 5 inch simulator. Instead, it is planned to submit for review and approval the final version of the 12 inch column testing program by October 1981.

The current experimental plan will therefore describe in detail the testing program to be carried out in the 5 inch simulator.

A. Apparatus

The 5 inch simulator and its associated gas and slurry recirculation equipment are illustrated diagramatically in Figure 13.

The column is constructed of plexiglass and is situated in a ventilated hood to prevent the buildup of flammable mixtures of kerosene vapor. Operating hazards are also reduced, and changes in solids concentration during the course of a test by evaporative losses of hydrocarbon are minimized by utilizing a gas recycle system.

Two 100 gallon tanks, equipped with stirrers designed to totally suspend the contained solids, will serve as slurry reservoirs. Slurry will be pumped into the column at a constant measured rate by an air driven 1" Warren Rupp Sandpiper pump via a dual diaphragm tranquilizer. Under normal operation, slurry and gas will flow concurrently through the distributor plate. However, if at the higher ranges of liquid velocities or solids loadings concurrent flow should result in too high a pressure drop across the distributor plate, we will optionally use a separate inlet immediately above the gas distributor for the slurry.

Gas and slurry exiting the top of the column will be allowed to separate in an 11-1/2" diameter closed cylinder attached to the column head. Gas will be recycled to the column inlet by a Gast, oil free, rotary vane pump driven by an explosion proof motor with automatic makeup from an external supply of any gas lost from the system.

The entire system will be fitted with all necessary safety devices, e.g., pressure relief and check valves.

The 5 inch column also features interchangeable gas distributor plates. Because of the potential importance of gas/liquid mass transfer in the operation of Fischer-Tropsch slurry reactors, the gas/liquid interfacial area will be maximized in the cold flow simulator studies by a suitable choice of gas distributor that is also commensurate with full scale industrial usage. The optimum distributor design is, however, a function of gas and slurry flow rates. In the 5 inch column program it is therefore proposed to utilize a compromise that should be suitable over a large part of the operating range, i.e., a 1 mm hole perforated plate with 13.8% hole area. This will avoid chain bubbling at the maximum gas velocities to be studied, while ensuring turbulent gas flow into the slurry at superficial velocities above 0.2 ft/sec. The effect of concurrent slurry flow on the gas flow behavior through this distributor is not easily calculable in advance. Therefore, one of the prime objectives of the initial tests will be to verify the suitability of this distributor over the range of slurry velocities and solids loadings to be studied. The type of distributor is not, however, a variable in this program, and, once tested out, will remain fixed during the course of the experimental tests.

B. Methods and Approach

1. Independent Variables

a. Solid Types and Particle Sizes

It is proposed to study two solids that are closely related to precipitated or supported Fischer-Tropsch catalysts: Fe_2O_3 and SiO_2. Their densities are listed in Table 1.

Three size ranges will be utilized: 1-5 μm, 45-53 μm, and 90-106 μm. Typically, Fischer-Tropsch slurry catalysts should be in the range of 30 μm (20). For particle diameters ≤50 μm and solids concentrations of ≤16 wt.%, three phase slurry reactors exhibit hydrodynamic behavior similar to two phase gas/liquid bubble columns (45). The chosen range of particle sizes should therefore both be typical of slurry catalysts and also indicate any transitions in column hydrodynamics away from two phase flow.

b. Liquids

Two liquids will be used: kerosene and water. Table 2 compares relevant physical properties at 20°C with those of a typical parafinic Fischer-Tropsch slurry oil at 260°C. While water presents no handling difficulties and facilitates mass transfer and liquid dispersion measurements, many of the physical properties of kerosene are closer to those of a heated paraffinic oil. In particular, kerosene has a lower surface tension than water, and should exhibit surface interactions with the suspended solids that are similar to those occurring in a Fischer-Tropsch slurry and which are relevant to solids dispersion effects.

Because of the large number of variables and the limitations of time, it is therefore proposed to concentrate measurements of gas hold-up, gas and solids dispersion in kerosene slurries while carrying out most of the determinations of mass transfer and liquid dispersion in water slurries.

c. Solids Concentration

Four solids concentrations will be studied: 0, 10, 20 and 30 wt.%.

The zero solids measurements will allow the operation of the 5 inch column to be checked against existing correlations for two phase bubble columns and will also facilitate the photographic determination of gas dispersion.

The other three concentrations are typical of Fischer-Tropsch slurry operations and are ranged about the 16% value at which, for solids $\leq$50 μm, it is claimed that three phase flow can be approximated by two phase flow (88).

d. Gas

Nitrogen will be used for all experiments except the determination of mass transfer for which air, and possibly CO_2, will be utilized.

e. Gas Velocity

Five superficial gas velocities will be studied: 0.05, 0.10, 0.20, 0.35, and 0.50 ft/sec.

For particle sizes $\leq$50 μm and zero liquid flow, gas velocities lower than 0.2 ft/sec are expected to produce a homogeneous (bubbly or quiescent) flow regime. With increasing gas velocity, a transition should occur to slug flow in the 5 inch column or heterogeneous (churn-turbulent) flow in the 12 inch column (42).

The range of gas velocities is therefore chosen to span the expected change in flow regimes, and includes typical operating values, e.g., the 0.3 ft/sec of the Rheinpreussen-Koppers demonstration plant. The lowest gas velocity of 0.05 ft/sec, particularly at zero liquid flow rate, is expected to lie on the boundary of incomplete solids suspension.

f. Liquid Velocity

Three superficial slurry velocities will be used: 0, 0.05, and 0.10 ft/sec.

At the space time yields of the Rheinpreussen-Kopper plant, the heat release per unit volume is of the order 20×10^3 BTU/h/ft^3 (20). With a $\Delta T \sim 9°F$ for passage through the column, this heat release in the 5 inch simulator would require a slurry flow rate of 0.1 ft/sec. The range chosen for study is therefore comparable with the velocity required for external heat transfer with a moderate temperature rise on transit through the column.

2. Dependent Variables

Because of the large number of combinations of independent variables, it is necessary to be selective in the measurements to be made in the two liquid slurry bases as already discussed in Section 6.3, subparagraph B.1.b.

The 5 inch column experimental program is divided into two six-month segments: first six months, gas hold-up, gas dispersion and solid dispersion; second six months, gas liquid mass transfer and liquid dispersion. The total number of experiments in each time segment will largely depend upon the time for the 5 inch column to reach equilibrium under the conditions of the particular experiment. Should the time to equilibrium be sufficiently great that all of the combinations of independent variables cannot be evaluated, every effort will be made to maximize the information obtained. At the end of the scheduled time, an assessment will be made of the results to date and in consultation with the DOE Project Manager, a decision will be made whether sufficient data have been obtained or whether additional experimental work is necessary.

During the first six months of operation of the 5 inch column, we will determine in chronological order:

a. Gas Hold-Up/Gas Dispersion in Kerosene and Water in the Absence of Solids

Measurement of gas hold-up at the 15 gas/liquid velocity combinations in the absence of solids is relatively rapid to to carry out and will provide a check on the column operation by comparison with existing correlations.

Gas hold-up will be measured by allowing the column to equilibrate at the set values of gas and liquid flow and subsequently stopping both flows, and measuring the decrease in height of the stagnant column contents.

Gas dispersion and bubble diameters will be estimated from photographs of the equilibrated column. It is envisaged that this will only be possible for the case of zero solids content.

b. Gas Hold-Up/Solids Dispersion in Kerosene Slurries

Determinations of these two parameters will be made for the 270 combinations of the independent variable. One of the major objectives of the initial tests will be to determine the suitability of the gas distributor plate over the entire range.

Gas hold-up will be determined by the above method, incorporating a known amount of solids into the recirculation liquid via the slurry reservoir tank. The major determining factor in the rate of acquisition of data points will be the time required for equilibration of the column/reservoir closed system.

Solids dispersion will be measured, after equilibration but prior to each gas hold-up determination, by sampling the column contents at five equidistant points up the length of the column.

c. Gas Hold-Up/Solids Dispersion in Water Slurries

It is planned to make representative measurements at selected data points in aqueous slurries of gas hold-up and solids dispersion to enable correlation to be made with the kerosene studies and with previous work carried out at APCI using larger particle sizes. The number of determinations will, however, depend on the column equilibration time.

During the second six months of operation of the 5-inch column, the following determinations will be made:

d. Gas Liquid Mass Transfer/Liquid Dispersion in Water Based Slurries

Overall gas liquid mass transfer rates will be measured by determining the rate of transfer of oxygen from air into a continuous deoxygenated aqueous slurry supply fed into the pre-equilibrated column. Oxygen concentrations will be measured in the outlet slurry system using dissolved oxygen electrodes.

Axial liquid dispersion coefficients will be determined by numerically fitting computer generated curves to the output of a conductivity probe in the slurry outlet stream following injection of a concentrated KCl solution spike into the inlet of the pre-equilibrated column.

It is intended to determine these two parameters for all 360 combinations of the independent variables. However, some selection of data points may be necessary depending on the equilibration time of the column/reservoir system.

e. Gas Liquid Mass Transfer/Liquid Dispersion in Kerosene Slurries

Depending on the available time and hence on the equilibration rate of the column/reservoir system, selected measurements will be made of these two parameters in kerosene slurries.

Liquid dispersion coefficients can be measured by monitoring the rise in concentration of an oil soluble dye injected as a spike at the column inlet in the outlet slurry flow using UV or visible spectroscopy.

It is anticipated that measurements of gas/liquid mass transfer rates or gas/liquid interfacial area in kerosene slurries could be made using a method that has been applied to xylene in small scale stirred or packed gas/liquid contactors (43). In this method, the rate of adsorption of CO_2 from CO_2/N_2 mixtures into cyclohexylamine solutions in kerosene would be determined. The addition of 10% isopropanol may be necessary to maintain the resulting carbamate in solution. Some development work would be necessary to utilize this method in the 5 inch slurry reactor simulator, e.g., to determine the optimum concentration of CO_2 in the inlet gas and the range of amine concentrations to be employed.

These measurements are therefore the most strongly effected by the time available at the end of the 12 month 5 inch column testing program.

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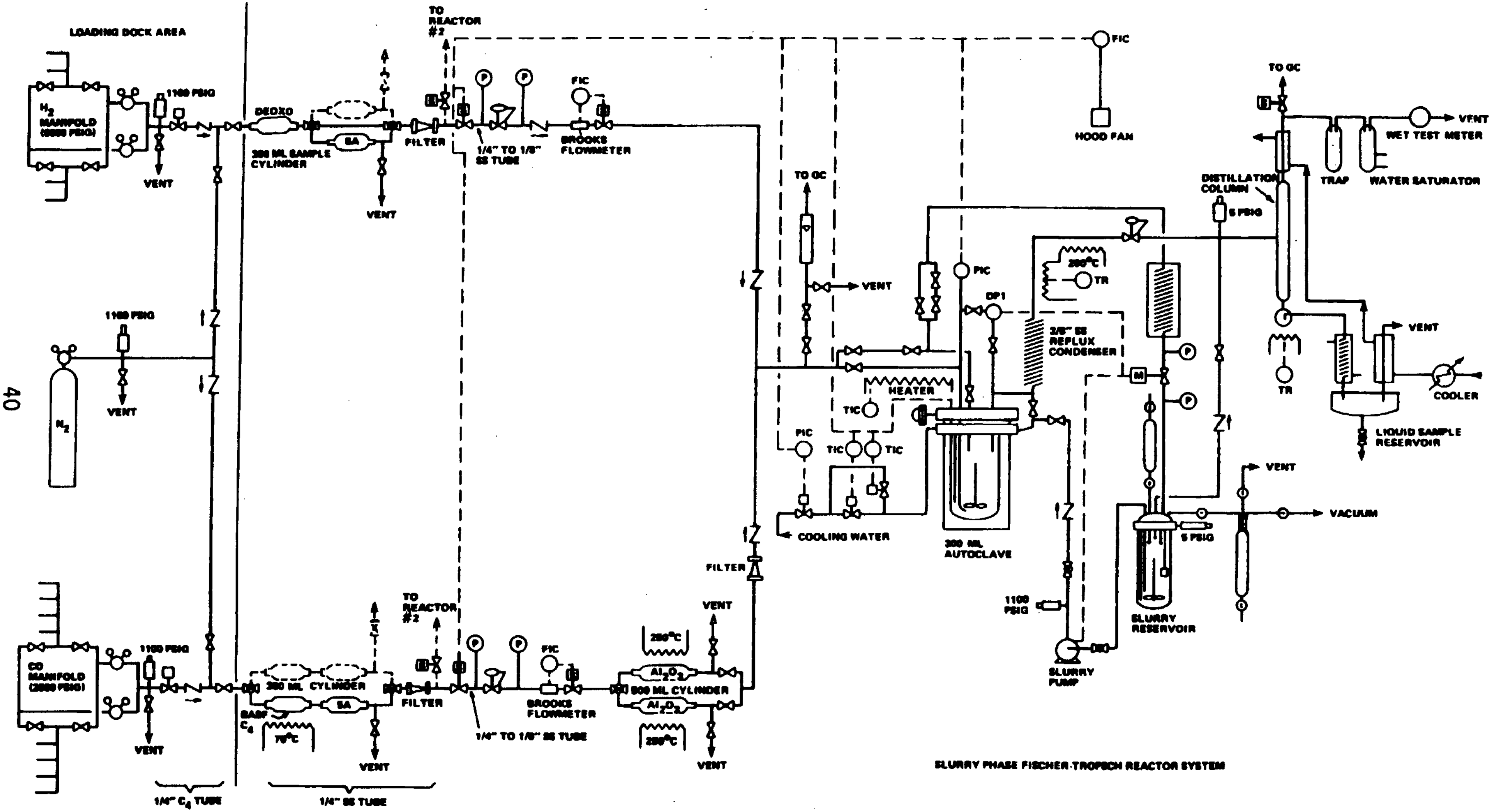
8.0 Figures

FIGURE 1

SLURRY REACTOR FLOW SHEET



SLURRY PHASE FISCHER-TROPSCH REACTOR SYSTEM

FIGURE 2

15-ML TUBULAR REACTOR

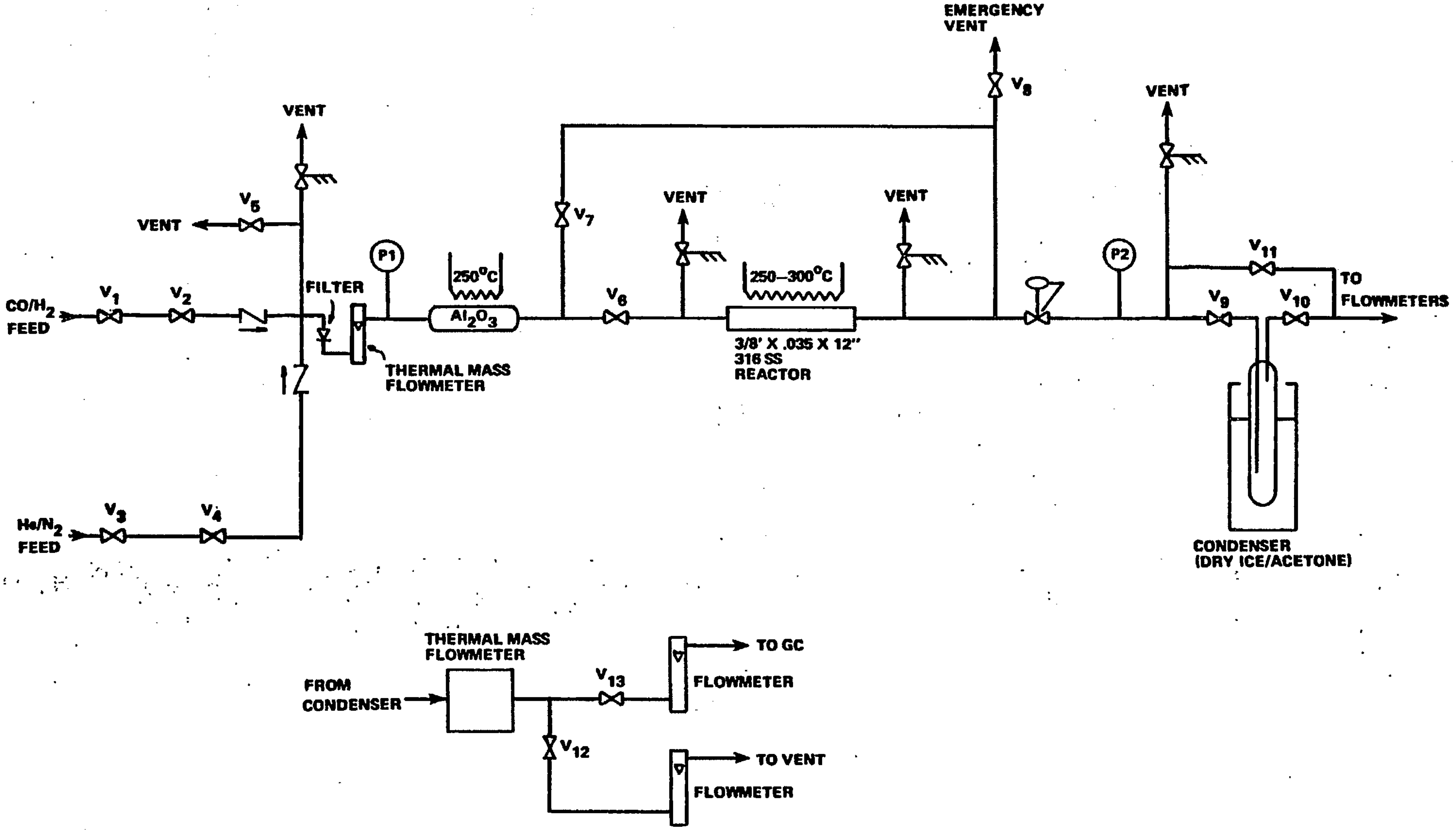
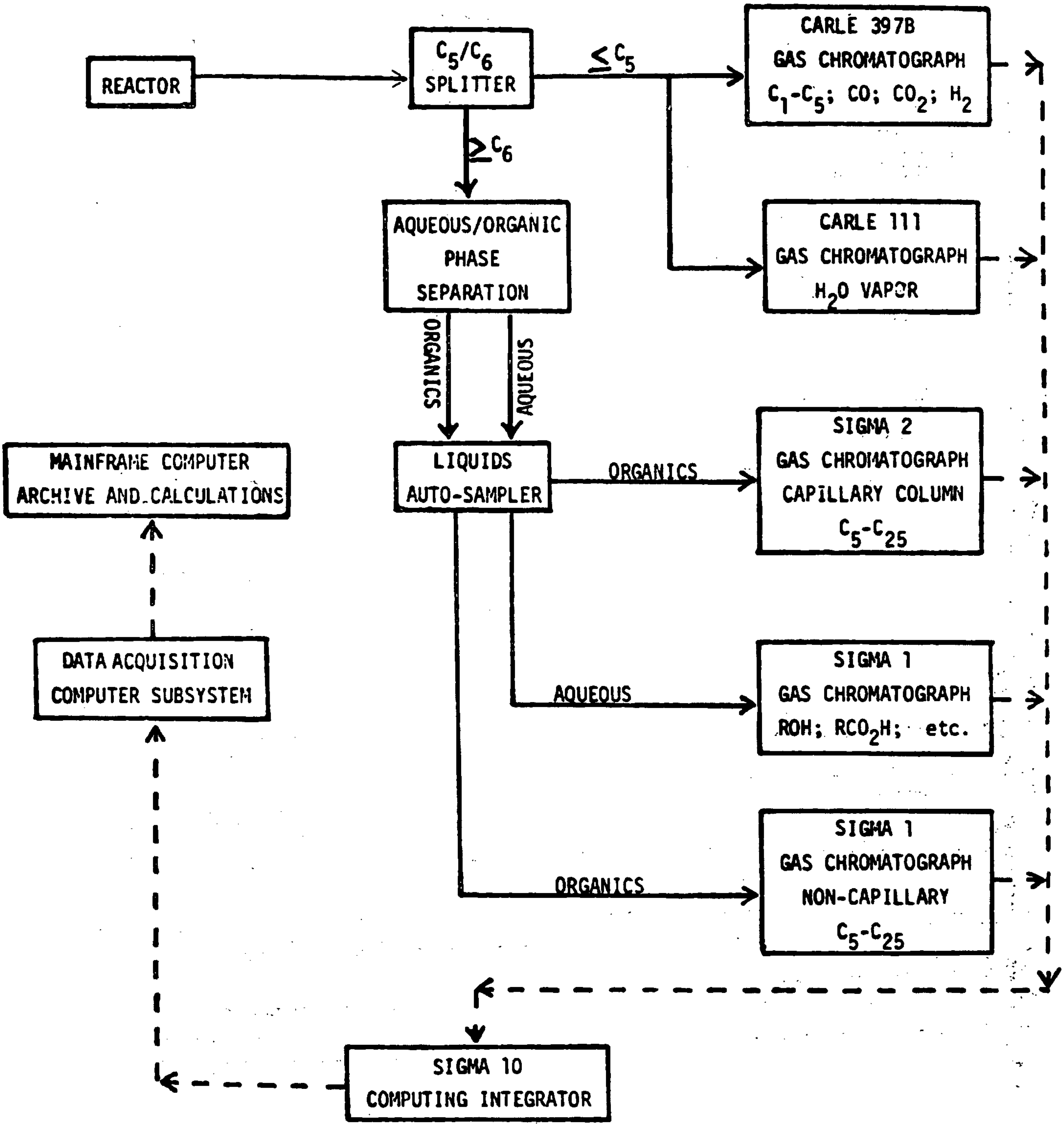


FIGURE 3

PRODUCT ANALYSIS SYSTEM



——— Sample Flow

– – – Data Flow

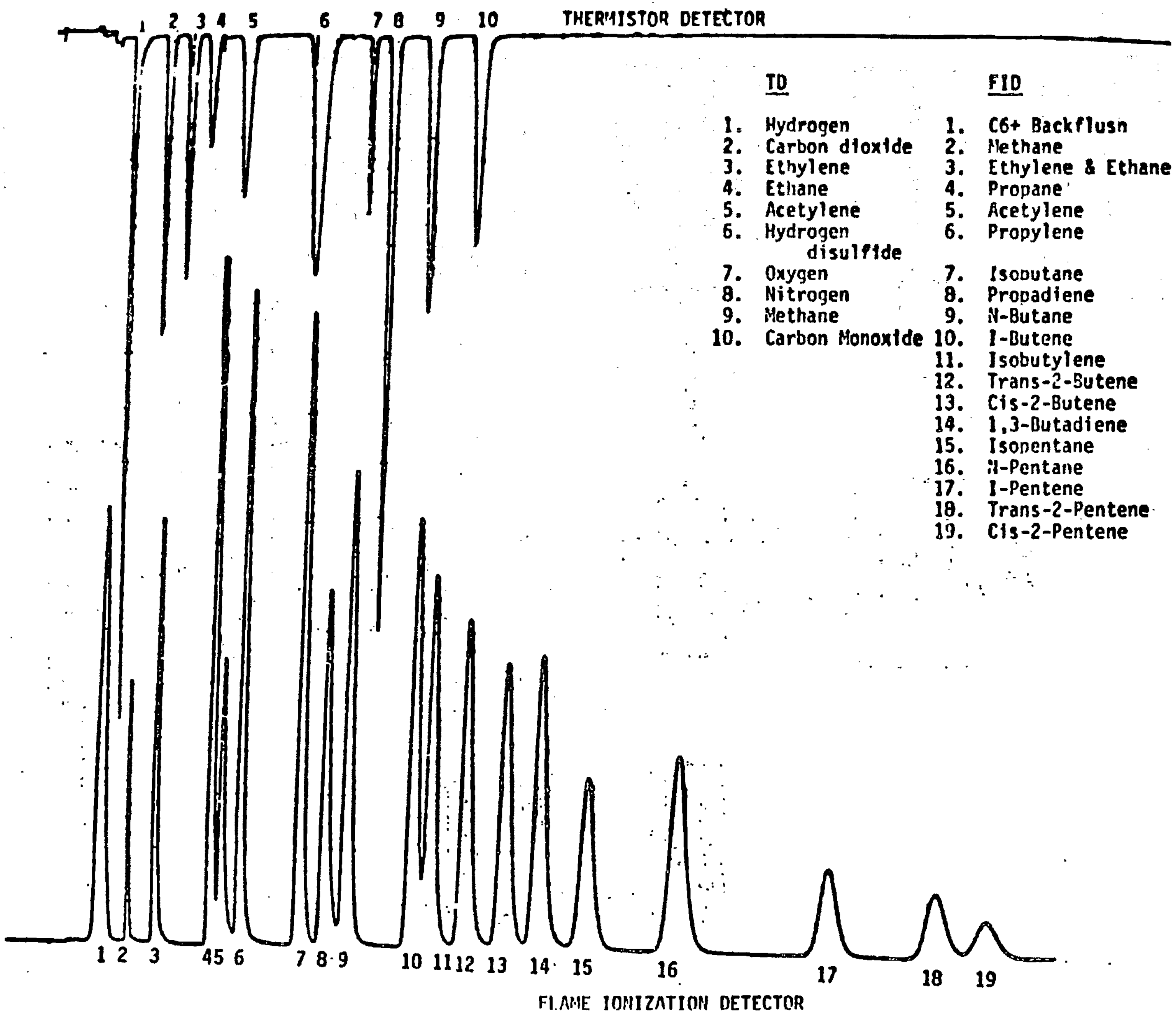


FIGURE 4

TYPICAL GAS ANALYSIS ON CARLE 357B

FIGURE 5

FUNCTIONAL BLOCK DIAGRAM

SIGMA 10 GC DATA SUBSYSTEM

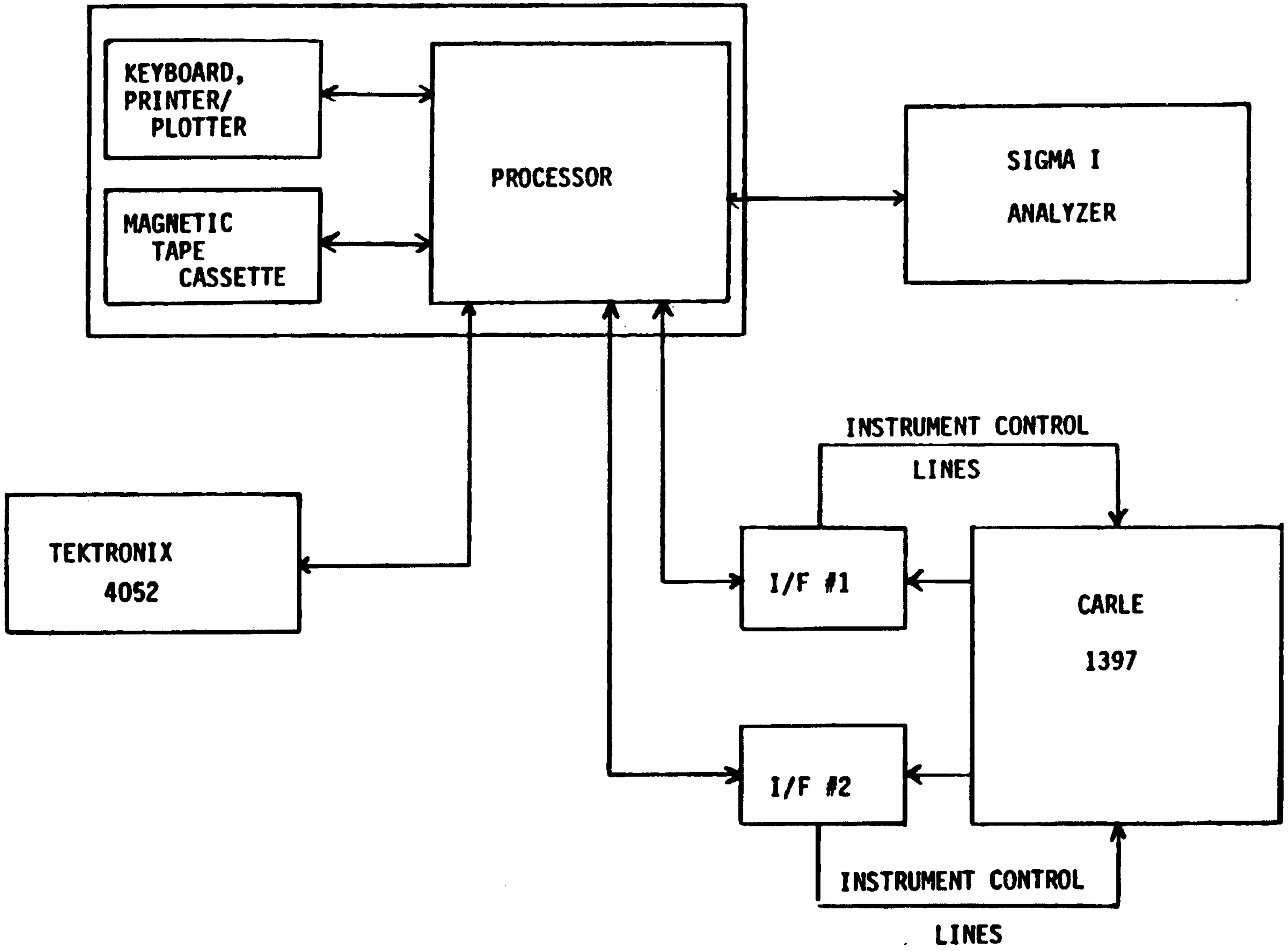


FIGURE 6

GAS ANALYSIS

DETAILED BLOCK DIAGRAM

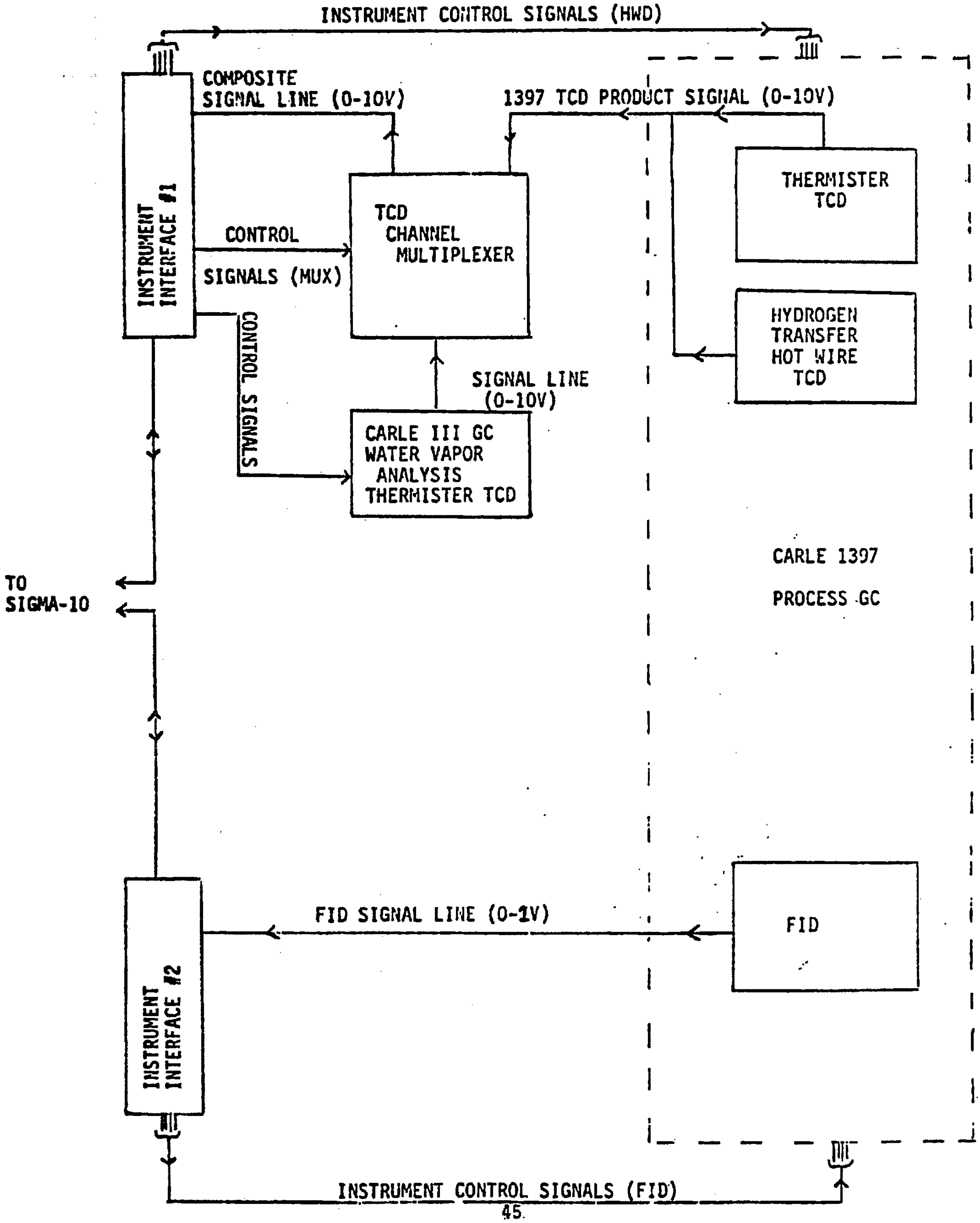
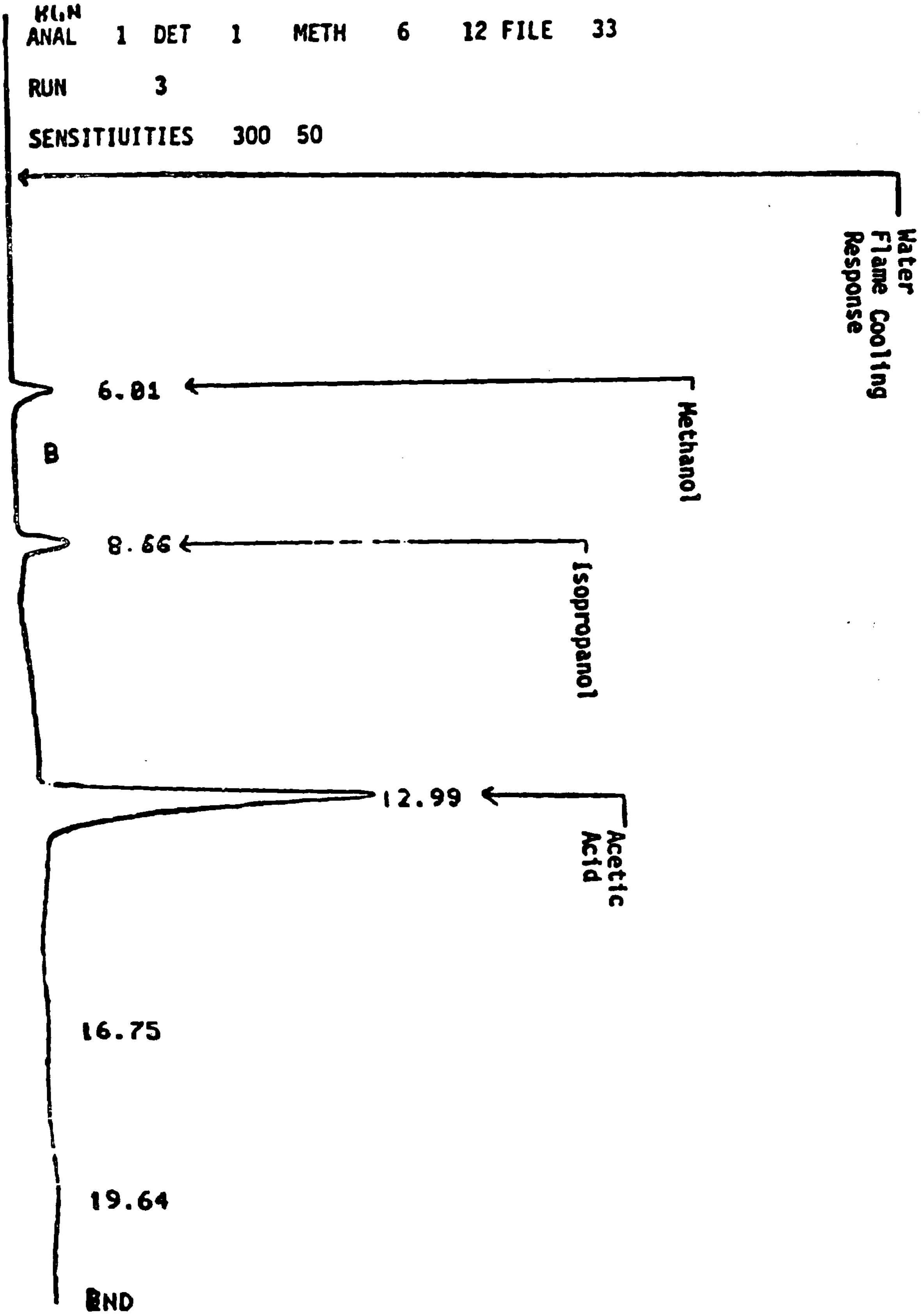


FIGURE 7

EXAMPLE OF AQUEOUS PHASE ANALYSIS



```
RUN
ANAL   1  DET   1    METH   6    12 FILE   33

RUN       3

SENSITIUITIES   300  50
```

FIGURE 8

Packed Column Separation Of C_7 - C_{19} Standard Mix
10% SP-2100/Supelcoport
1/8 in. X 6 ft

```
ANALYZER CONTROL

INJ TEMP     200
DET ZONE 1,2     250    250
AUX TEMP     200
FLOW A,B     50    50
INIT OVEN TEMP,TIME      40    10

TEMP  RATE  TIME
 200    2.0   60

DATA PROC


ANAL  1  DET     1  METH 4        2  FILE   35

RUN       1

SENSITIVITIES   350  50
```

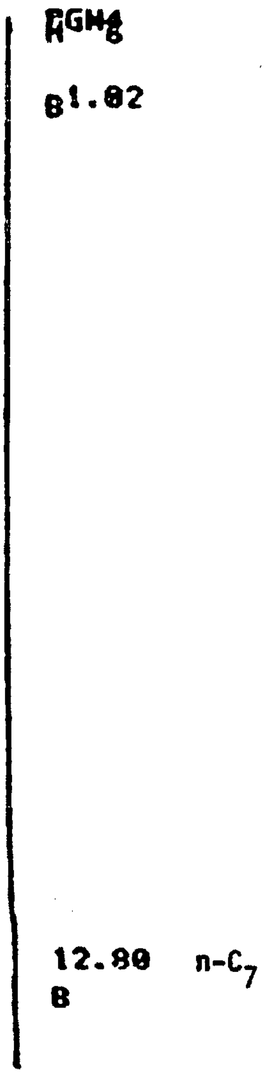


FIGURE 8
(cont'd)

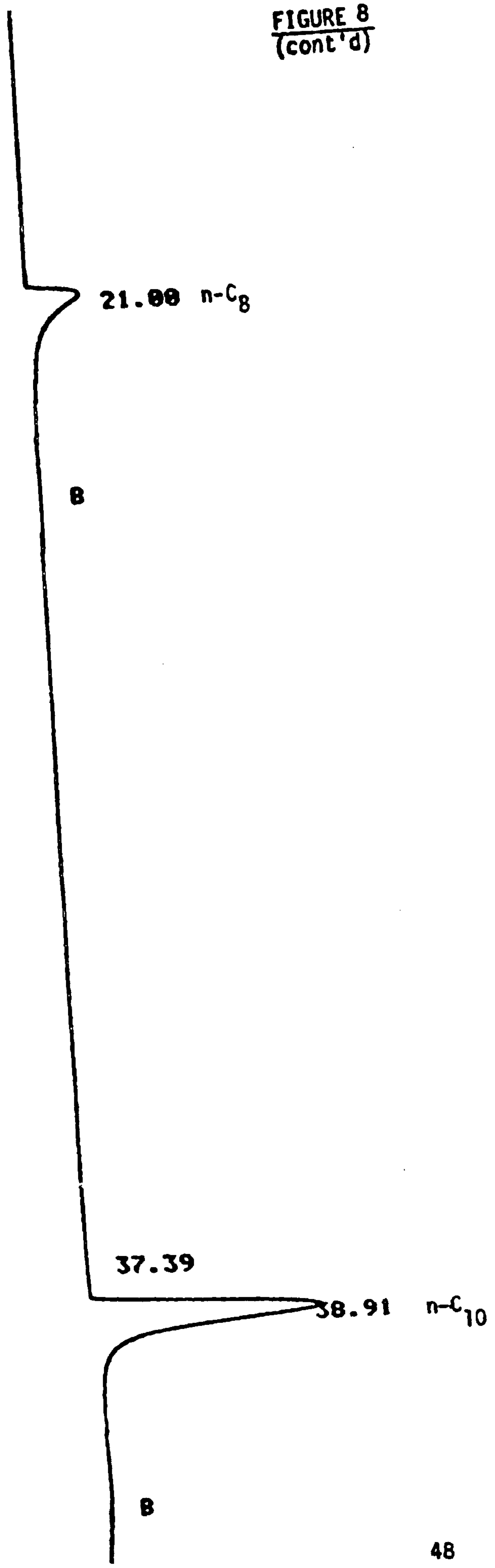


FIGURE 8
(cont'd)

Page 3 of 4

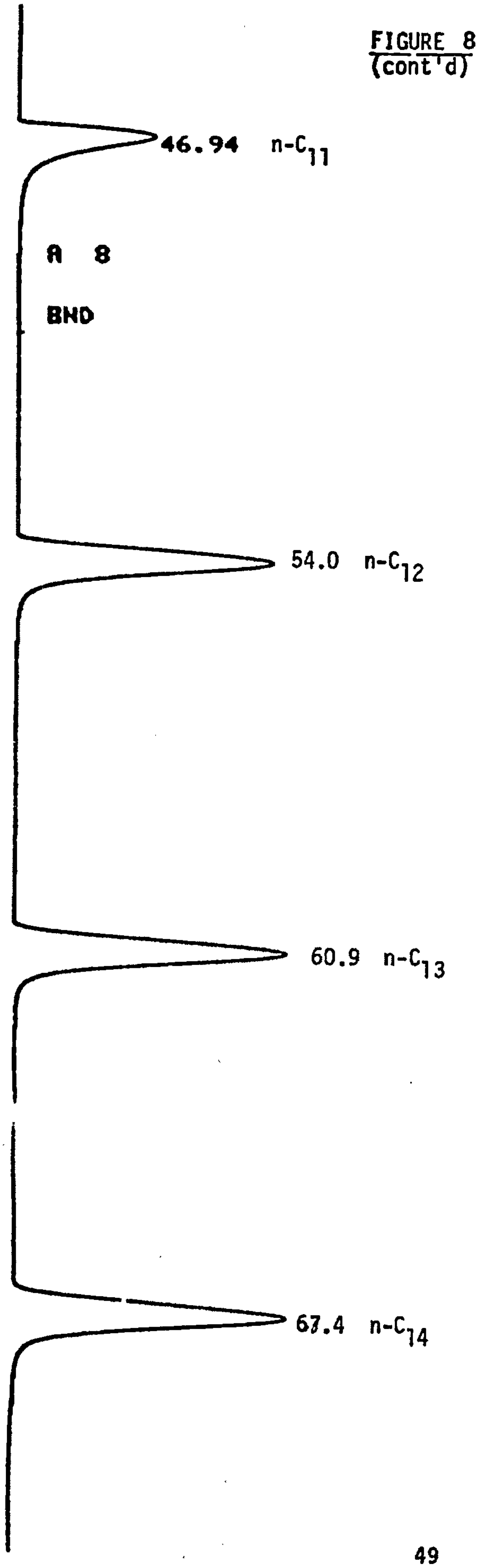


FIGURE 8
(cont'd)

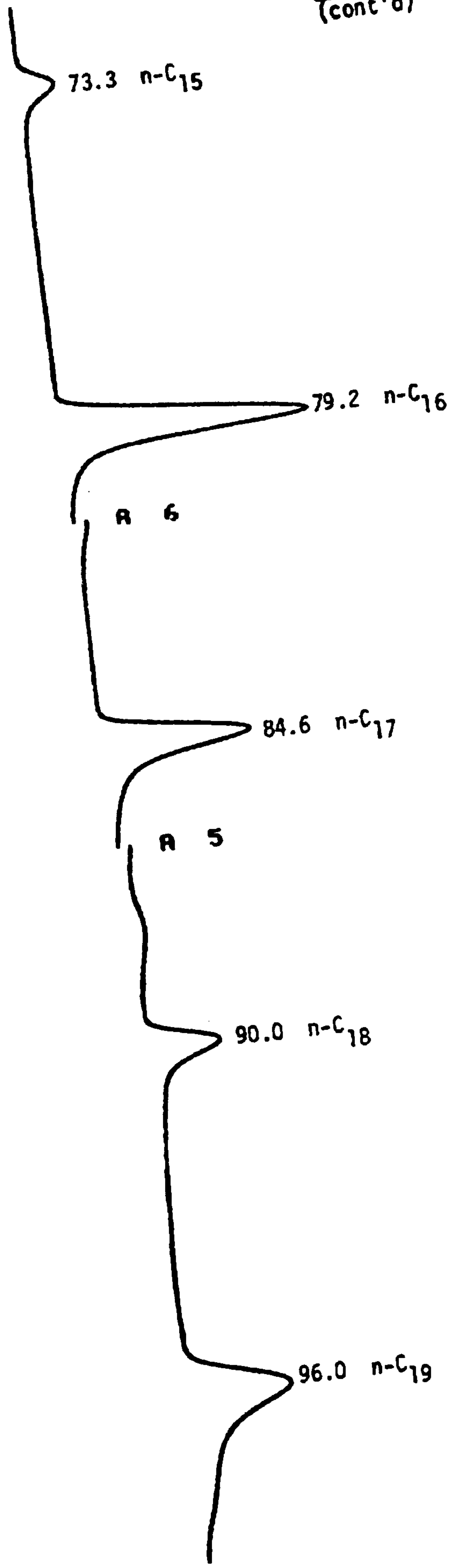


FIGURE 9

CAPILLARY SEPARATION OF #2 HEATING OIL

```
INST   4   METH     1   FILE    11

RUN       1

SENSITIVITIES    50    4
```

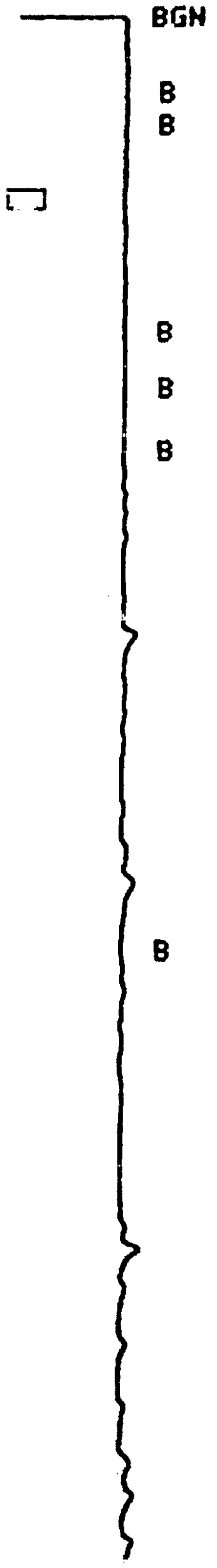


FIGURE 9
(cont'd)

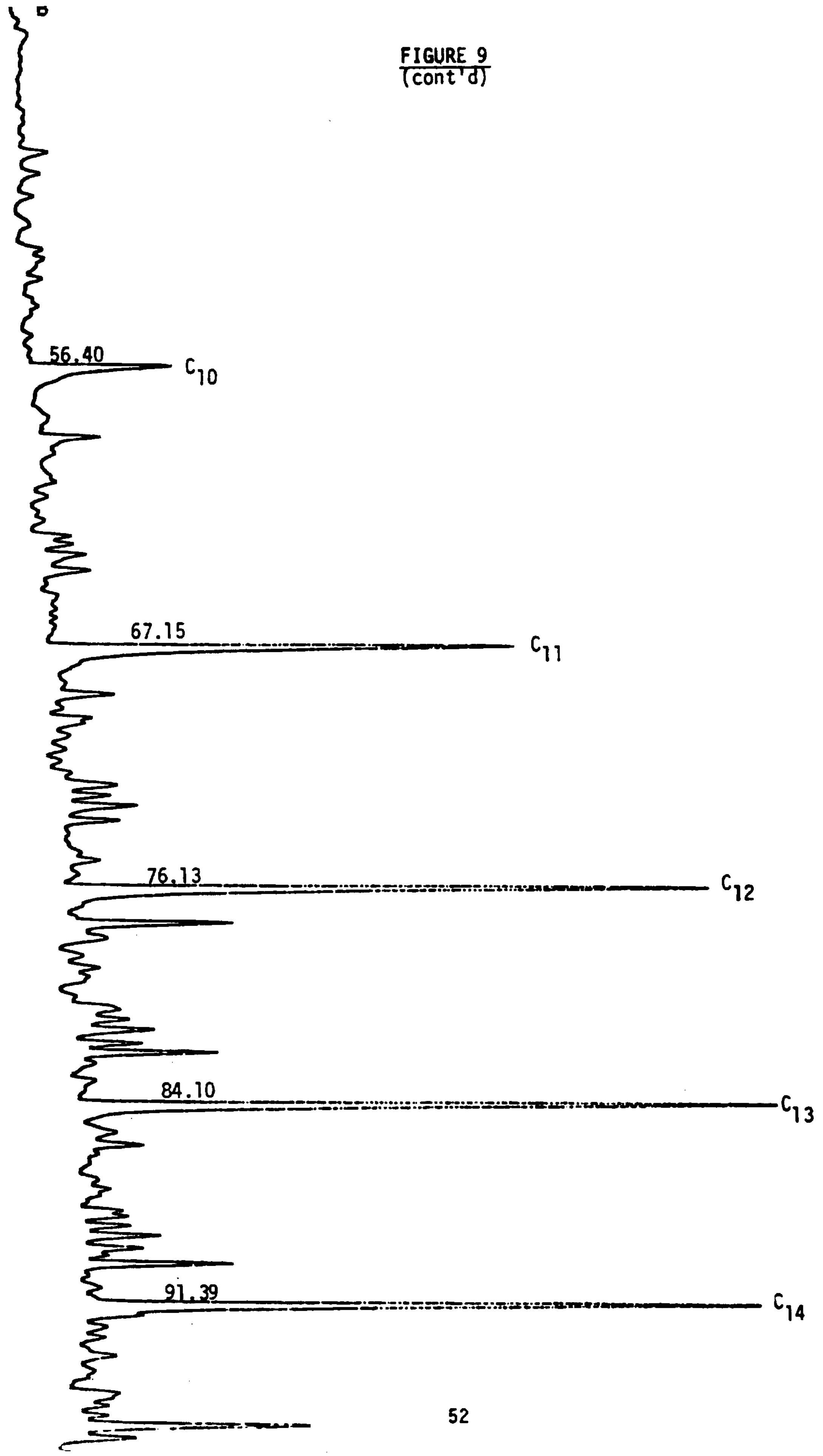


FIGURE 9 (cont'd)

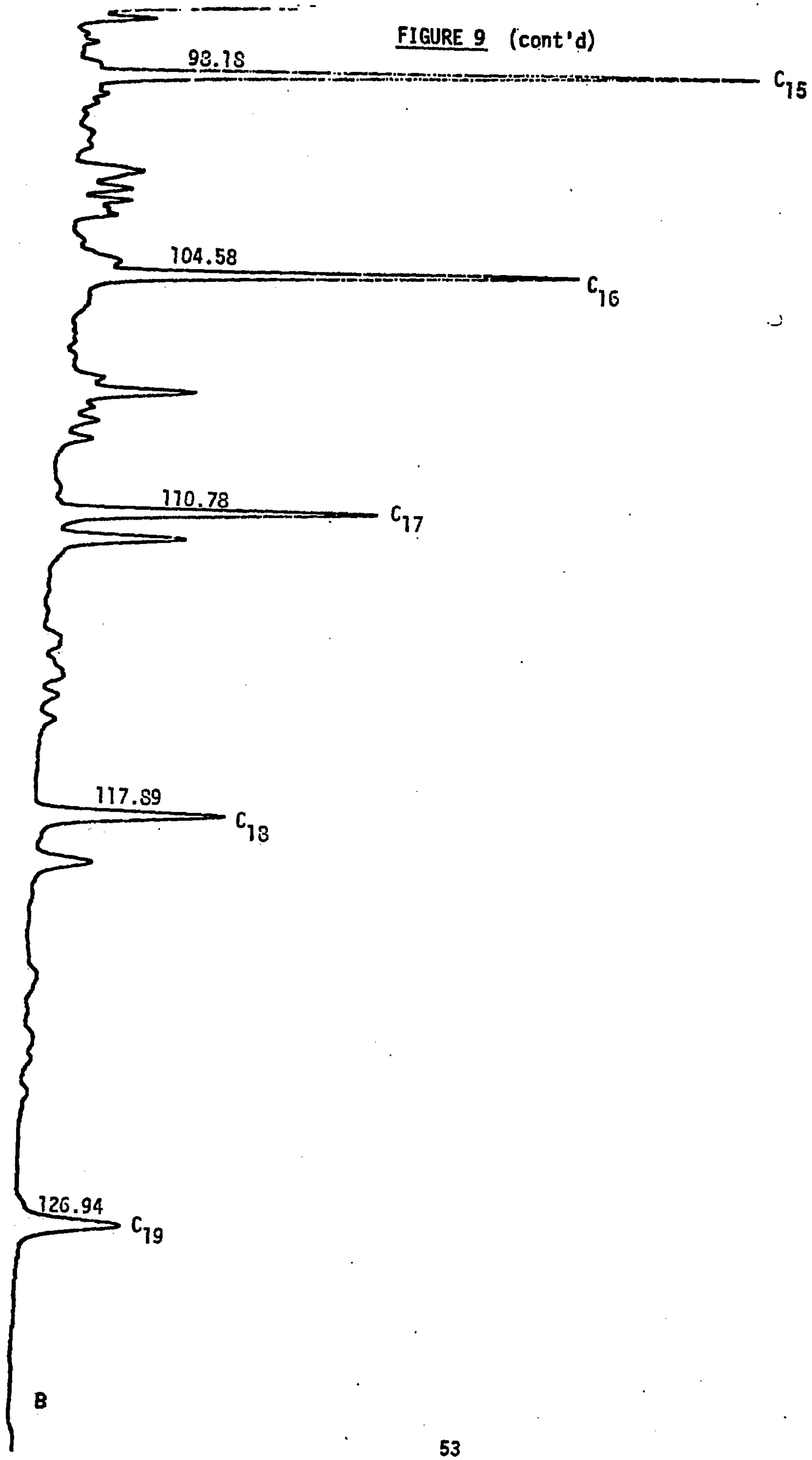


FIGURE 10

COMPUTER REPRESENTATION OF CAPILLARY SEPARATION OF #2 HEATING OIL

```
C #      CONC.
  5      0         X
         0         X
  6      0         X
         .0844     X
  7      0         X
         .5598     XBB
  8      0         X
         1.0925    XBBBB
  9      0         X
         3.5919    XBBBBBBBBBBBBBB
  10     1.7142    XNNNNNN
         5.4259    XBBBBBBBBBBBBBBBBBBBBB
  11     3.5616    XNNNNNNNNNNNNNN
         7.218     XBBBBBBBBBBBBBBBBBBBBBBBBBBBB
  12     3.6476    XNNNNNNNNNNNNNN
         8.2796    XBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBB
  13     4.2329    XNNNNNNNNNNNNNNNN
         6.8672    XBBBBBBBBBBBBBBBBBBBBBBBBBBB
  14     4.9945    XNNNNNNNNNNNNNNNNNNN
         7.8431    XBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBB
  15     6.3389    XNNNNNNNNNNNNNNNNNNNNNNNNN
         3.4628    XBBBBBBBBBBBBB
  16     4.8794    XNNNNNNNNNNNNNNNNNNN
         6.0765    XBBBBBBBBBBBBBBBBBBBBBBBB
  17     3.5867    XNNNNNNNNNNNNNN
         5.9011    XBBBBBBBBBBBBBBBBBBBBBBB
  18     2.3271    XNNNNNNNNN
         3.3334    XBBBBBBBBBBBBB
  19     1.8805    XNNNNNNN
         3.1001    XBBBBBBBBBBBB
  20     0         X
         0         X




 THE TOTAL CONC. LESS THAN C5 IS =  0
THE TOTAL NORMAL ISOMER CONTENT IS  37.1634
THE TOTAL BRANCHED ISOMER CONTENT IS  62.8363
         TOTAL AREA ACCOUNTING =  99.9997 %

13 : 10  3000 H 100
```

FIGURE 11

STIRRED TUBULAR FLOW REACTOR FOR CATALYST PRECIPITATION

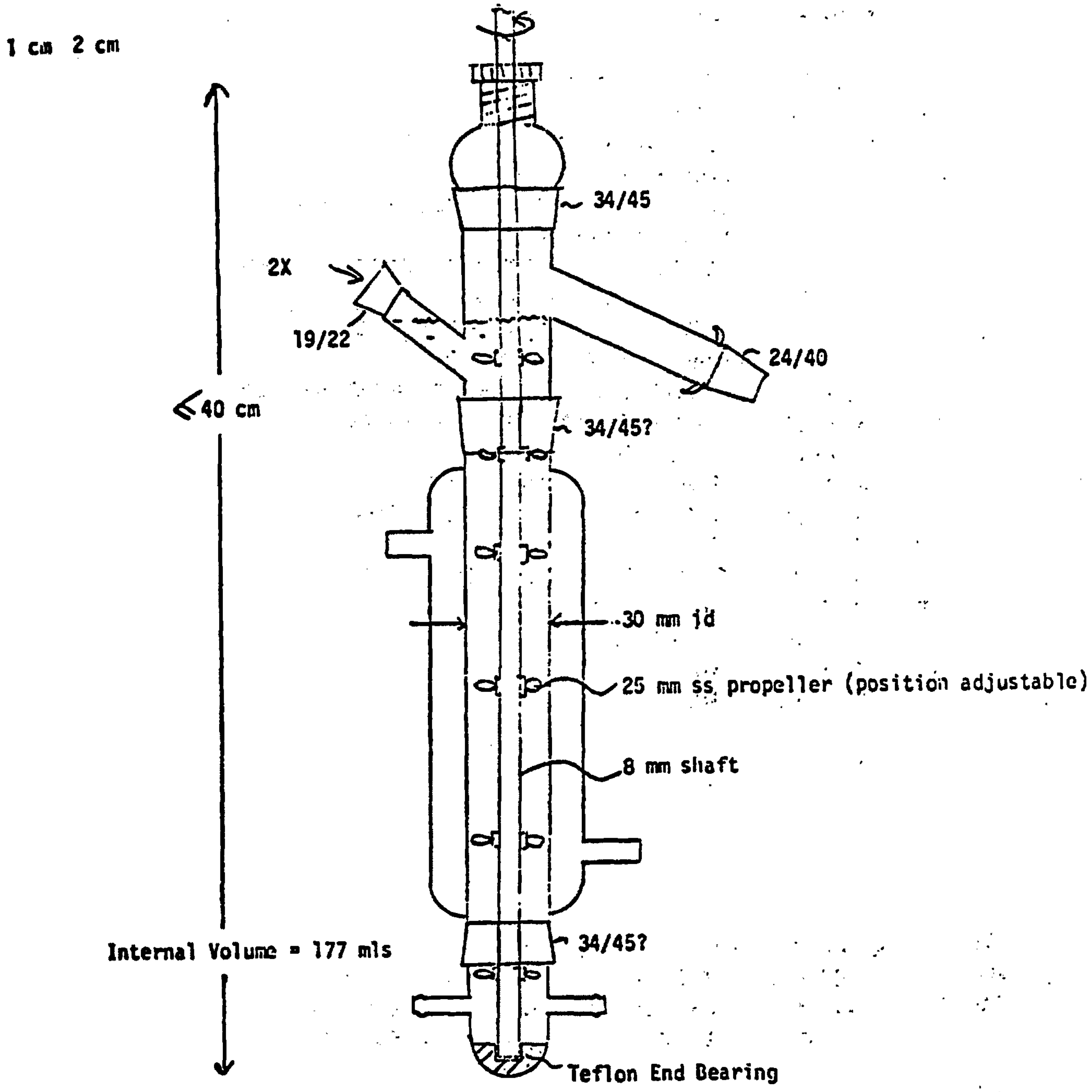


FIGURE 12

PRECIPITATION REACTOR FLOW DESIGN

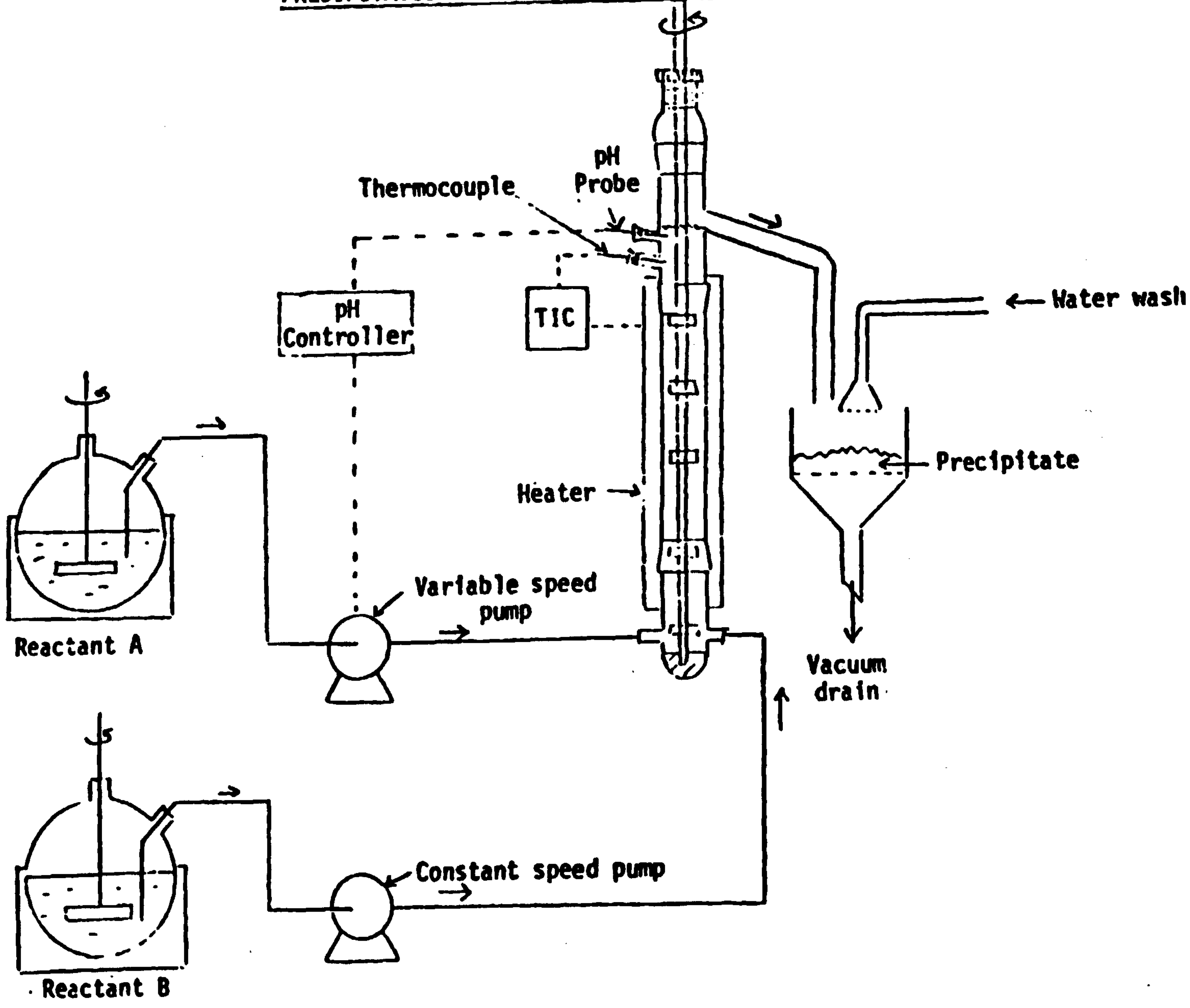
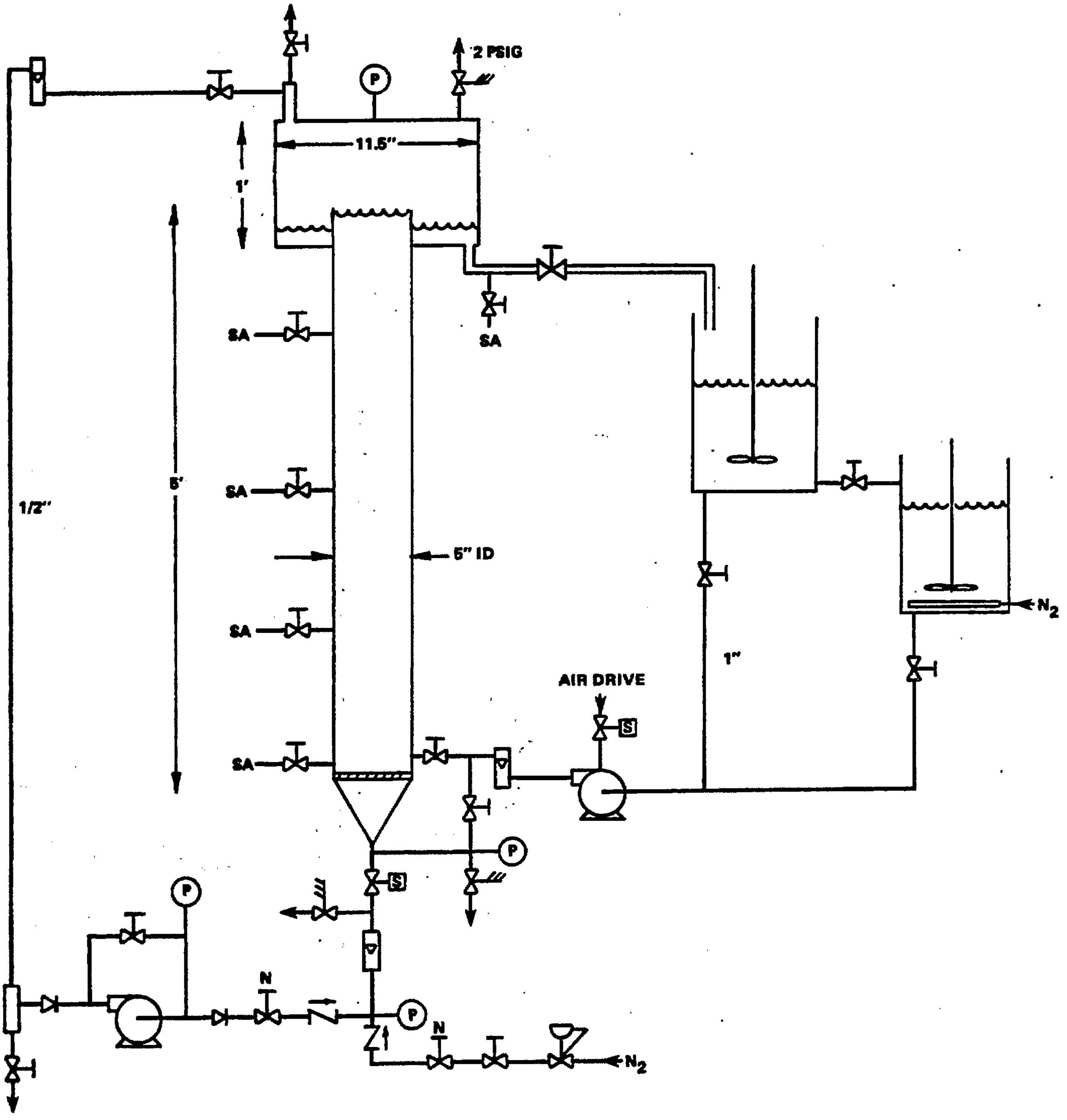


FIGURE 13

5-INCH SLURRY COLUMN



SA = SOLID DISPERSION
SAMPLING POINT

TABLE 1
SOLID DENSITIES

Solid	Specific Gravity	Bulk Density g/cm^3
SiO_2	2.65	0.34-0.51
Fe_2O_3	5.2	0.3-2.1

TABLE 2

PHYSICAL PROPERTIES OF LIQUIDS

Liquid	Temp. 0°C	Surface Tension dynes/cm	Viscosity cp	Density g/cm^3	Gas Diffusivity cm^2/sec	Specific Heat cal/g/°C	Thermal Conductivity cal/cm/sec/°C
Water	20	72.7	1.00	1.00	2.5×10^{-5} (O_2)	1.00	1.41×10^{-3}
Kerosene	20	27.2	3.6	0.81	1.2×10^{-5} (O_2)*	0.47	3.5×10^{-4}
Rheinpreussen type paraffinic oil	260	11	0.33	0.67	8×10^{-5} (CO)*	0.70	3.1×10^{-4}

*Estimated

Air Products

10.0 Appendix

PROJECT WORK PLAN
FOR
CATALYST AND REACTOR DEVELOPMENT FOR A LIQUID PHASE FISCHER-TROPSCH PROCESS

SUBMITTED TO
UNITED STATES DEPARTMENT OF ENERGY
OCTOBER 31, 1980

BY
PAUL N. DYER, RONALD PIERANTOZZI AND JAMES W. BROCKINGTON
AIR PRODUCTS AND CHEMICALS, INC.
ALLENTOWN, PA 18105

UNDER CONTRACT NO. DE-AC22-80PC30021

INTRODUCTION

This detailed project work plan is submitted in compliance with Task 1 of the work statement in the DOE-APCI contract "Catalyst and Reactor Development for a Liquid Phase Fischer-Tropsch Process". The objective of this program is to evaluate catalysts and slurry reactor systems for the selective conversion of synthesis gas into transportation fuels in a single stage, liquid phase process. The program covers 36 months and is divided into four tasks.

This work plan presents in detail all the activities which will be performed in this program and includes the following:

1. Description of the methods and technical approach which will be used to achieve the objectives and requirements set forth in the contract.
2. A detailed program schedule for each task.
3. Graphs reflecting cumulative estimated costs and man-hours expended by month for each task. (Not included)
4. A project work chart which shows the key personnel/groups which are planned for each task and the percentage of their time which will be devoted to the tasks. (Not included)
5. A list of critical deadlines and action items.

METHODS AND TECHNICAL APPROACH

Task 1 - Project Work Plan

The requirements of this Task are fulfilled by submission of this work plan. Appropriate revisions will be submitted to the DOE Project Manager as requested by him or as deemed desirable by the contractor.

Task 2 - Slurry Catalyst Development

In this Task, we will evaluate and test catalysts for their potential to convert synthesis gas into gasoline, diesel fuel or a mixture of transportation fuels suitable for the U.S. markets. In these tests, we will evaluate catalyst activity, selectivity, stability, and aging with a target concept involving a single stage, liquid phase reactor system. The work in this Task is divided into four sub-Tasks.

Sub-Task 2a - Background Studies

From October to mid-December 1980, an evaluation will be made of the performance of previously published catalysts for the conventional and slurry phase Fischer-Tropsch processes, and of data concerning the operation of slurry reactors. An assessment will be made of the activity, selectivity and stability of the catalysts with information drawn from available literature, patents and personal contacts. Emphasis will be placed on the comparative performance of slurry and fixed or entrained bed operation.

The evaluation will identify the potential catalysts and characteristics of slurry reactors to be studied, and the results will be reported at the end of December. A list of approximately twenty precipitated, fused or supported catalysts recommended for slurry phase testing will be submitted to the DOE Project Manager for approval.

This background study will be regularly updated at bi-weekly intervals throughout the contract period by a computerized search of the Fischer-Tropsch and slurry reactor subject areas.

Sub-Task 2b - Bench Scale Reactor Set-Up

A design for the gas phase reactor and associated analytical equipment to be used to screen metal cluster catalysts prepared in sub-Task 2d will be submitted to the DOE Project Manager for review in November 1980. This reactor will be a commercial unit manufactured by Chem Data Systems.

In addition, a 15 ml tubular reactor will be provided by APCI. This reactor will be used to determine the gas phase performance of the conventional catalysts that will subsequently be tested in the slurry phase so that a comparison can be made between the two modes of operation.

The designs for a 300 ml and a 1000 ml slurry reactor system will be submitted to the DOE Project Manager for review in November 1980. It is essential that components for these reactors be ordered in the beginning of December so that their construction and shakedown can be completed by the beginning of April and May 1981, respectively. To commence the catalyst testing program, a 300 ml slurry reactor of similar design, provided by APCI, will be employed.

Sub-Task 2c - Catalyst Preparation and Slurry Reactor Testing

(a) General Description

In January 1981, initial tests will be made in the 300 ml slurry reactor provided by APCI to establish mass transfer controlled operating regimes. This will be done, for example, by studying synthesis gas methanation catalyzed by a nickel catalyst slurried in oil. Gas/liquid mass transfer may be an important factor in determining conversion and selectivity when operating in the slurry phase with active catalysts, and the information gained in this initial test will be used to avoid or make use of such limitations in subsequent runs.

To provide a baseline for further comparison, a slurry test will be made in February 1981 of an established Fischer-Tropsch catalyst; a commercially available iron oxide catalyst promoted with 0.6% K_2O, 1.0% CaO and 2.5% Al_2O_3 will be used. This catalyst will be subjected to a gas phase test in the APCI tubular reactor at the end of November 1980 prior to slurry testing.

Following approval of the list of recommended slurry phase catalysts, their preparation and screening in the APCI tubular reactor will begin in January and continue through November 1981. The catalyst particle size and loading, together with the oil vehicle to be used in the slurry tests, will be submitted to the DOE Project Manager in January 1981. The solubilities and diffusivities of reactant and major product gases in the chosen oil will be determined during the slurry phase tests.

The first four tests of selected catalysts in the slurry phase will last for up to approximately twenty days each and will be made in the APCI 300 ml reactor from March to June 1981. The details of the proposed method, product analysis and handling of data are given in the accompanying description (section b, following).

The 300 ml slurry reactor constructed for the contract (reactor I) will be brought on stream in May 1981. Following tests in June to establish gas/liquid mass transfer limiting regimes, the larger size, 1000 ml reactor (reactor II) will be commissioned in July. After this, the APCI 300 ml reactor will be returned to internal APCI use.

The availability of two sizes of slurry reactors will give flexibility in the choice of reaction conditions during the test program. The more active catalysts giving good conversions at high space velocities will be assigned to the 300 ml reactor.

Slurry phase testing of the twenty recommended catalysts for twenty day periods will be concluded in February 1982. Approximately 10 cluster catalysts shown to have promise in the gas phase screening program will then be subjected to slurry testing for periods up to 20 days each from March to July 1982 in sub-Task 2d. In addition, four lesser active catalysts will be slurry tested for up to five days each.

From the overall results of these slurry phase tests, four catalysts will be chosen for approval for extended testing. Long term continuous tests of approximately 175 days each will be made from September 1982 to August 1983. Changes in activity and selectivity with time will be studied. A model will be developed for the reaction kinetics and rates of feed consumption and product fraction generation.

(b) Detailed Program Steps

Flow charts for a typical slurry phase catalyst test and product analysis are shown in Figures 1 and 2.

1. Catalyst Preparation

Precipitated, fused and supported catalysts will be prepared by proprietary techniques and will be ground and sieved to less than 50 μm. They will be characterized by the measurements indicated in Figure 1.

2. Gas Phase Testing

For comparative purposes, a sample of each catalyst will be initially tested for Fischer-Tropsch activity in a solid bed using a 15 ml tubular reactor. Synthesis gas will be premixed 1:1 CO/H_2, and the tests will be run at 450 psig, 250°C and space velocities of 300-1000 GHSV.

3. Activation for Slurry Phase Testing

Preferentially, this will be carried out in situ, with the procedure dependent upon catalyst type. Typically, activation will involve heating the slurry under nitrogen at 100 psig and 200°C, replacing the nitrogen with synthesis gas and slowly raising the temperature and pressure to reaction conditions over a period of 72 hours. An alternative procedure, useful for iron containing catalysts, is to maintain the slurry at reaction temperature for 24 hours under 100 psig of nitrogen, followed by successive reduction under the same conditions with CO and H_2 for a further 24 hours each.

If necessary, the catalyst will be activated as a solid bed in an additional tubular reactor, and then slurried in oil under nitrogen before transfer to the slurry reactor.

4. Slurry Phase Testing

Tests will be carried out continuously for up to twenty days. Inlet CO/H_2 ratios will be 2:1, 1:1 and 1:2, with emphasis placed on the CO rich ratio. Space velocities will be in the range 300-1000 GHSV, based on slurry volume, and will be chosen together with reactor stirring speed for the maximum conversion while avoiding mass transfer limitations.

The operating pressure and temperature will be varied between 225 and 450 psig and 250 and 300°C, although tests may be extended to 1000 psig and 350°C. The re-establishment of steady state conditions will be ensured following changes in operating parameters, and a reference point will be reproduced periodically to determine catalyst stability over the twenty day test.

The slurry reactor will be operated at 50% volume loading, i.e. the 300 ml reactor will contain 150 ml slurry, to allow adequate space for gas/slurry disengagement, and the solids content of the slurry will be in the range 15-30 wt%.

The slurry reactor also has the capability of recirculating slurry under automatic control via an external holding and treatment reservoir at rates up to 3.3 vol/vol/h. This will be used as required to:

a) simulate continuous gas and slurry flow
b) maintain catalytic activity by withdrawing deactivated catalyst and replacing with fresh catalyst
c) maintain slurry volume by filtering off excess oil if a net synthesis of high boiling hydrocarbons occurs
d) alter the solids content of the slurry during the course of a run.

5. Product Analysis

As illustrated in Figure 2, the analytical method will give as complete as possible a total product profile to provide data on conversion per pass, catalyst activity and product selectivity, and the change of these measured parameters with reaction conditions and with time. As much of the data handling as possible will be done by computer in order to provide rapid feedback during the course of each test.

The Fischer-Tropsch reaction product will first pass to a C_5/C_6 splitting column. Gaseous product from the top of this column will be analyzed by a multicolumn Carle SX-397B g.c. equipped with TCD and FID, capable of resolving all C_1-C_5 isomers plus CO, H_2 and CO_2. Water vapor in the gaseous product will be analyzed by a separate sample on a Carle 111 g.c.

Liquid product from the column will exist as two phases. Samples will be collected, weighed, separated and reweighed and analyzed according to Figure 2. The organic phase will be analyzed for C_5-C_{25} on a 1/8" SP2100 column in a PE Sigma 1 g.c., or, for greater resolution, on a 0.01" x 150' stainless steel capillary OV-101 column in a PE Sigma 2 g.c. The latter will give a carbon number distribution in the range C_5-C_{25}, isomers in the C_6-C_{12} range, and normal and branched hydrocarbon ratios for C_{12}-C_{25}. In addition, representative samples will be analyzed for PONA by a fluorescence indicator column chromatography method or low resolution mass spectrometry.

The aqueous phase will be analyzed for oxygenates on a 3% Carbowax, 0.5% H_3PO_4 Carbopack open tubular 1/4" x 5' glass column. This will yield C_1-C_{10} alcohols and acids as well as phenols.

Operations of the chromatographs will be controlled by a Sigma 10 computing integrator. Treated data from this, plus process parameters describing each sample, will be inputted to a microcomputer for correlation before being transmitted to a mainframe computer archive. The microcomputer will also be used to check successive process parameters, produce rapid selectivity profiles and intermediate mass balances.

Intermediate analyses will also be performed on the slurry vehicle oil using a high temperature capillary column, e.g. an SE30 or SE52.

6. Conclusion of Test

Data collected on the computer file during the course of the tests will be used to derive graphs and correlations showing:

a) changes in the selectivity profile or product fractions with process conditions and with time

b) departures from a Schulz-Flory distribution of products

c) changes in activity and conversion with time.

Final analyses of selected product fractions, such as boiling range measurements and PONA, will also be carried out.

Oil from the slurry at the conclusion of the test will be analyzed and the catalyst will be characterized again as shown in Figure 1. This information will be used to derive and project the catalyst's aging characteristics.

Sub-Task 2d - Metal Cluster Catalyst Preparation and Screening Tests

(a) General Description

A recommended list of monometallic, bimetallic and bifunctional metallic clusters to be evaluated will be submitted to the DOE Project Manager in early November with approval expected by early December. The clusters will be prepared, characterized and supported on high surface area supports. γ-Al_2O_3, MgO and CeO_2 will be the inorganic supports used in order to give a representative range of surface basicities. Selected clusters will be attached to poly(styrene-divinylbenzene) supports. The supported clusters will be characterized and then thermally treated under various atmospheres to determine decomposition point. Fifty supported cluster catalysts will be prepared; preparation will begin in late November-early December 1980 and will continue through June 1982 at the rate of approximately three catalysts per month.

The catalysts prepared in this sub-Task will be tested in a gas phase screening reactor beginning in February 1981 and continuing through July 1982. Ten of the catalysts which display good Fischer-Tropsch activity will be recommended to the DOE Project Manager for additional screening in the slurry reactors for up to 14 days. Four of the less active catalysts will also be tested in the slurry reactors for about 5 days to verify the validity of gas phase testing as a useful screening test. These tests will begin in March 1982 and last through July 1982. At the completion of the slurry reactor screening tests, two cluster catalysts will be recommended to the DOE Project Manager for long term aging tests. These runs will be similar to the long term testing described in sub-Task 2c,

(b) <u>Detailed Program Steps</u>

Figure 3 describes the general plan for the preparation, characterization and gas phase testing of the supported metal cluster catalysts.

1. <u>Catalyst Preparation</u>

The metal clusters will be prepared by literature procedures and characterized by infrared spectroscopy, NMR spectroscopy and elemental analysis, when necessary. Each metal cluster will be supported on high surface area γ-Al_2O_3, MgO and CeO_2 to give a representative range of surface basicities. Selected clusters will also be attached to poly(styrene-divinylbenzene) supports. The total number of catalysts prepared will be fifty. The amount of cluster on the support will be varied to give between 0.5-2% metal loading. The clusters will be attached to the support by either standard or proprietary techniques. The supported cluster will then be characterized by infrared spectroscopy and elemental analysis. To determine the decomposition temperature of the supported cluster, a variable temperature infrared spectral study will be performed. The cluster will be heated at 50°C intervals in the presence of H_2, CO, CO/H_2, N_2, O_2, or under vacuum to determine the decomposition points. At least five supported clusters will be prepared by 1 February 1981. Catalyst preparation will continue until 30 June 1982 at the rate of approximately three per month. Large scale preparations for the slurry testing will begin on 1 January 1982 and continue for seven months or until fourteen catalysts are prepared.

2. Gas Phase Testing

The catalysts prepared by the above method will be tested as Fischer-Tropsch catalysts in a continuous tubular flow reactor. The initial reaction temperature will be determined by the decomposition temperature found in the IR experiments described above. Two different temperatures will be examined including one temperature below the decomposition temperature and one temperature of at least 250°C, providing the support does not decompose. The effect of pressure on activity and selectivity will be examined at pressures of 20 atm and 60 atm initially. The CO/H_2 ratio will be varied from $CO/H_2 = 2$ to $CO/H_2 = 0.5$. At least three different points will be examined (e.g. $CO/H_2 = 2$, 1 and 0.5). The space velocities used will be 200 hr^{-1} and 500 hr^{-1}. These variables will be examined with the same catalyst charge. A center point will be repeated periodically to determine catalyst stability. If serious deactivation occurs, the catalyst charge will be replaced. The gas phase screening reactor will have a built in gas chromatograph for product analysis; column selection will be similar to that described in Section 5, Product Analysis, under sub-Task 2c. Catalyst testing will begin on 1 February 1981 and continue at the rate of three per month until 31 July 1982. The duration of each screening run will be about fourteen days.

Catalysts will be analyzed by IR and elemental analyses after the gas phase screening runs. Catalysts which display good activity (relative to a baseline Fe catalyst) or unusual selectivity will be analyzed by surface area measurements (BET), CO chemisorption and particle size distribution.

3. Slurry Phase Testing

Ten of the catalysts which display good activity will be tested in the slurry reactor for up to twenty days. Four of the catalysts exhibiting lower activity will also be tested in the slurry reactor for up to five days.

The procedures followed in slurry phase testing will be generally as described in Section 4, Slurry Phase Testing, under Sub-Task 2c. Operating temperatures will be based on the results of the gas phase screening.

From the results of these tests, two cluster catalysts will be selected for long term aging studies. The general procedure described for slurry testing will again be followed.

Task 3 - Slurry Reactor Design Studies

The objective of this Task is to evaluate through the use of cold-flow reactor simulators the flow characteristics and behavior of slurry reactors for the production of hydrocarbons from synthesis gas. From the data developed in this Task, we will (1) define the heat, mass and momentum transfer parameters which affect the design of slurry reactors, (2) establish operating limits for slurry reactors with respect to system physical parameters, (3) develop or confirm correlations for predicting the flow characteristics and heat/mass transfer of slurry reactors, and (4) define the needed requirements for design of larger-scale reactors.

This Task will span 36 months and will consist of five specific units: literature evaluation and detailed experimental plan; three phase flow in a 5-inch column; three phase flow in a 12-inch column; engineering evaluation; final report (to be combined with final report from Task 2).

Beginning in October (month one), we will update our literature reviews to insure inclusion of current work and will maintain literature surveillance throughout the contract. Based on this literature review, information within APCI from similar studies and discussions with others working in similar areas, we will develop a detailed experimental plan. This plan will be submitted to the DOE Project Manager on or before 2 January 1981.

This plan will include use of a 5-inch diameter and 12-inch diameter cold-flow reactor simulator. We originally planned on using an existing 5-inch diameter simulator, but it will not be available. Therefore, APCI will provide at its own cost a new 5-inch diameter simulator. This reactor simulator will be identical to the existing one and will be constructed during the first three months of the contract. During December 1981 and January 1982 a 12-inch diameter glass cold-flow reactor simulator will be constructed. This unit will be constructed to operate with hydrocarbon liquid phase and will contain exchangeable internal heat transfer surface inserts and distributor plates.

The 5-inch diameter simulator will be used to define design requirements in the absence of internal heat transfer surfaces. Cold-flow experiments in the 5-inch simulator will commence in January 1981 and will be completed in December 1981. The 12-inch diameter simulator will be used to define the affects of alternative internal heat transfer surfaces. Experiments in the 12-inch simulator will begin in February 1982 and will be completed in January 1983.

The 5-inch diameter simulator will be used to investigate the effect of superficial gas and slurry velocities, solids concentration and characteristics, and liquid phase characteristics on gas holdup, mass transfer, phase dispersion and solids distribution. The results of these studies will be used to define the experimental regimes to be investigated with 12-inch diameter simulator using alternative configurations of internal heat transfer surfaces.

Following completion of the cold-flow studies, we will conduct further engineering evaluations to better define the performance of internal versus external heat transfer, optimum operating conditions with respect to gas and slurry superficial velocities, solids concentration and size, solid/liquid separation techniques, and staged reaction systems. These evaluations will also incorporate the results of catalyst screening studies in Task 2 and will define the need for additional data.

Detailed Experimental Plan

The final detailed experimental plan for this Task will be submitted to the DOE Project Manager on or before 2 January 1981. This plan will contain a complete recommended schedule of experiments. We expect this plan to include the following ranges of variables:

I. 5-Inch Diameter Simulator - No Internal Heat Transfer Surface

  A. Experiments in Kerosene and Water

  - Independent Variables:
    1. Five gas superficial velocities: 0.05-0.5 ft/sec
    2. Three liquid superficial velocities: 0-0.1 ft/sec
    3. Two different solids: silica and iron oxide
    4. Four solids concentrations: 0, 10, 20, 30 wt%
    5. Three solid sizes: 1-5 μm, 45-53 μm, 90-106 μm
  - Dependent Variables:
    1. Gas hold-up
    2. Solids dispersion
    3. Gas dispersion

  B. Experiments in Water Only

  - Independent Variables:
    Same as in (A)
  - Dependent Variables:
    1. Mass transfer
    2. Liquid dispersion

In addition, selected liquid dispersion experiments will be performed in kerosene and a search will be made for an acceptable method of measuring mass transfer in kerosene under the cold-flow conditions.

II. 12-Inch Diameter Simulator - With Internal Heat Transfer Surfaces

  A. Experiments in Kerosene and Water

  - Independent Variables:
    The same variables that were investigated in IA above will be examined in the 12-inch simulator. The range and number of values for each variable may differ depending upon the results obtained in the 5-inch simulator. For example, the liquid (slurry) superficial velocities do not need to be as large when internal heat transfer surfaces are present since external circulation need only be done to maintain catalyst activity.

- Dependent Variables:
  Same as in IA plus heat transfer

B. Experiments in Water Only

- Independent Variables:
  Same as in IIA
- Dependent Variables:
  Same as in IB

The engineering evaluation will commence in January 1983 and will continue for six months. This evaluation will utilize all the available data from Task 2 and 3 of this work, the current literature and similar work being performed at APCI and by other DOE contractors.

Optional Task 4 - Pilot Facility Design

In this Task, we will develop a preliminary design for a pilot-scale liquid phase reactor for converting synthesis gas into liquid transportation fuels. We will base this design upon either the construction of a new pilot plant or modification of an existing facility owned by DOE. The choice will be recommended to DOE based upon availability of an existing facility and a preliminary estimate of the most cost effective route. The design will be based upon all data then currently available to us and will draw primarily upon the results of Tasks 2 and 3, data available from other contractors, and recommendations from DOE.

The design will include detailed flow sheets, material balances, major equipment specifications, and operating conditions. A preliminary cost estimate will be prepared. These design specifications and preliminary cost estimates will be provided to the DOE Project Manager in a separate report.

PROGRAM SCHEDULE

A Detailed Program Schedule is shown in Figure 4. This schedule contains the key elements of each Task.

FIGURE 1

FLOW DIAGRAM FOR SLURRY PHASE CATALYST TESTING

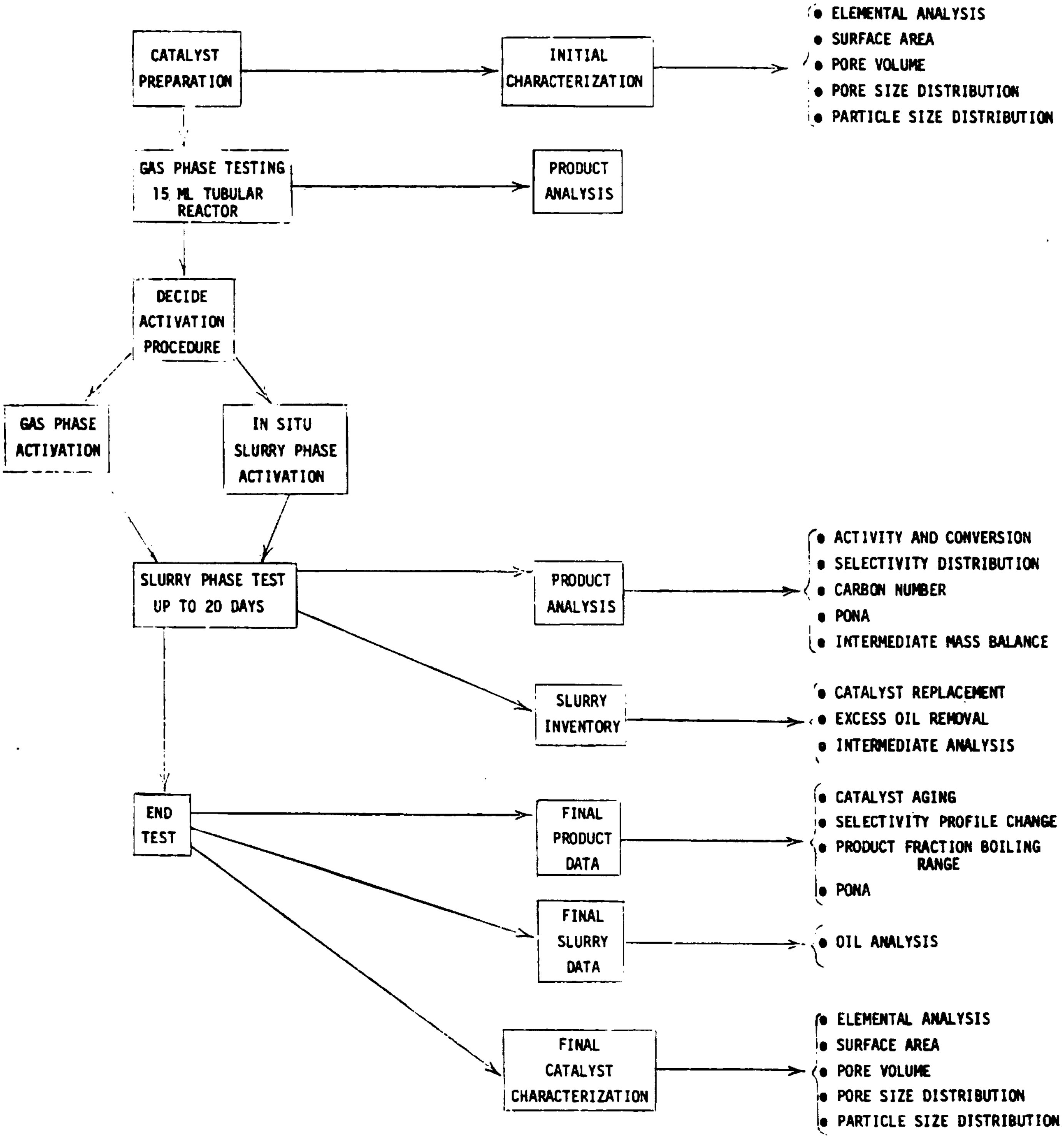


FIGURE 2

PRODUCT ANALYSIS SYSTEM

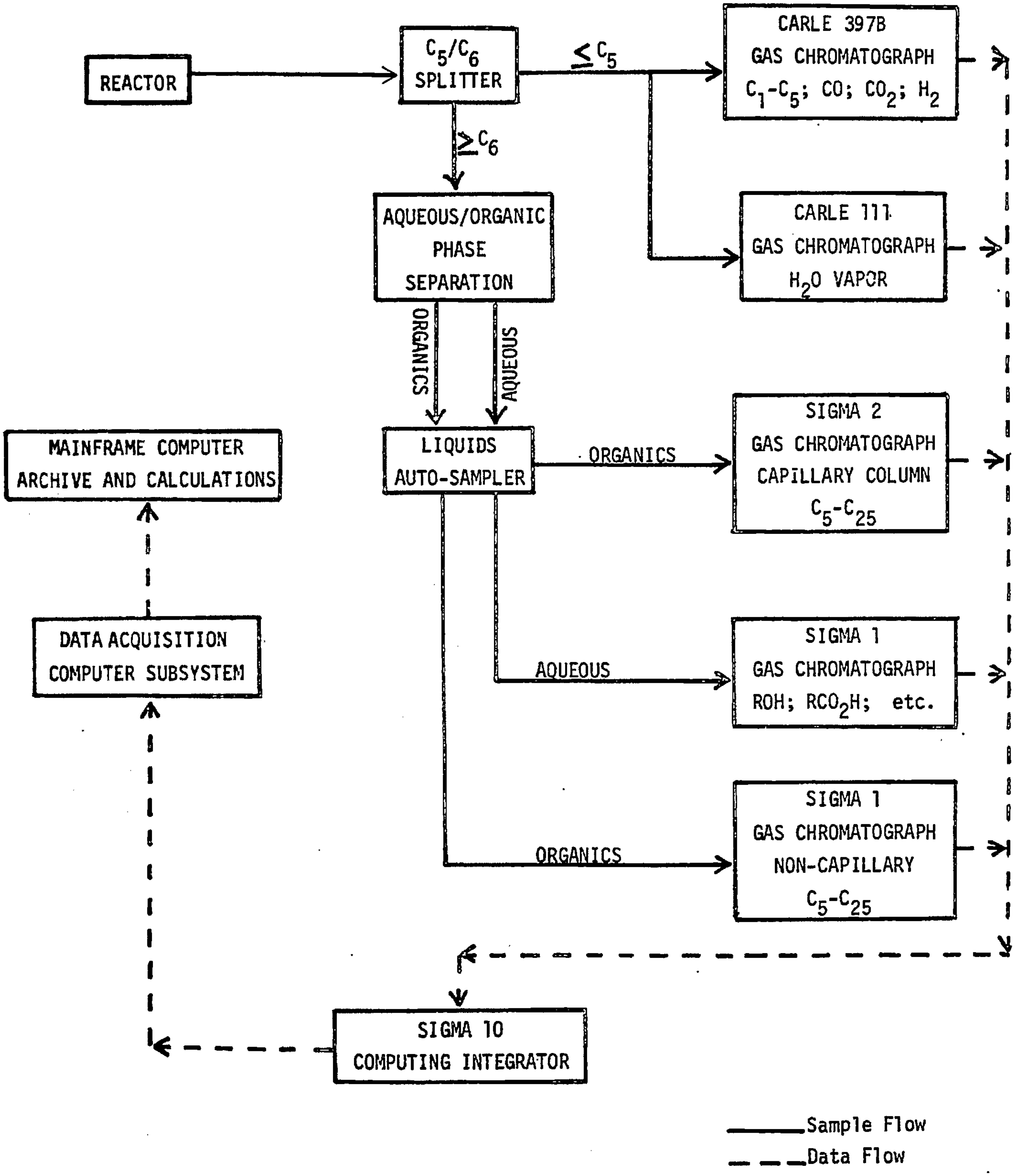


FIGURE 3

GENERAL PLAN FOR THE PREPARATION, CHARACTERIZATION AND GAS PHASE TESTING FOR SUPPORTED METAL CLUSTER CATALYSTS - Task 2d

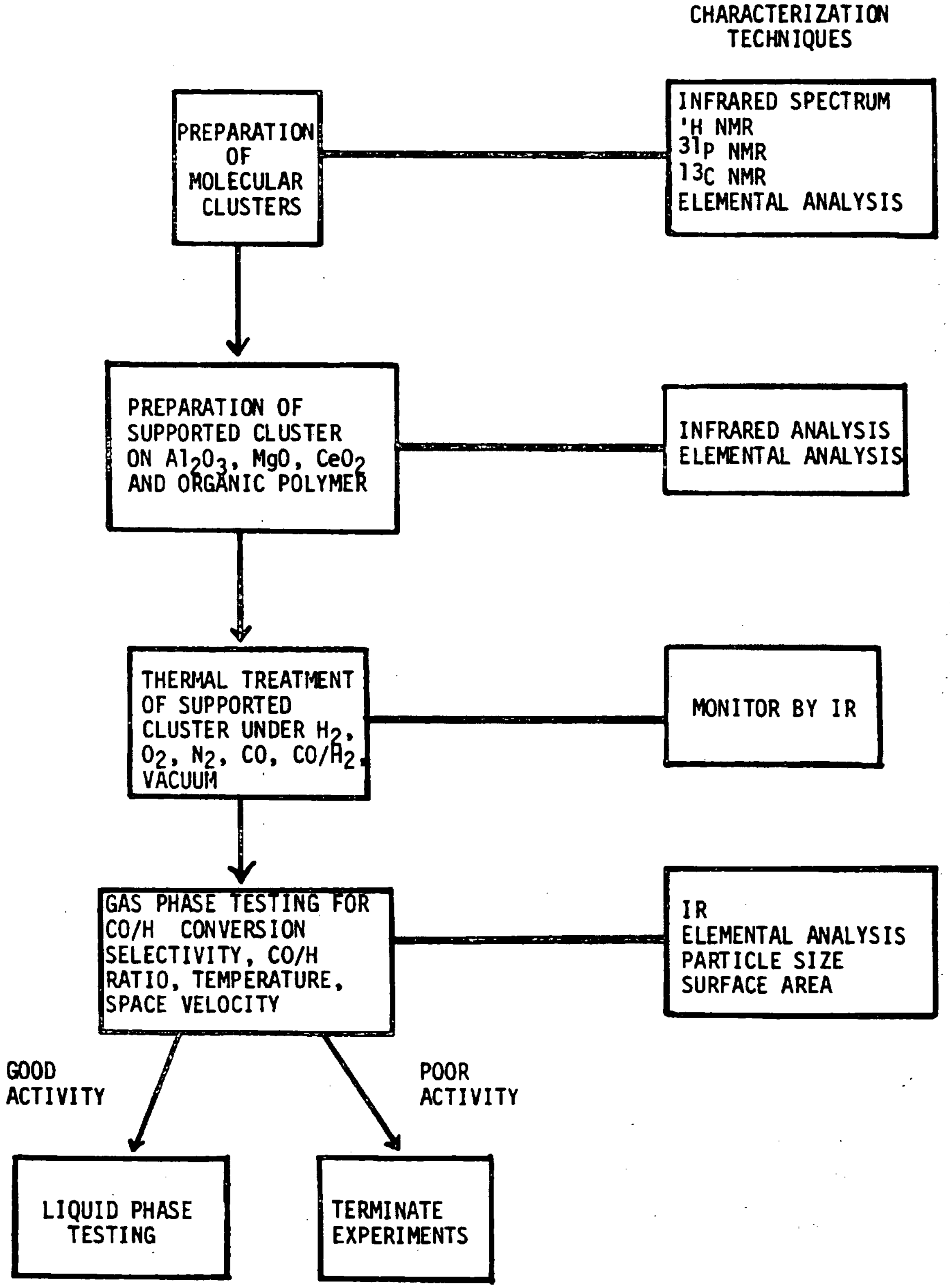


Figure 4

MILESTONE SCHEDULE - FISCAL YEARS AND MONTHS

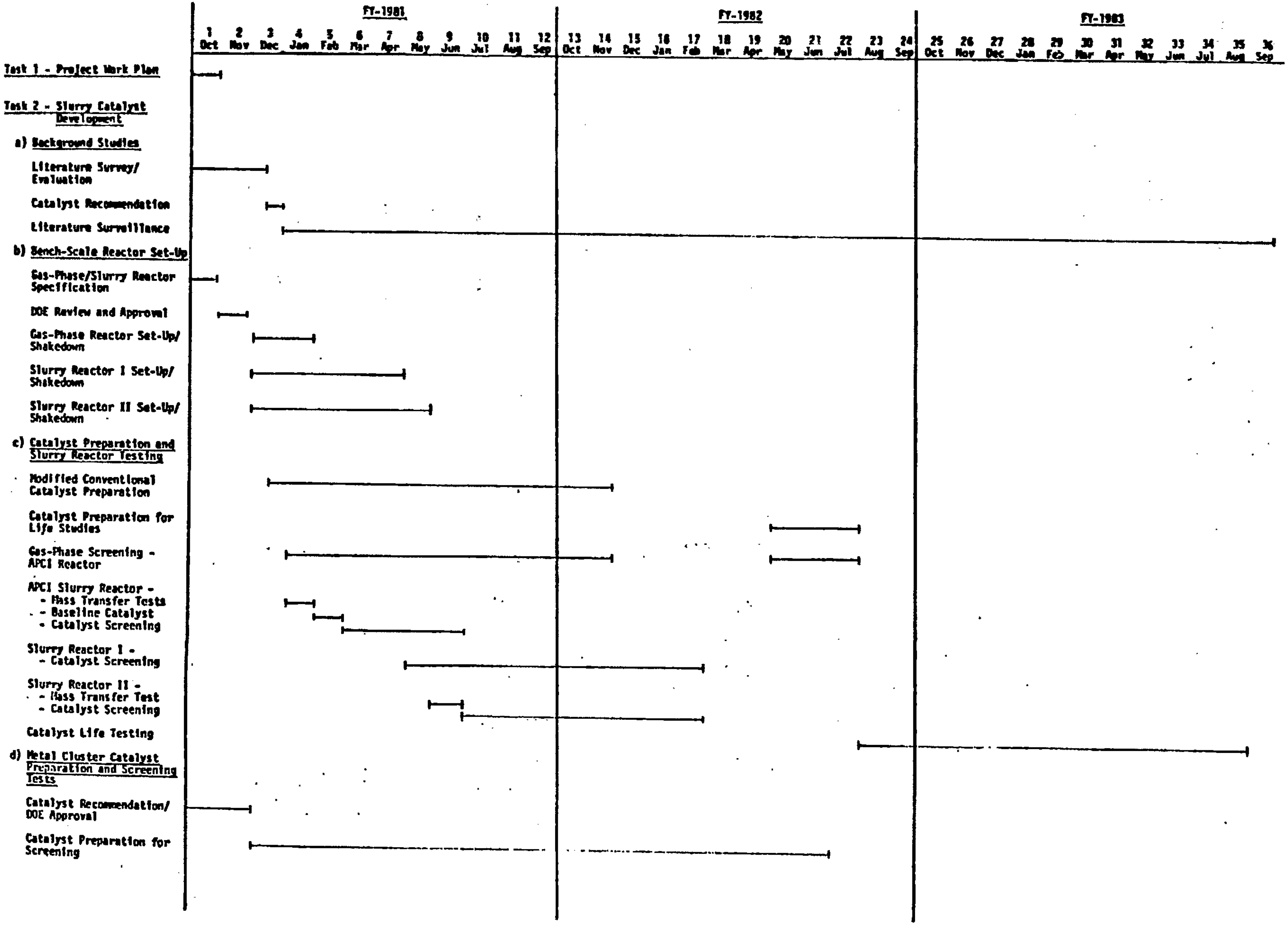


Figure 4 - Continued

MILESTONE SCHEDULE - FISCAL YEARS AND MONTHS - CONTINUED

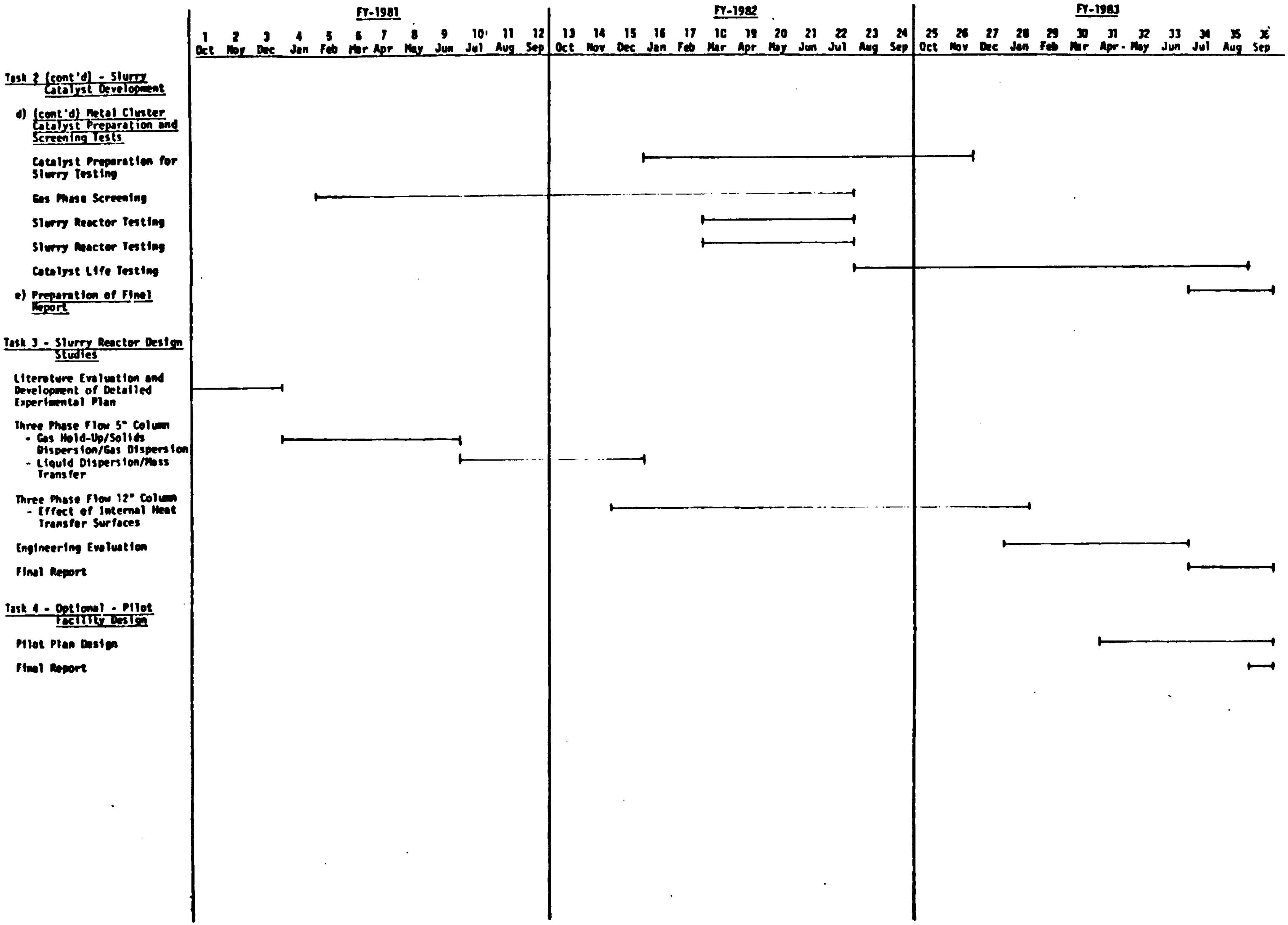


TABLE II

CRITICAL DEADLINES/ACTION POINTS

1.	Project Work Plan to DOE (Task 1)	31 October 1980
2.	Slurry Reactor Design to DOE (Task 2b)	7 November 1980
3.	Gas Phase Screening Reactor Design to DOE (Task 2b)	7 November 1980
4.	Recommended Cluster Catalysts to DOE (Task 2d)	7 November 1980
5.	Slurry Reactor Design Approval by DOE (Task 2b)	5 December 1980
6.	Gas Phase Screening Reactor Design Approval by DOE (Task 2b)	5 December 1980
7.	Cluster Catalysts Approval by DOE (Task 2d)	5 December 1980
8.	Initiate Operation of Gas Phase Screening Reactor (Task 2b)	5 December 1980
9.	Order Components for Slurry Reactors (Task 2b)	12 December 1980
10.	Recommended Conventional Catalysts to DOE (Task 2a)	19 December 1980
11.	Initiate Operation of Slurry Reactor (APCI Reactor) (Task 2c)	2 January 1981
12.	Detailed Program Plan for Task 3 to DOE (Task 3)	2 January 1981
13.	Initiate Cold-Flow Experiments in 5-Inch Simulator (Task 3)	2 January 1981
14.	Approval by DOE of Conventional Catalysts (Task 2a)	16 January 1981
15.	Conventional Catalyst Screening - Slurry Reactor (Task 2c)	1 March 1981
16.	Start Slurry Testing in Slurry Reactor I (Task 2c)	1 May 1981
17.	Start Slurry Testing in Slurry Reactor II (Task 2c)	1 June 1981
18.	Start Construction of 12-Inch Diameter Simulator	1 December 1982
19.	Initiate Cold-Flow Experiments in 12-Inch Simulator	1 February 1982
20.	Initiate Slurry Reactor Screening of Cluster Catalysts (Task 2d)	1 March 1982
21.	Initiate Catalyst Life Testing	1 August 1982
22.	Initiate Slurry Reactor Engineering Study (Task 3)	1 January 1983
23.	Approval by DOE to Begin Pilot Facility Design (Task 4)	1 April 1983
24.	Submit Final Report	30 September 1983

Catalyst and Reactor Development for a Liquid Phase Fischer-Tropsch Process

Quarterly Technical Progress Report
for Period 1 January 1981 - 31 March 1981

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April 1981

Prepared for the United States Department of Energy
Under Contract No. DE-AC22-80PC 30021

ABSTRACT

Air Products and Chemicals, Inc., under contract to DOE, has begun a three year program in "Catalyst and Reactor Development for a Liquid Phase Fischer-Tropsch Process". This program contains four major tasks: (1) Project Work Plan, (2) Slurry Catalyst Development, (3) Slurry Reactor Design Studies, and (4) Pilot Plant Facility Design. During the first quarter, Task 1 was completed. During this, the second quarter, work in Tasks 2 and 3 was actively underway. In Task 2, the computerized literature search of Fischer-Tropsch literature was continued, refinements in analytical procedures were implemented, the first 300 mL slurry reactor was completed, and catalyst screening tests were begun in the 15 mL gas-phase tubular reactor. Two of ten modified "conventional" slurry catalysts were prepared. Two batches of one of these catalysts, representing different pretreatment procedures, and a baseline Fischer-Tropsch catalyst were tested in the gas phase reactor. Eight metal cluster catalysts were screened in a gas phase reactor. In Task 3, construction of the 5" cold flow reactor simulator was completed and initial experiments begun. The persistant foaming problem associated with the use of kerosene as a cold flow liquid was overcome by using a C_9-C_{11} isoparaffin mixture instead of kerosene.

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1.0 INTRODUCTION

The national need for an adequate domestic supply of distillate hydrocarbon liquids for transportation and heating fuels is becoming critical. Coal liquefaction can be an important source of liquid fuels in the future. Coal liquefaction can be accomplished by both the direct route (hydrogenation of coal in a donor solvent) or by indirect routes (gasification of coal followed by recombination reactions, e.g. Fischer-Tropsch).

Many factors influence the viability of Fischer-Tropsch indirect liquefaction technology as a source of liquid fuel. Some of these factors, such as the price and availability of petroleum-based fuels, are nontechnical, virtually uncontrollable, and seemingly unpredictable. However, a major technical problem influencing the viability of the Fischer-Tropsch reaction is its poor selectivity for liquid fuels.

Product selectivity of the Fischer-Tropsch reaction has been the focus of extensive research for many years, yet still remains a prime target for technical innovation. Fischer-Tropsch technology, as it is currently practiced commercially for liquid fuels production, provides a broad range of hydrocarbon products which require costly downstream refining. Ideally, technology should be available for the selective production of gasoline and other fuels.

Selectivity can be influenced by variations in the catalyst composition and process conditions. Yet, in spite of the extensive effort devoted to this problem, a suitable catalyst has not been developed for producing a narrow range hydrocarbon product such as gasoline or diesel fuel without the coproduction of lighter and heavier undesirable products. Development of a highly selective catalyst certainly has the largest potential impact on the desired product distribution.

The Fischer-Tropsch reaction is highly exothermic, and improved heat transfer would also be expected to have a major beneficial effect on product selectivity. Higher selectivity through improved temperature control provided the impetus for research during the 1940's and 1950's to develop a liquid phase process. These efforts began in Germany in 1938 and continued until 1953, culminating with a demonstration plant in Rheinpreussen. Additional liquid phase work was undertaken in Great Britain and at the U.S. Bureau of Mines. Liquid phase operations always resulted in improved selectivity to liquid products, usually through lower methane production. However, considerable differences were reported in the space-time yield, catalyst life and ease of operation of liquid phase reactors.

In addition to improved product selectivity, liquid phase operation offers the advantages of ease of scale-up and the ability to directly utilize the carbon monoxide-rich synthesis gas produced by coal gasifiers. The full potential of the liquid phase Fischer-Tropsch process has clearly not yet been realized, and its further development is an important part of our country's program to establish viable technology for converting coal to hydrocarbon fuel.

Therefore, Air Products (APCI) under contract to the DOE has undertaken a program in catalyst and reactor development for a liquid phase Fischer-Tropsch process. This contract spans 36 months and is divided into four major tasks. This report describes the work accomplished during the second quarter.

2.0 OBJECTIVE

The overall objective of this program is to evaluate catalysts and slurry reactor systems for the selective conversion of synthesis gas into transportation fuels via a single stage, liquid phase process.

Task 1 - To establish a detailed Project Work Plan.

Task 2 - To evaluate and test catalysts for their potential to convert synthesis gas to gasoline, diesel fuel, or a mixture of transportation fuels suitable for domestic markets, and to quantify catalyst activity, selectivity, stability and aging with a target process concept involving a single stage, liquid phase reactor system.

Task 3 - To evaluate through the use of cold-flow reactor simulators the flow characteristics and behavior of the slurry reactors for the production of hydrocarbons from synthesis gas. This includes (1) defining heat, mass and momentum transfer parameters which affect the design of slurry reactors, (2) establishing operating limits for slurry reactors with respect to system physical parameters, (3) developing or confirming correlations for predicting the flow characteristics and heat/mass transfer of slurry reactors, and (4) defining the necessary requirements for the design of larger scale reactors.

Task 4 - To develop a preliminary design for a pilot-scale slurry phase Fischer-Tropsch reactor.

3.0 SUMMARY AND CONCLUSIONS

3.1 Task 1 - Project Work Plan

This task was completed last quarter.

3.2 Task 2 - Slurry Catalyst Development

3.2.1 Sub-Task 2a - Background Studies

A computerized survey of available literature and patents dealing with the conventional and slurry phase Fischer-Tropsch processes and the hydrodynamics of 3 phase slurry reactors was continued.

3.2.2 Sub-Task 2b - Bench Scale Reactor Set-Up

The first 300 mL slurry reactor was constructed and shakedown tests were begun.

The 15 mL gas phase tubular reactor was commissioned and used to screen precipitated catalysts and the baseline Fischer-Tropsch catalyst.

Development of the analytical methods was continued. The aqueous phase analysis was quantified for alcohols, acids, aldehydes and ketones found to occur in actual reactor samples. Quantitation errors in the organic phase capillary analysis were traced to peak tailing caused by the stainless steel capillary walls. Less active column materials are being investigated.

The Tektronix 4052 computing graphics system was installed. Programs were written to organize and correlate sample chromatographic and operating data, and to reduce these data to weight, molar and Schulz-Flory distributions, together with selectivity and molar conversion and mass balance information. Automatic graphing became available.

3.2.3 Sub Task 2c - Catalyst Preparation and Slurry Reactor Testing

Gas phase screening was carried out in the 15 mL tubular reactor of the baseline Fischer-Tropsch catalyst. It behaved exactly as expected producing a near-linear Schulz-Flory distribution plot.

The remainder of this section contains potentially patentable material and has therefore been issued under a supplementary report marked "Not for Publication".

3.2.4 Sub-Task 2d - Metal Cluster Catalyst Preparation and Screening Tests

This section contains potentially patentable material and has therefore been issued in a supplementary report marked "Not for Publication".

3.3 Task 3 - Slurry Reactor Design Studies

Construction of the 5" cold flow simulator for gas holdup, solid and liquid dispersion and mass transfer measurements was completed. Initial gas holdup results in the simulator for an air/water system agree directionally with the Akita and Yoshida correlation. To prevent foaming, the decision was made to use a C_9-C_{11} isoparaffin mixture instead of kerosene as the organic liquid. The hydrodynamic properties of these liquids are expected to be similar. Procedures were written for the column's safe operation, and gas holdup and foam tests. A method of determining the viscosity of a slurry was established.

3.4 Task 4 - Pilot Facility Design

No action is planned until March 1983.

4.0 ACKNOWLEDGEMENTS

The contributions to this program made by T. G. Dunlap, J. M. LaBar, L. E. Schaffer and E. G. Valagene are gratefully acknowledged.

5.0 RESULTS AND DISCUSSION

5.1 Task 1 - Project Work Plan

This task was completed last quarter.

5.2 Task 2 - Slurry Catalyst Development

5.2.1 Sub-Task 2a - Background Studies

Background studies, including a computerized search of current literature and patents, have been continued this quarter.

5.2.2 Sub-Task 2b - Bench Scale Reactor Set-Up

The first 300 mL slurry reactor was constructed and shakedown tests were begun.

The 15 mL gas phase tubular reactor was commissioned and used to screen two precipitated catalyst preparations and the baseline catalyst.

Development of the analytical methods was continued with the quantitation of the aqueous phase analysis, based on an external methanol solution standard, for C_1-C_6 alchols, C_2-C_6 aldehydes, C_3-C_6 ketones, and C_2-C_6 carboxylic acids.

The observation of small errors in the the integration of the organic phase capillary analysis was investigated and found to be due to peak tailing in the stainless steel capillary column. A change to a less active capillary column material such as glass or silica should eliminate this problem.

The Tektronix 4052 computing graphics system was delivered and installed. A program was written to logically organize chromatographic data and operator input by reactor type, day number and sample sequence number. A complete analysis contains a minimum of 5 files: TCD and FID gas analyses, aqueous and organic liquid phase analyses, and operator log sheet data. Additional information, e.g. capillary analyses, PONA results and elemental analyses, are stored in optional files.

A data correlation program was written to scan the database, test for the presence of the required files, and organize the chromatographic data into a series of standardized matrices.

A second data correlation program utilizes these data matrices to produce overall weight %, mole % and Schulz-Flory distribution plots for the sample, as well as selectivity and molar balance data. The Tektronix graphics routines can be used to automatically produce graphs from these results.

5.2.3 Sub-Task 2c - Catalyst Preparation and Slurry Reactor Testing

a) Preparation of Modified "Conventional" Catalysts

This section contains potentially patentable material and has therefore been issued in a supplementary report marked "Not for Publication".

b) Gas Phase Screening

i) Gas Phase Screening Test No. 5870-9-B - Baseline Catalyst - Fused Fe_2O_3:2.5% Al_2O_3:1.0% CaO:0.6% K_2O

A gas phase screening test of the baseline Fischer-Tropsch catalyst, fused Fe_2O_3 promoted with 0.6% K_2O, 1.0% CaO and 2.5% Al_2O_3, was carried out at 455 psig, 253°C and GHSV 295 h^{-1} with 43% CO/57% H_2. The full results are presented in Tables 1-3 and Figures 1-3.

The hydrocarbon product distribution followed a standard Schulz-Flory distribution ($\alpha = 0.76$) with positive deviations shown by CH_4 and the C_6 fraction (Figure 3). A noticeable feature of the results is the high olefinic content of the hydrocarbon product with 1-alkene/n-alkene ratios of 2.0 to 5.2 in the C_2-C_5 region (Table 2 and Figures 2 and 3).

The concentration of oxygenates in the product and their distribution were also typical of this type of catalyst, with zero CH_3OH, but a small amount (1.2 mol %) of dimethyl ether formed (Table 3).

Conversion of the inlet gas under these conditions was high. The formation of high boiling point waxes was also observed, leading to the eventual plugging of the reactor, which presumably accounted for the discrepancies in the molar conversions shown between the observed total conversion and sum of the component conversion given in Table 1.

The remainder of this section contains potentially patentable data and therefore has been issued under a supplementary report marked "Not for Publication".

5.2.4 Sub-Task 2d - Metal Cluster Catalyst Preparation and Screening Tests

This section contains potentially patentable data and therefore has been issued in a supplementary report marked "Not for Publication".

5.3 Task 3 - Slurry Reactor Design Studies

5.3.1 5" Cold Flow Simulator

a) Gas Holdup

The construction of the 5" cold flow simulator column was completed and initial shakedown tests were carried out.

Initial measurements of gas holdup in water at zero liquid velocity were carried out as a system test, using 12.8% open area, 1/28" hole diameter, triangular pitch distributor plate. The results are listed in Table 22 and plotted in Figure 37, where the solid line is the correlation derived by Akita and Yoshida(4). Agreement is good particularly at lower gas velocities.

b) Organic Liquid

A suitable organic liquid was found for the cold flow simulator tests. It was required to meet the following constraints: 1) The organic fluid should not foam when sparged with nitrogen, since this would result in highly inaccurate gas holdup, solids dispersion and bubble diameter measurements. 2) The flash point of the organic liquid should be greater than 100°F. 3) The liquid should be as economical as possible while still meeting the general hydrodynamic properties of an n-paraffin mixture.

The results of foam testing a variety of paraffins meeting conditions (2) and (3) are given in Table 23.

Bed height difference of a foaming versus nonfoaming solution was quite striking. Gas hold-up values of 0.4 vs 0.88 resulted. In all cases but one, the addition of a defoamer to the deodorized kerosene aggravated the foaming problem. One defoamer, Dow FS1265, a fluorinated silicone oil, was effective at a concentration of 1% by weight. However, such a large addition of surfactant would make suspect any results of the study, and the search for an alternative non-foaming paraffin liquid was continued.

Samples of reagent grade n-alkanes from C_5 to C_{16} that were tested did not foam, nor did technical grade paraffins and paraffin mixtures. No commercial source of n-paraffin mixtures was located, and therefore a decision was made to use a C_9-C_{11} isoparaffin mixture as the organic liquid in the simulator tests.

The physical properties of the isoparaffin mixture may be compared against water, kerosene, and the Rheinpreussen type paraffin oil. It is expected that the gas diffusivities, specific heat and thermal conductivity of the isoparaffin mixture will be similar to that of kerosene, although actual measurements or estimations have not yet been made. While most of the physical properties of the Rheinpreussen type paraffin oil are well matched by the isoparaffin, the viscosity is about a factor of 4 greater. It is not possible in cold flow studies to easily obtain such a low viscosity, except by using hazardous liquids, such as pentane, or expensive fluids, such as Dow Corning silicone oil. If any of the existing correlations are confirmed by this work, then we will be able to extrapolate to lower viscosities with some confidence. However, if a new correlation is developed, then a recommended extension of the present work would be to obtain data for a low viscosity liquid.

c) Liquid Dispersion

In the area of liquid dispersion, the question has been raised as to whether a single residence time distribution (RTD) at the outlet of the column would be sufficient to characterize the mixing behavior of the 5" column. Alvarez-Cuenca and Nerenberg(5) have postulated a 2 zone model for 2 phase bubble columns with the region near the distributor plate having different mass transfer and dispersion characteristics. To correctly model these zones, the 5" column could be segregated into several zones, and the extent of dispersion and mass transfer could be determined in each. It would then be possible to distinguish, for example, between a distributor region, which acts like a continuous stirred tank reactor (CSTR), and the rest of the bubble column, which may act like a plug flow reactor (PFR). Because of the many-fold increase in the amount of data to be collected and reduced, data sampling would need to be computer interfaced, which is currently being considered.

6.0 EXPERIMENTAL

6.1 Task 1 - Project Work Plan

No experimental work.

6.2 Task 2 - Slurry Catalyst Development

6.2.1 Sub-Task 2a - Background Studies

No experimental work.

6.2.2 Sub-Task 2b - Bench Scale Reactor Set-Up

a) Slurry Reactors

The construction and instrumentation of the first 300 mL slurry reactor, provided by APCI, was completed this quarter, and shakedown tests have now begun. It is expected that determination of the mass transfer characteristics of the reactor will begin in mid-April. An internal safety review of the system was also successfully completed.

Most of the components of the 1000 mL and 300 mL slurry reactors ordered for the contract have now been received, and construction, to the same design which was published in the previous quarterly report, is scheduled to begin in April.

b) 15 mL Gas Phase Tubular Reactor

The 15 mL gas phase tubular reactor, whose design was also published in the previous quarterly report, was constructed and commissioned. It was used to conduct screening tests on two precipitated catalyst preparations, as well as the baseline Fischer-Tropsch catalyst.

c) Analytical Procedures

(i) Aqueous Phase Analysis

The method of aqueous phase analysis was previously demonstrated but not fully developed because of a lack of actual reactor samples for analysis. Catalyst testing utilizing the 15 mL tubular reactor produced aqueous phase samples which were used as a basis for developing an aqueous phase analysis system. A 10% SP-2100/1% H_3PO_4 on Chromosorb/WAW (20' x 1/8" column) was utilized in conjunction with a Sigma-1 chromatograph fitted with an auto-sampler and dual differential flame ionization detectors.

The analysis currently quantifies C_1-C_6 alcohols, C_2-C_6 aldehydes, C_3-C_6 ketones, and C_2-C_6 carboxylic acids (see Figure 38). A series of GC standard kits were acquired which contain authentic samples of alcohols, aldehydes, ketones and acids (and methyl esters) for most of the isomers in the range of C_1 to C_{10}. Since the bulk of the phase is water, and therefore invisible to the detector, the analysis quantitation was based on a methanol external standard. Literature FID response factors were then used to determine components concentrations from their absolute areas. The linearity of the FID response was checked with a standard solution supplied by Perkin-Elmer. The injection size was maintained at a constant volume by the use of an auto-sampler, and the amount of water present was assumed to be the difference between the weight of known components and the gross sample weight. The accuracy of the analysis was checked by comparison to total carbon analyses of the sample.

(ii) Capillary Organic Phase Analysis

The quantitation of the capillary analysis method for the organic liquid phase was examined as part of an overall quality assessment of the analysis stream. The quantitation of mixtures of normal hydrocarbons and olefins was found to be good; however, difficulties were encountered in the analysis of actual reactor samples. Small quantitation errors were observed within C_5-C_8 isomer sets, and although these errors were not large, it was felt that the analysis quantitation could be improved. The problem was found to be due to mis-assignment of area due to tailing peaks. The method of integration was changed to accommodate skimming or riding peaks from tails. This, however, caused quantitation errors for small peaks which were not assigned as tailing peaks because of a failure to establish baseline conditions between major peaks.

The cause of the quantitation problem is the tendency of peaks of large concentration to tail. The column currently in use is a 150' stainless steel capillary. The injector system of the chromatograph has been changed to allow use of capillary columns constructed of less active materials such as glass and fused silica. We have recently sent reactor samples to capillary suppliers to identify a new capillary which will yield the desired separation without the observed tailing of major components.

(iii) Organic Phase Packed Column

The SP-2100 column previously used for routine phases analyses was replaced with a 3% SP-2100/Chromosorb/WAW (6' x 1/8"). This column has been found to give equivalent separation and quantitation with much reduced analysis time (see Figure 39).

d) Data Reduction

The Tektronix model 4052 computing graphics system was delivered. The new system consists of the 4052 processor, three 600 kbyte 8" floppy disk drives and a hard-copy device. This represents a significant increase in capability over the 4051 system previously sited. Work was initiated to utilize this system for complete data collection and reduction operations for the contract. Data will also be archived on the corporate computer to serve as a back-up and to allow large scale data operations.

The transfer programs previously developed for the 4051 system have been modifed to run on the new system. Transferred data from the Sigma computing integrators will now be directly stored in the 1.8 megabyte disk storage area of the 4052 system. This will allow quicker access to the data and extend the data storage capacity to a point where all data from a catalyst test can be stored on one diskette. The three disk drives have been designated for storage as below:

Drive 0 - Programming Storage
Drive 1 - Reactor System #1
Drive 2 - Reactor System #2

Data from the tubular gas phase catalyst testing unit will be stored on a separate diskette and can be located in either drive 1 or 2.

The multi-level directory system of the 4052 graphics disk system is used to organize the transferred data. The directory consists of 5 levels of libraries and files. A library is a logical grouping of files. The data organization is shown in Figure 40. Incoming data from the chromatographs is placed in the applicable day library for that sample. Each day of the catalyst test has been assigned a separate library or data file. It is only necessary, therefore, to specify the day and number sequence of the desired data when accessing the data from any particular analysis.

A complete analysis contains a minimum of 5 files and consists of all the tests performed on the reactor at any particular sampling time. The 5 files are the results from the gas analysis (hot wire detector and flame ionization detector), the aqueous phase analysis, the organic phase analysis, and the operator log sheet. Each of these files is assigned a separate suffix. Optional files may also be present consisting, for example, of capillary analyses, results from PONA analysis and elemental analyses, and these are also assigned unique suffix designations. The organization of the analytical and operating data in this fashion allows the data reduction system to automatically examine the database for any particular day/sequence number and report which tests are present and which tests have not been completed. This capability is required for automatic data correlation.

A data correlation processor was programmed and is currently in use. This processor automatically examines the stored data base for any particular day/sequence number dataset and verifies that sufficient data exists to allow reporting of product distributions, etc. Complete data reduction for an analysis requires that at least 4 separate gas chromatographic files are present. In addition to the required 4 files, an optional 5th file for capillary analysis may be present. The processor asks the operator for the reactor number of the data. The day of the test is then entered along with the sequence number for the particular analysis desired. The processor then checks the data base to ensure that the 4 required files are present.

If only capillary data is present for that analysis, the system informs the operator that capillary data has been selected. If both capillary and standard organic phase analyses are present, the system questions the operator to determine which one he wishes to utilize. Each data file is then scanned and the pertinent numerical information is extracted and placed in a series of standardized matrixes (see Figures 41-43). These matrixes are stored within the data base and can be used by subsequent data reduction processors.

A second processor was written which utilized the numerical matrixes produced by the above processor to compute the weight %, mole %, and Schulz-Flory product distribution (see Figures 44-46). The program also produces selectivity information in the form of mol % conversion of CO and H_2 into selected product ranges and compares the sum of these with the observed total conversion. The Schulz-Flory distribution plot can be immediately examined by the operator (Figure 46). The output from this processor is also stored within the database and can be accessed directly by the standard graphics routines of the Tektronix plot-50 graphics library. This allows the operator to use the many graphics programs supplied by Tektronix to produce graphs directly from the reduced data. Figures 1-12 were produced by this process.

6.2.3 Sub-Task 2c - Catalyst Preparation and Slurry Reactor Testing

a) Catalyst Preparation

This section contains potentially patentable material and has therefore been issued under a supplementary report marked "Not for Publication".

b) Gas Phase Screening

(i) Gas Phase Screening Test No. 5870-9-B - Baseline Catalyst -Fused Fe_2O_3:2.5% Al_2O_3:1.0% CaO:0.6% K_2O

The first screening test carried out in the 15 mL gas phase tubular reactor utilized 32.2 g of the baseline Fischer-Tropsch catalyst (an ammonia synthesis catalyst) ground to <300 µm.

The activation history of the catalyst was an initial treatment with 1:1 CO/H_2 at 100-400 psig and 250°C for 19 hours followed by reduction at 300°C and 450 psig of H_2 for 26 hours. A further 43 hours on stream at reaction conditions was required for the activity to increase to the level shown by the results quoted here. For the slurry phase test of this baseline catalyst, it is therefore proposed to preactivate the ammonia synthesis catalyst under H_2 at 450°C in the gas phase before loading into the slurry phase.

The remainder of this section contains potentially patentable material and has therefore been issued under a supplementary report marked "Not for Publication".

6.2.4 Sub-Task 2d - Metal Cluster Catalyst Preparation and Screening Tests

This section contains potentially patentable material and therefore has been issued under a supplementary report marked "Not for Publication".

6.3 Task 3 - Slurry Reactor Design Studies

6.3.1 5" Cold Flow Simulator

a) Gas Holdup

The procedure for obtaining gas holdup involved simultaneously shutting off the liquid and gas flow rates by closing valve 32 (see Figure 47) to the column and then measuring the settled liquid height. No correction to the settled liquid height is required unless there is weeping through the distributor plate (initial tests with water do not show any weeping). In addition to flow rates, temperatures and time to visual steady state were recorded.

b) Determination of Steady State

It is difficult to determine when a slurry bubble column has reached steady state. Visually, the column appears to be at steady state after a minute or so of operation, but this may be misleading. A more reliable method is to take slurry samples from the column to determine when the solids concentration no longer varies with time, as determined by measuring the weight of a known volume of the slurry sample. When mass transfer studies are being done, a second method that will be used to determine steady state will be to measure the oxygen concentration as a function of time.

c) Foam Test Procedure

This test is a qualitative determination of liquid foaming caused by nitrogen sparging. A 1-1/2" ID x 24" high fritted glass column was partially filled to the 3" line with the liquid to be tested. A 0.25 liter/minute flow of nitrogen was then sparged through the column and the height of the bed was measured immediately, after five minutes, and after sparging was stopped. These were then compared with the original bed height.

d) Filling Procedure

The following procedure for filling the column refers to Figure 47. Lines 61-64 and the reservoir tank are first purged with nitrogen. If a slurry is to be pumped into the reservoir tank, the lid of the 55 gallon storage drum is replaced with an agitator, 3b, which is the only time that the fluid is exposed to the atmosphere. The amount of liquid or slurry to be transferred is monitored by the scales, 6a, on which the 55 gallon drum is placed. By turning valves 47 and 48 into the "fill" position and turning on the slurry pump, 5a, the reservoir tank is filled with slurry to the desired weight change on scales, 6a. Pure liquid is then added to the tank through the same fill lines in order to obtain the desired slurry weight concentration and also to purge the fill lines of the solid.

e) Draining Procedure

The draining procedure is almost the reverse of the filling procedure except that 2 drums are connected in series by line 78. Line 71 is connected to ball valve 16 or 17, depending upon which tank is to be drained. Ball valves 47 and 48 are turned to drain and pump 5a is turned on. The tank and drain lines are then flushed several times by pumping liquid from line 66 up into the reservoir tank and then draining that liquid. The drain procedure is considered complete when only liquid is being drained from the reservoir.

f) Cleaning Procedure

This procedure is used when the slurry phase is changed. If the change to be made is from water to organic, the system is purged overnight with fresh nitrogen to evaporate the water. To confirm that all water has been evaporated, a fresh dessicant is attached to the nitrogen outlet at port number 58.

To change from organic to water, the entire system is cleaned with detergent and then rinsed with water.

g) Slurry Viscosity Measurements

An apparatus was constructed and is being evaluated for the measurement of apparent viscosities of rapidly setting slurries.

The Viscometer is a Brookfield model LVT. A spindle, immersed in the liquid being tested, is rotated at a constant speed. The torque required to maintain the spindle rotation is a measure of the viscosity of the liquid. The full scale torque for the model LVT is 674 dyn-cm.

The spindle is a modification of Brookfield's "Tee-Bar" spindle. There are twelve cylindrical bars extending radially from a central shaft which swing in horizontal planes through the liquid. The modifed spindle has greatly increased sensitivity.

The apparatus (Figure 48) is based on a design by W. M Underwood(6) of Monsanto Company. To maintain the slurry in suspension, the beaker holding the sample contains an annular sleeve. The slurry is pumped, by means of a stirrer, up through the annular space between the sleeve and the wall of the beaker, and flows back down through the central space of the sleeve. The bottom of the sleeve contains a honeycomb of small diameter thin wall tubing which permits the liquid to flow through easily while at the same time, eliminating any swirls and eddies created by the pump from reaching the spindle in the space above the honeycomb.

The "Eddy Control Basket" was installed in a glass beaker and operated with model slurries to observe the mixing pattern. Dyes injected into the slurry showed the agitation described by Underwood to be acceptable for the work proposed.

7.0 REFERENCES

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(5) M. Alverez-Cuenca, M. A. Nerenberg, AIChE J, Jan 1981, 1 27, p. 66.

(6) W. M. Underwood, Rev. Sci. Instrum., 1976 47 no. 9.

8.0 FIGURES

FIGURE 1

HYDROCARBON WEIGHT DISTRIBUTION

5870-9-B-23-27

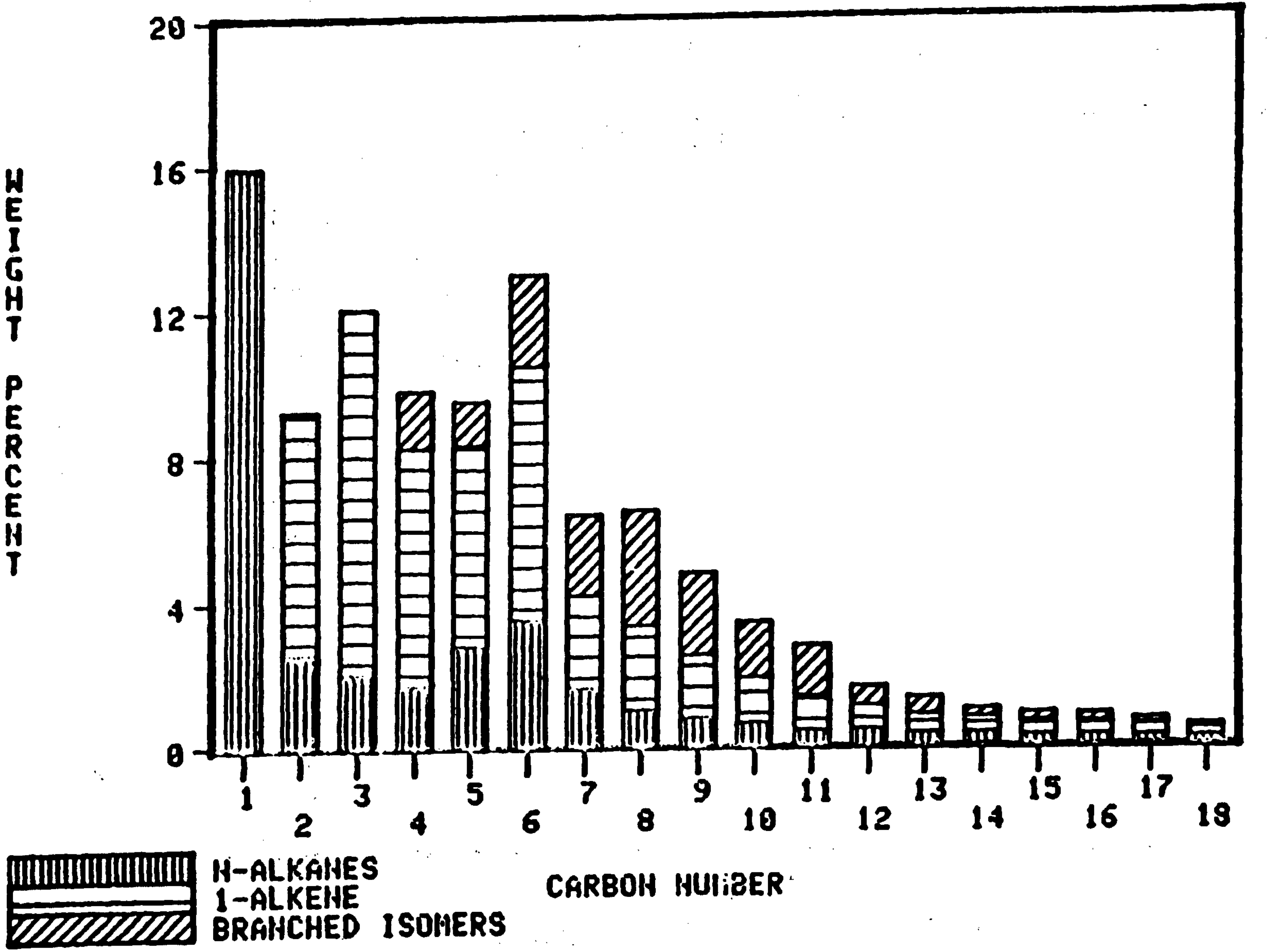


FIGURE 2

HYDROCARBON MOLAR DISTRIBUTION

5870-9-B-23-27

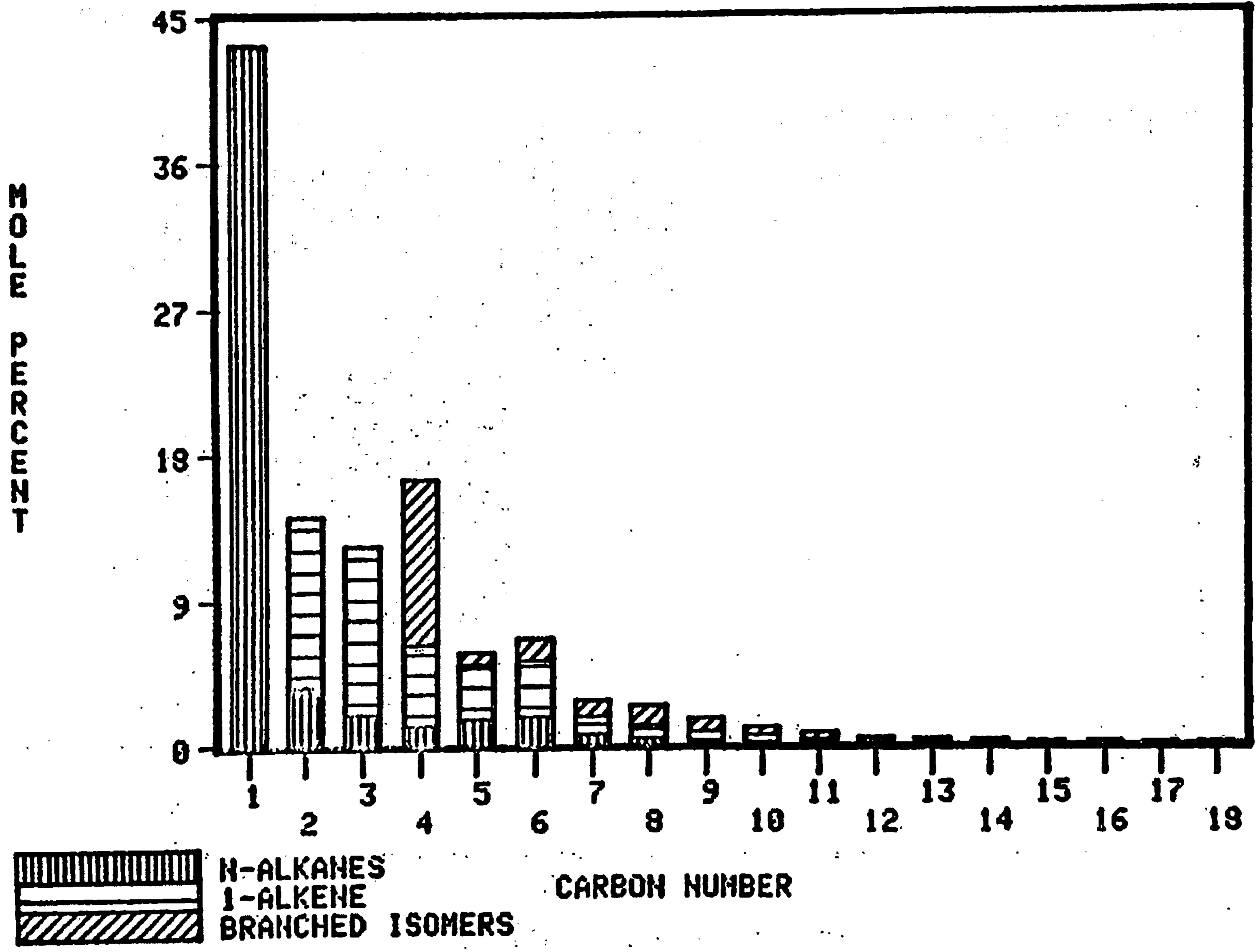


FIGURE 3

HYDROCARBON SCHULZ-FLORY DISTRIBUTION

5870-9-B-23/27

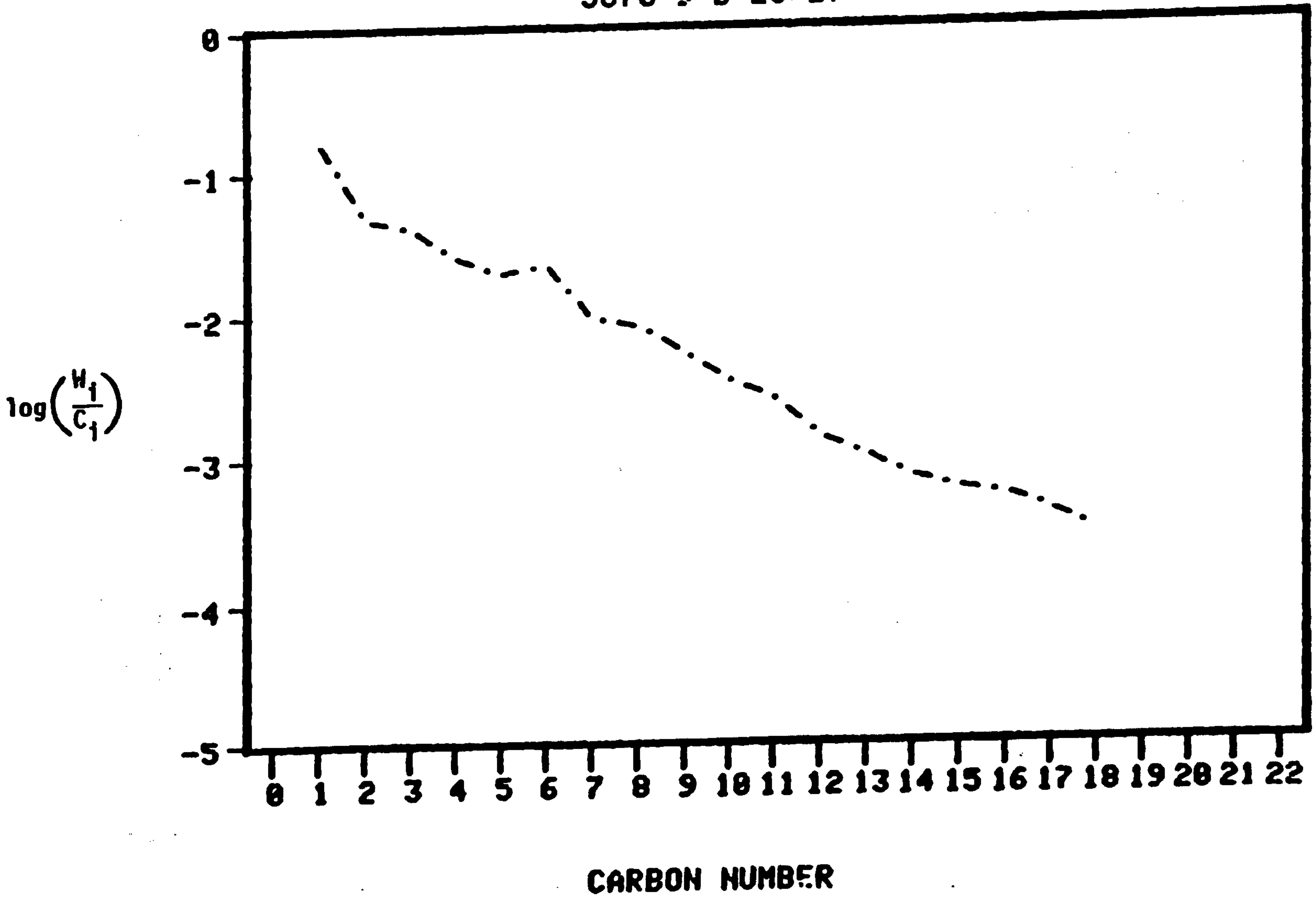


FIGURE 37

GAS HOLDUP

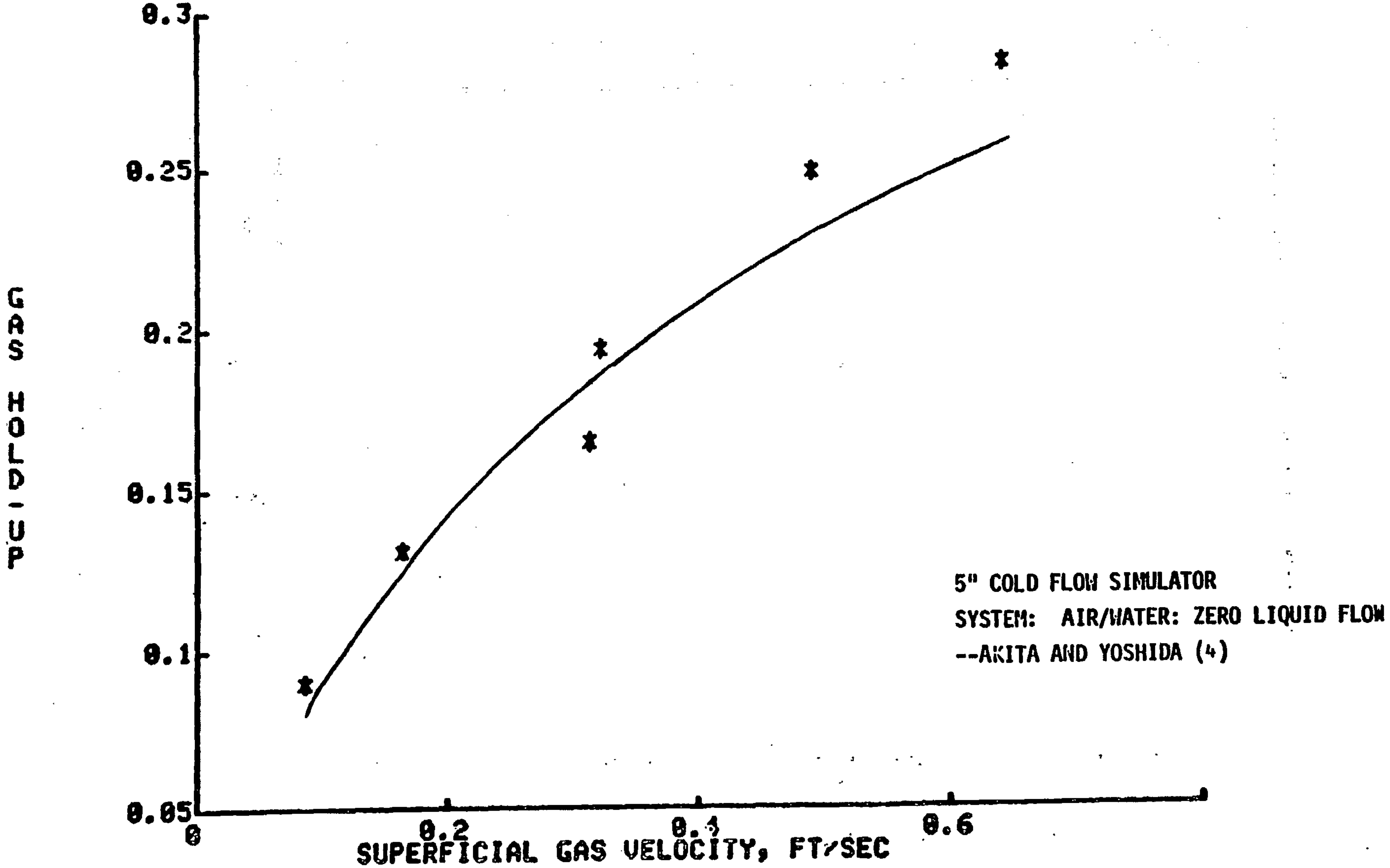
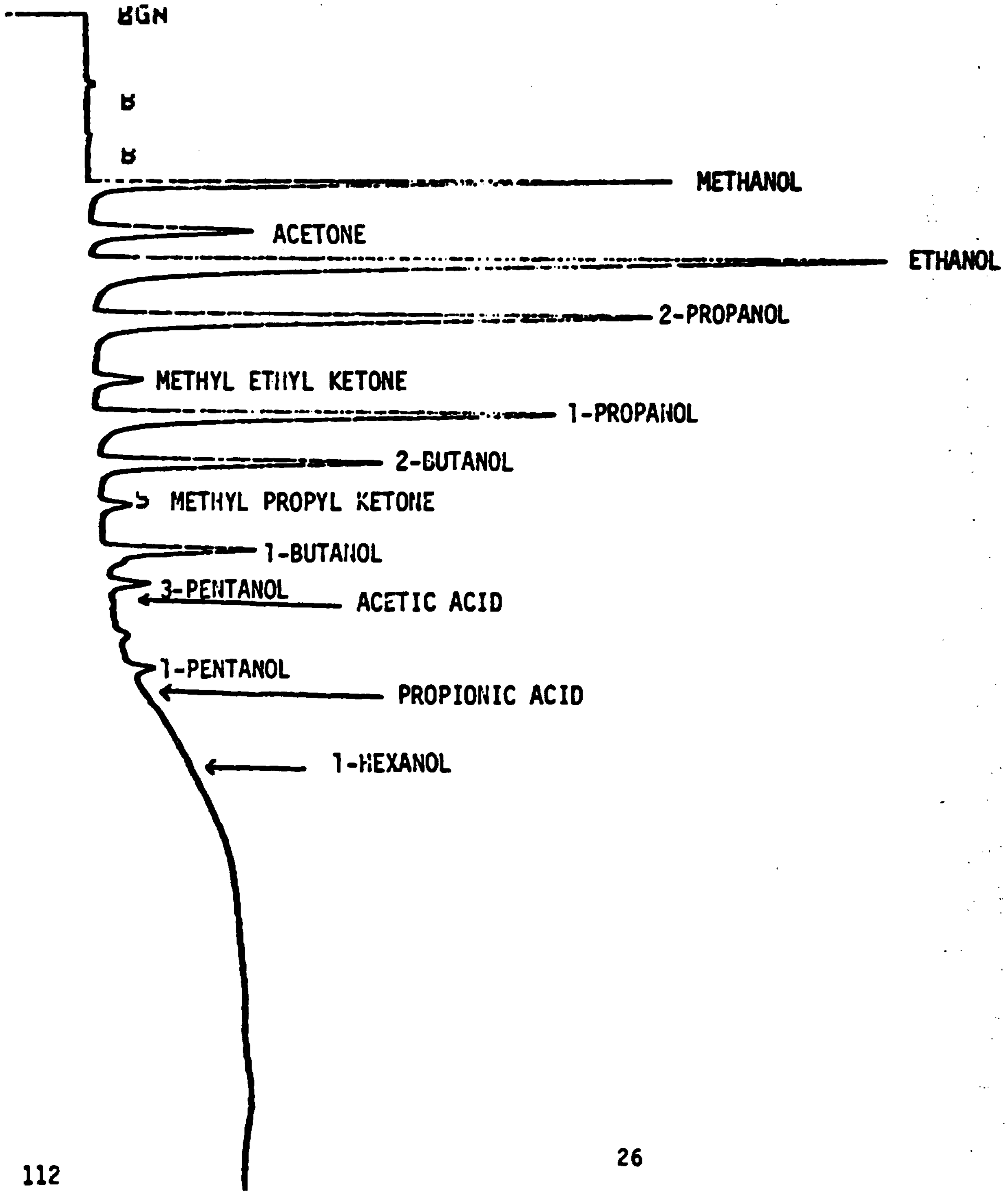


FIGURE 38

TEST SAMPLE AQUEOUS PHASE ANALYSIS



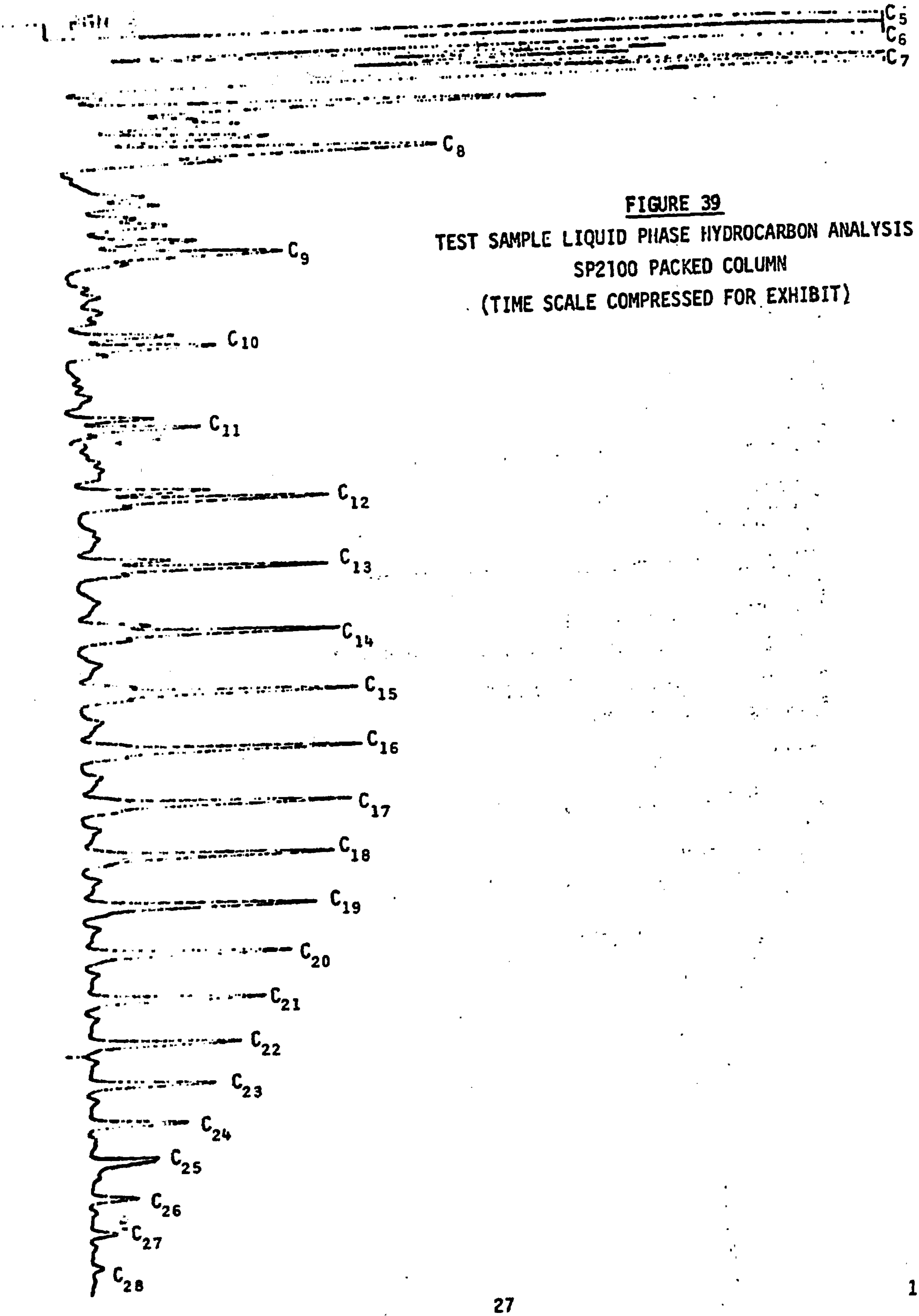
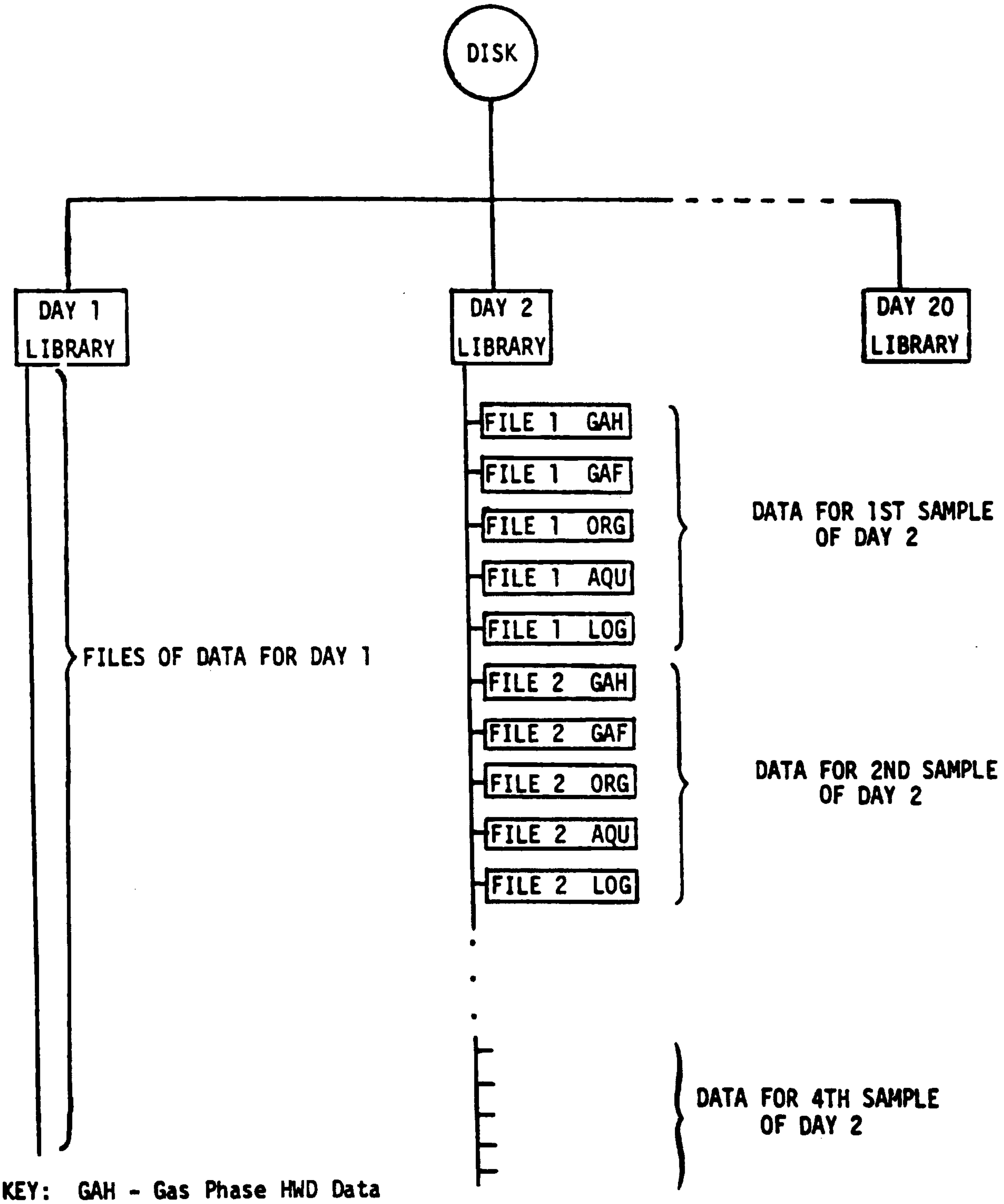


FIGURE 39
TEST SAMPLE LIQUID PHASE HYDROCARBON ANALYSIS
SP2100 PACKED COLUMN
(TIME SCALE COMPRESSED FOR EXHIBIT)

FIGURE 40

DATA ORGANIZATION ON DISK



KEY: GAH - Gas Phase HWD Data
GAF - Gas Phase FID Data
ORG - Organic Phase Data
AQU - Aqueous Phase Data
LOG - Operator Log Sheet Data

FIGURE 41

TEST SAMPLE

```
COMPILED GAS PRODUCT DISTRIBUTION :

HYDROGEN EXIT = 31.789 CORRECTED
CARBON MONOXIDE = 5.702

CARBON DIOXIDE = 40.2077
DI-METHYL ETHER = 0.4865

CARBON NO.         N-ALKANE        ALKENE            BRANCHED ALKANE
----------         --------        ------            ---------------
    C1              10.7898         0                      0
    C2              2.5272          0.3091                 0
    C3              0.8             1.7103                 0
    C4              0.3351          0.6435                0.3679
    C5              0.1041          0.0509                0.079
    C6              0.3494          0.1676                0.0959
DEPRESS RETURN TO CONTINUE
```

FIGURE 42

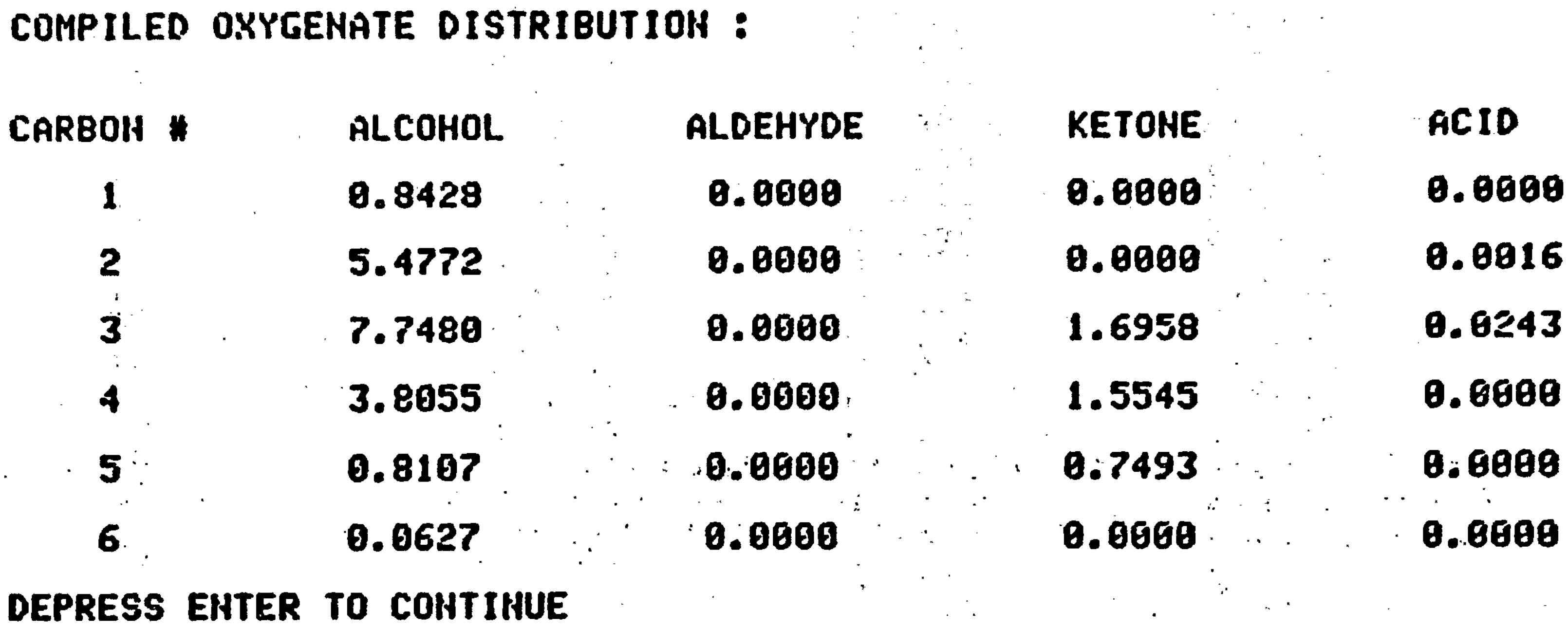
TEST SAMPLE (FROM FIGURE 39)

COMPILED LIQUID PHASE ORGANIC ANALYSIS :

CARBON #	N-ALKANE	1-ALKENE	BRANCHED
1	0.0000	0.0000	0.0000
2	0.0000	0.0000	0.0000
3	0.0000	0.0000	0.0000
4	0.0000	0.0000	0.0000
5	11.6844	2.1710	0.5119
6	11.1421	5.3438	3.0513
7	8.9463	3.2911	5.4485
8	3.8528	1.8059	6.0917
9	1.8672	1.1847	4.8130
10	1.0558	0.8540	2.2345
11	0.8472	0.6342	1.2965
12	0.7973	0.4880	0.9535
13	0.8067	0.3816	0.8244
14	0.8636	0.3191	0.7503
15	0.9615	0.2592	0.7620
16	1.3472	0.0000	0.8174
17	1.6590	0.0000	1.2209
18	2.1172	0.0000	1.9096
19	1.0018	0.0000	0.3295
20	0.8685	0.0000	0.1948
21	0.6979	0.0000	0.1596
22	0.5453	0.0000	0.0892

FIGURE 43

TEST SAMPLE (FROM FIGURE 3B)



```
COMPILED OXYGENATE DISTRIBUTION :

CARBON #        ALCOHOL        ALDEHYDE        KETONE        ACID
    1           0.8428          0.0000          0.0000        0.0000
    2           5.4772          0.0000          0.0000        0.0016
    3           7.7480          0.0000          1.6958        0.0243
    4           3.8055          0.0000          1.5545        0.0000
    5           0.8107          0.0000          0.7493        0.0000
    6           0.0627          0.0000          0.0000        0.0000
DEPRESS ENTER TO CONTINUE
```

FIGURE 44

TEST SAMPLE (FROM FIGURES 41 and 42)

```
HYDROCARBON WT% DISTRIBUTION IS

C1                  21.7473337418      0                  0
C2                  9.5506627496       1.08673179023      0
C3                  4.43420028471      9.04886748215      0
C4                  2.4483588038       2.59531727119      4.70236862466
C5                  5.08268166896      1.7794909738       0.897836390758
C6                  7.73166701937      3.66619986071      2.12144950833
C7                  3.13327228722      1.165675189        1.92980500965
C8                  1.36462379392      0.639631984387     2.15762011146
C9                  0.661343840328     0.419609065786     1.70471717197
C10                 0.373953955987     0.302478384554     0.791437880898
C11                 0.300069891563     0.224627390497     0.455665622634
C12                 0.282395803285     0.172844791174     0.337720304066
C13                 0.285725190656     0.135158959656     0.291994356237
C14                 0.305878609955     0.11302207554      0.26574886643
C15                 0.340553825233     0.0918060858039    0.269892891136
C16                 0.477164964487     0                  0.289515025216
C17                 0.587601451962     0                  0.432430749066
C18                 0.74989137679      0                  0.676361502512
C19                 0.354827688111     0                  0.116705653057
C20                 0.307614141669     0                  0.0689962404112
C21                 0.247189302787     0                  0.0565287472774
C22                 0.193139886531     0                  0.0315937610097
READY? (YES OR NO)
```

FIGURE 45

TEST SAMPLE (FROM FIGURES 41 and 42)

```
HYDROCARBON DIST IN MOL % IS

C1                 51.4952071106     0                  0
C2                 12.0589274509     1.47014701948      0
C3                 3.81732429596     8.16096217921      0
C4                 1.59898171447     1.7554920106       3.0710373961
C5                 2.6739719147      0.96292880169      0.472346971392
C6                 3.40542341744     1.65323000164      0.934395366028
C7                 1.18684653158     0.450555094299     0.730987342428
C8                 0.453424012227    0.216325928776     0.716913168419
C9                 0.195710339684    0.126145204458     0.504474006479
C10                0.0997530572615   0.0818394565258    0.211117831456
C11                0.0728608528464   0.0552507806352    0.1106415899
C12                0.0629224673944   0.0389711697742    0.0752496835076
C13                0.0588202865105   0.0281300095571    0.060110876657
C14                0.0585167698755   0.0218425648857    0.0509396623872
C15                0.0608480029768   0.0165595527959    0.0482227543092
C16                0.0799754213199   0                  0.048524279533
C17                0.092740203809    0                  0.0692498592461
C18                0.111830706955    0                  0.100865255855
C19                0.0501509466281   0                  0.0164950458314
C20                0.0413193628605   0                  0.00926771662087
C21                0.0316325635298   0                  0.00723392626358
C22                0.023599712133    0                  0.00386043338028
READY?(YES OR NO)
```

FIGURE 46

TEST SAMPLE SCHULZ-FLORY DISTRIBUTION PLOT (FROM FIGURES 41 and 42)

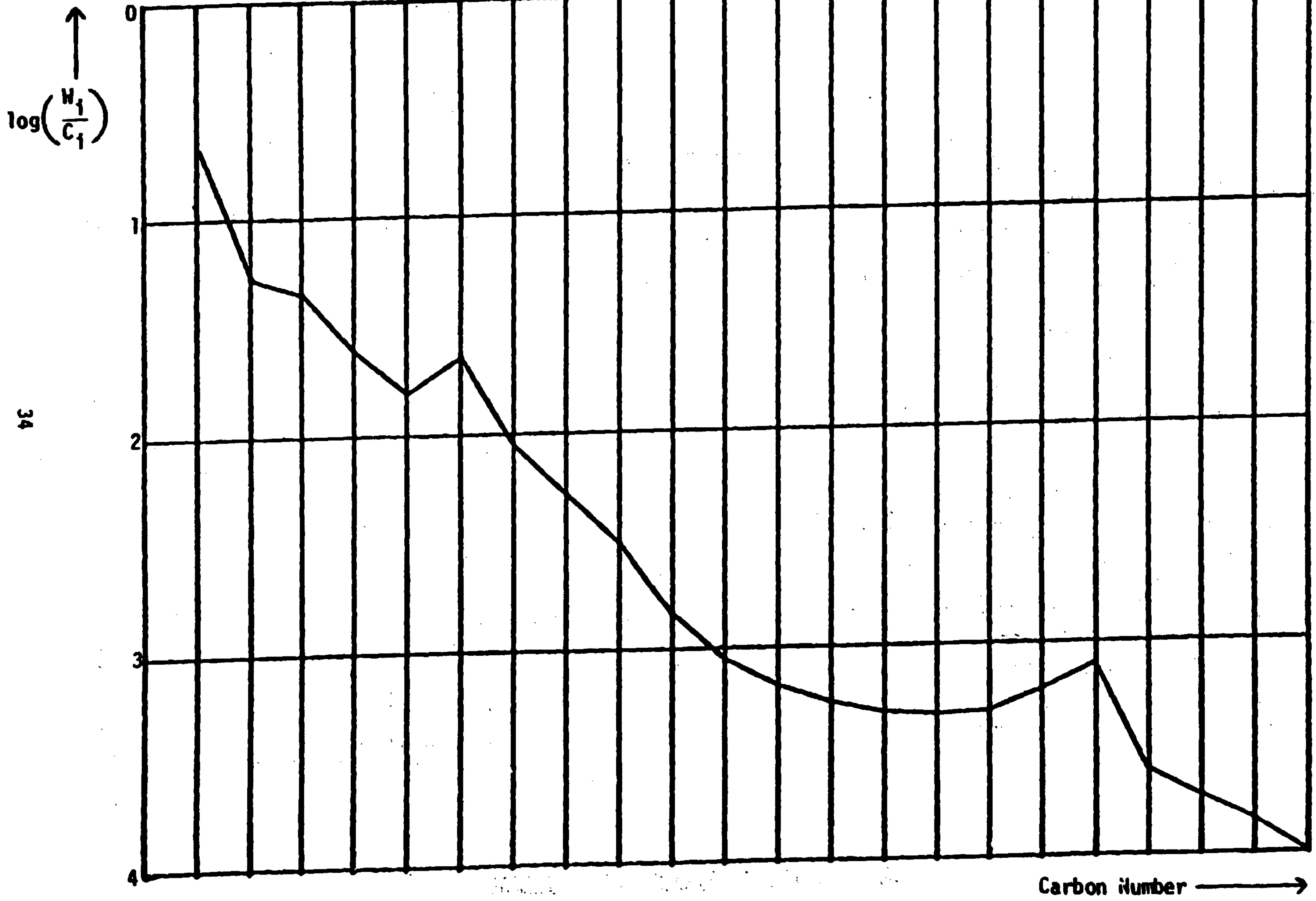
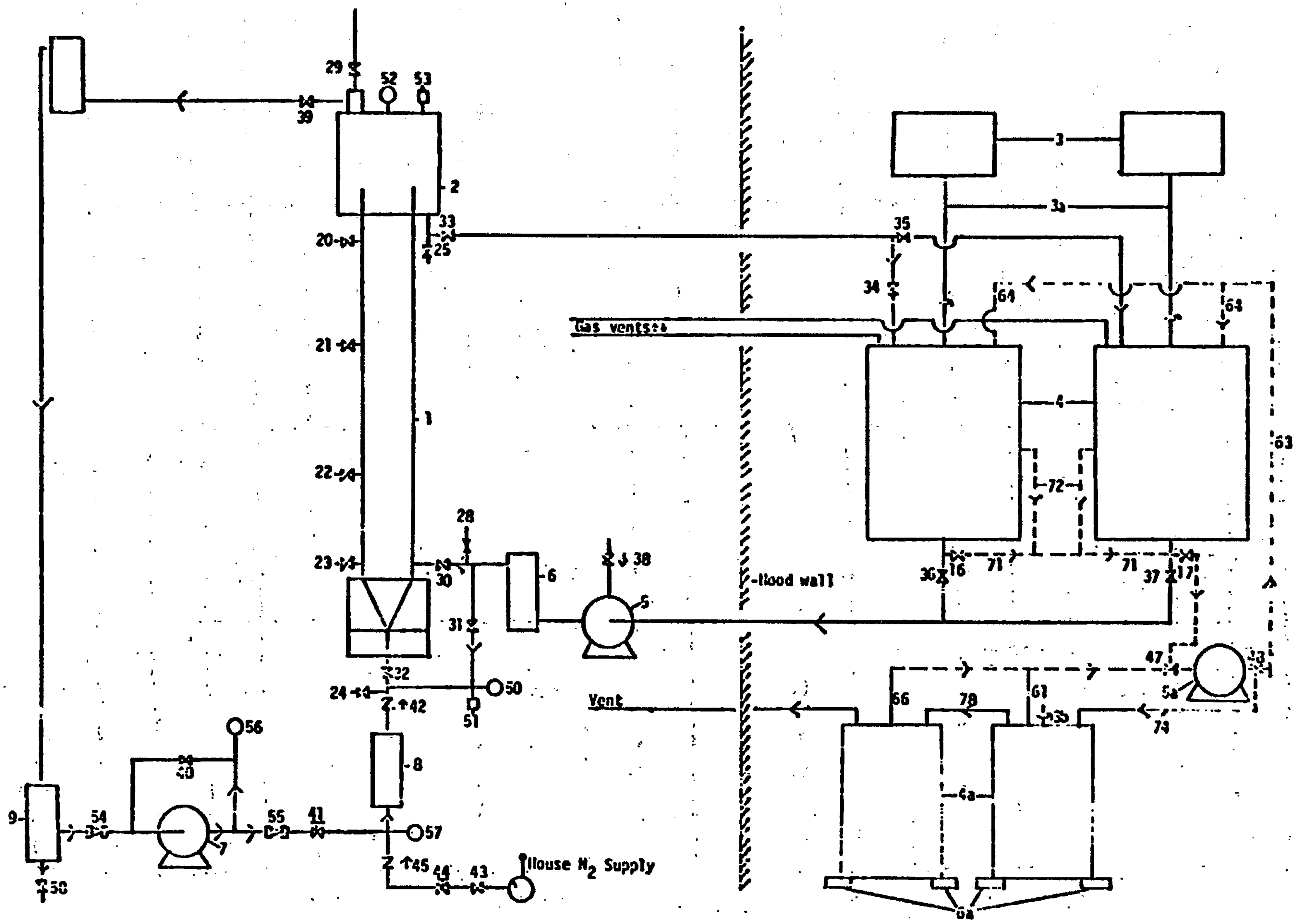


FIGURE 47

PROCESS FLOW DIAGRAM FOR 5" SLURRY COLUMN



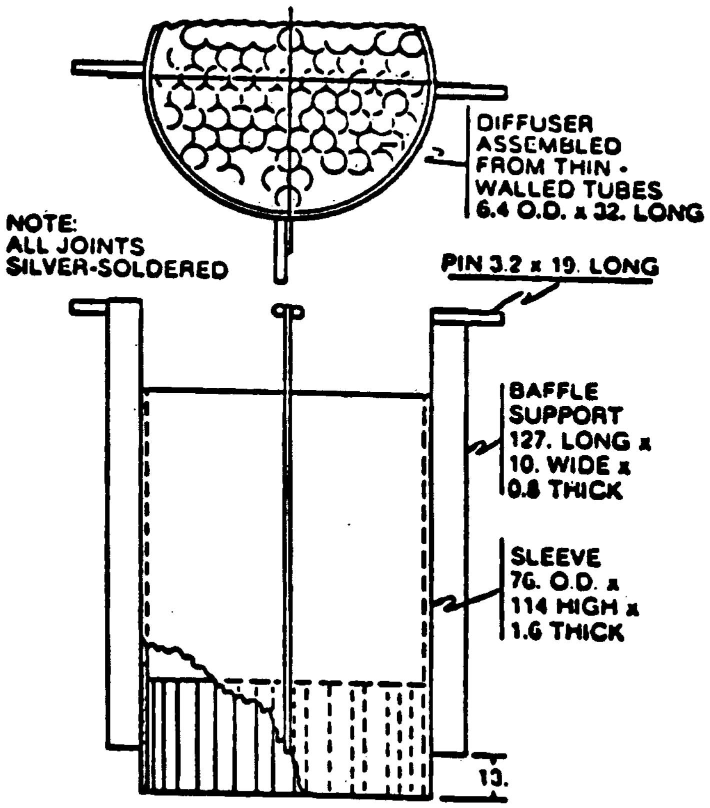


*FIGURE 48 Eddy control basket.

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9.0 TABLES

TABLE 1
PROCESS AND CONVERSION DATA

IDENTIFICATION

Run # : 5870-9-B	Catalyst: Baseline	Time on Stream: 43 hours
Sample #: 23-27	Loading : 32.2g	Reactor : 15 ml tubular

PROCESS DATA

CO/H_2 Ratio : 0.732	GHSV h^{-1}: 295
Inlet CO rate mol/min: 1.22×10^{-3}	P psig : 455
Inlet H_2 rate mol/min: 1.67×10^{-3}	T °C : 253

PRODUCT DISTRIBUTION, MOL %

C_1 : 10.71	C_{18+}: 0.02
C_2-C_4 : 8.42	CO_2 : 51.42
C_5-C_{11} : 5.25	H_2O : 21.90
C_{12}-C_{17}: 0.35	Oxygenates: 1.38

MOL % CONVERSION

Product / Reactant	C_1	C_2-C_4	C_5-C_{11}	C_{12}-C_{17}	C_{18+}	CO_2	H_2O	Oxygenates	Sum Component Conversion	Observed Total Conversion
CO	7.7	17.0	25.3	3.5	0.3	37.0	-	3.7	94.5	97.6
H_2	11.3	13.5	20.0	2.7	0.2	-	11.5	3.5	62.7	70.7

TABLE 2

Run # : 5870-9-B
Sample #: 23-27

Hydrocarbon Product Distribution

Carbon Number	n-alkane		1-alkene		Branched Isomers	
	Wt %	Mol %	Wt %	Mol %	Wt %	Mol %
1	15.90	43.3	-	-	-	-
2	2.58	3.75	6.67	10.38	-	-
3	2.03	2.01	10.00	10.36	-	-
4	1.69	1.27	6.54	5.09	1.57	1.12
5	2.79	1.69	5.52	3.43	1.20	0.73
6	3.51	1.78	6.95	3.60	2.48	1.26
7	1.60	0.70	2.56	1.14	2.21	0.96
8	1.01	0.39	2.31	0.89	3.14	1.20
9	0.77	0.26	1.73	0.60	2.27	0.77
10	0.61	0.19	1.26	0.39	1.54	0.47
11	0.42	0.12	0.92	0.26	1.40	0.39
12	0.45	0.12	0.67	0.18	0.48	0.12
13	0.35	0.08	0.50	0.12	0.46	0.11
14	0.32	0.07	0.45	0.10	0.23	0.05
15	0.27	0.06	0.39	0.08	0.21	0.04
16	0.27	0.05	0.36	0.07	0.22	0.04
17	0.23	0.04	0.31	0.06	0.16	0.03
18	0.17	0.03	0.23	0.04	0.11	0.02

TABLE 3

Run # : 5870-9-B
Sample #: 23-27

Oxygenates Product Distribution

Oxygenate	Mol % Fraction	Wt % of Aqueous Phase
CH_3OH	0	0
CH_3OCH_3	1.2	-
C_2H_5OH	33.2	4.95
CH_3CHO	3.2	0.50
$n\text{-}C_3H_7OH$	22.5	4.79
CH_3COCH_3	18.4	3.44
$n\text{-}C_4H_9OH$	7.6	2.01
$C_2H_5COCH_3$	5.6	1.44
$n\text{-}C_5H_{11}OH$	3.6	1.13
$C_3H_7COCH_3$	3.0	0.87
$n\text{-}C_6H_{13}OH$	1.8	0.64

TABLE 22

GAS HOLDUP, 5" COLD FLOW SIMULATOR

System: Air/water, zero liquid flow

RUN	V_{GS} Ft/sec	ε_G Measured	ε_G Akita & Yoshida
1	.490	.247	.2263
2	.314	.164	.1817
3	.166	.130	.1252
4	.088	.089	.0809
5	.641	.281	.2547
6	.323	.193	.1841

TABLE 23

FOAM TESTS SUMMARY

RUN	LIQUID	ADDITIVE	BED HEIGHT (IN.)		FOAM
			Unsparged	Sparged	
1	Water	--			No
2	Kerosene, reagent grade	--	3	>24	Yes
3	Kerosene, reagent grade	Heptanoic acid	3	>24	Yes
4	Kerosene, deodorized	Silica	3	>24	Yes
5	Kerosene, deodorized, United Refining	--	3	>24	Yes
6	Kerosene, deodorized, Quaker State	--	3	>24	Yes
7	Kerosene, deodorized, Penreco	--	3	>24	Yes
8	Kerosene, deodorized, United Refining	Diamond Shamrock Foamaster	3	>24	Yes
9	Kerosene, deodorized, Quaker State	Diamond Shamrock Foamaster	3	>24	Yes
10	Kerosene, deodorized, Penreco	Diamond Shamrock Foamaster	3	>24	Yes
11	Kerosene, deodorized, United Refining	Air Products Surfonyl	3	>24	Yes
12	Kerosene, deodorized, Quaker State	Air Products Surfonyl	3	>24	Yes
13	Kerosene, deodorized, Penreco	Air Products Surfonyl	3	>24	Yes
14	Kerosene, deodorized, United Refining	GE AF70	3	>24	Yes
15	Kerosene, deodorized, Quaker State	GE AF70	3	>24	Yes
16	Kerosene, deodorized, Penreco	GE AF70	3	>24	Yes
17	Kerosene, deodorized, United Refining	Dow FS 1265	3	5	No
18	Kerosene, deodorized, Quaker State	Dow FS 1265	3	5	No
19	Kerosene, deodorized, Penreco	Dow FS 1265	3	5	No
20	Hexane, reagent grade	--	3	5	No
21	Octane, reagent grade	--	3	5	No
22	Hexadecane, C_{16}, reagent grade	--	3	5	No
23	n-decane, technical grade	--	3	5	No
24	Isoparaffins, Phillips Chemical	--	3	5	No

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