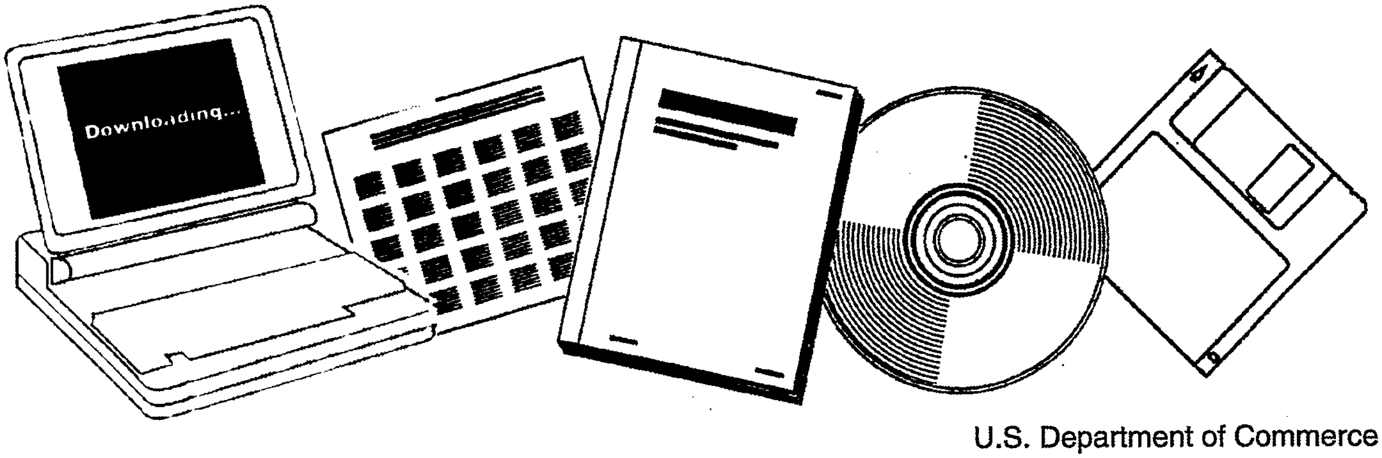
CATALYST AND REACTOR DEVELOPMENT FOR A LIQUID-PHASE FISCHER-TROPSCH PROCESS. QUARTERLY TECHNICAL PROGRESS REPORT, 1 JANUARY 1981-31 MARCH 1981

AIR PRODUCTS AND CHEMICALS, INC.
ALLENTOWN, PA

APR 1981



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DOE/PC/30021-T4
(DE81028209)
Distribution Category UC-90d
DE81-028209

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.

TABLE OF CONTENTS

Page

TABLE OF CONTENTS
(Continued)

Page

List of Figures

TABLE OF CONTENTS

Page

List of Tables

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 non-technical, 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

(4) K. Akita, F. Yoshida, Ind. Eng. Chem. Proc. Des. Dev. 1973 12 76.

(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.

FIGURE 1

HYDROCARBON WEIGHT DISTRIBUTION

5970-9-B-23-27

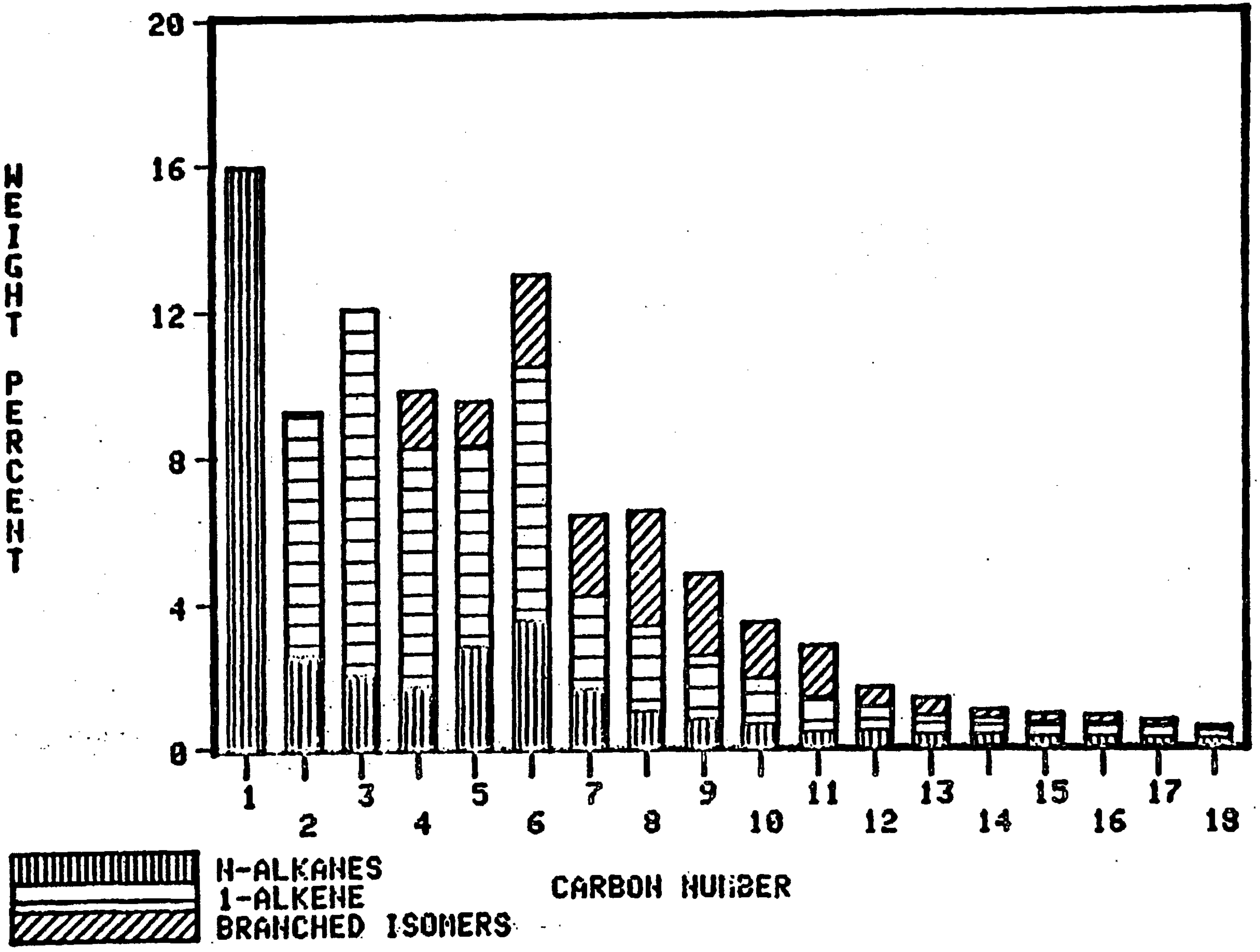

FIGURE 2

HYDROCARBON MOLAR DISTRIBUTION

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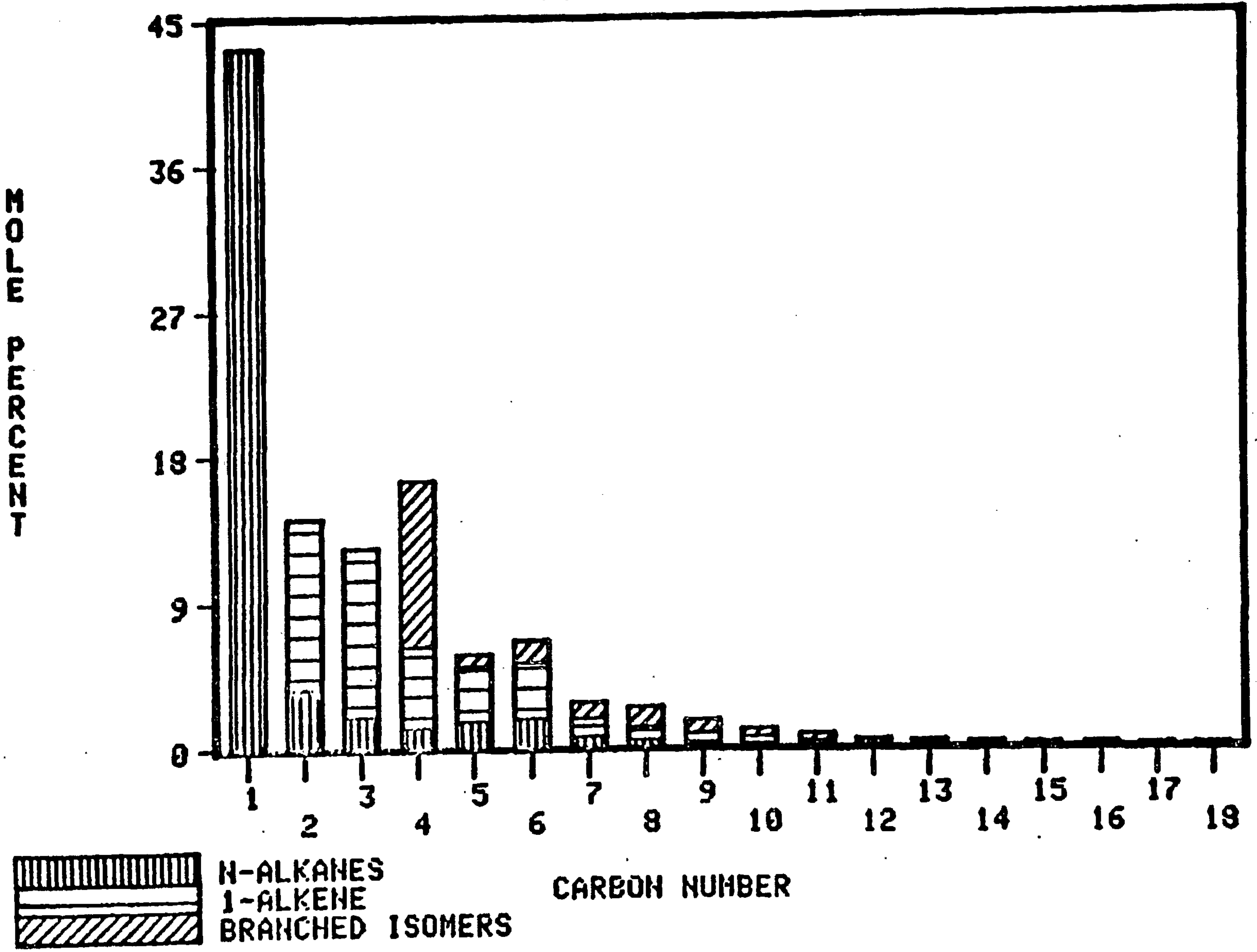


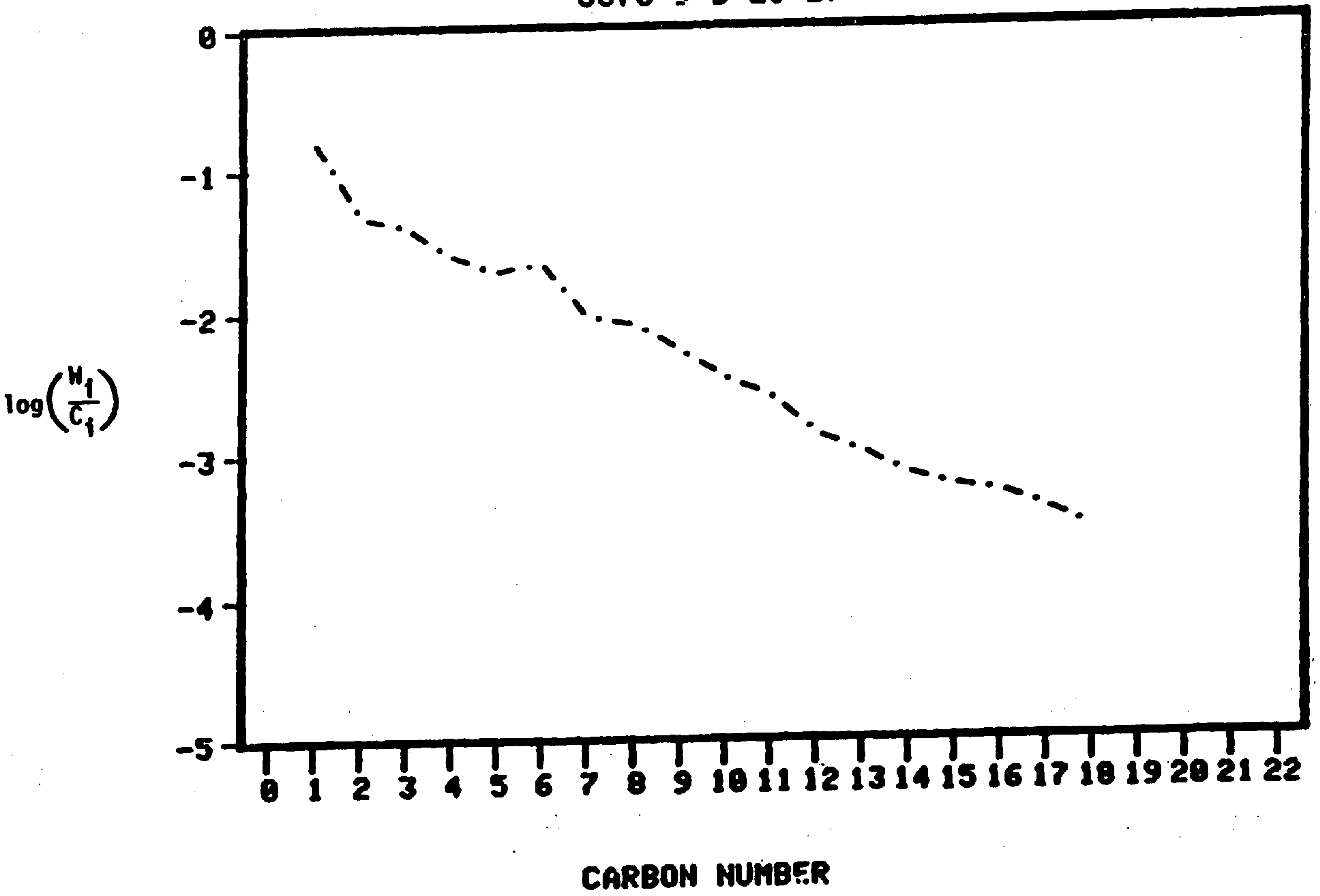


FIGURE 3

HYDROCARBON SCHULZ-FLORY DISTRIBUTION

5870-9-B-23/27

FIGURE 37

GAS HOLDUP

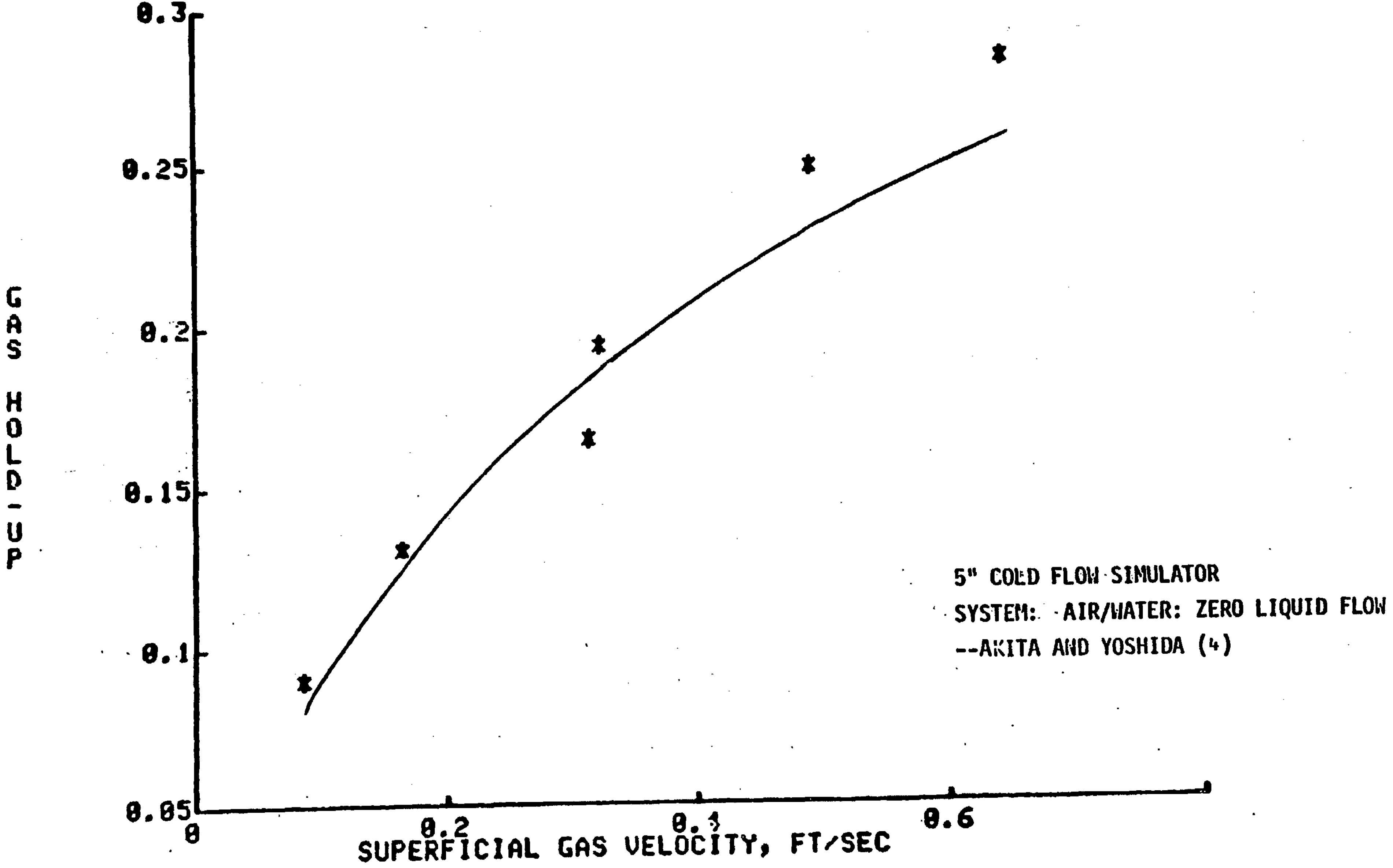
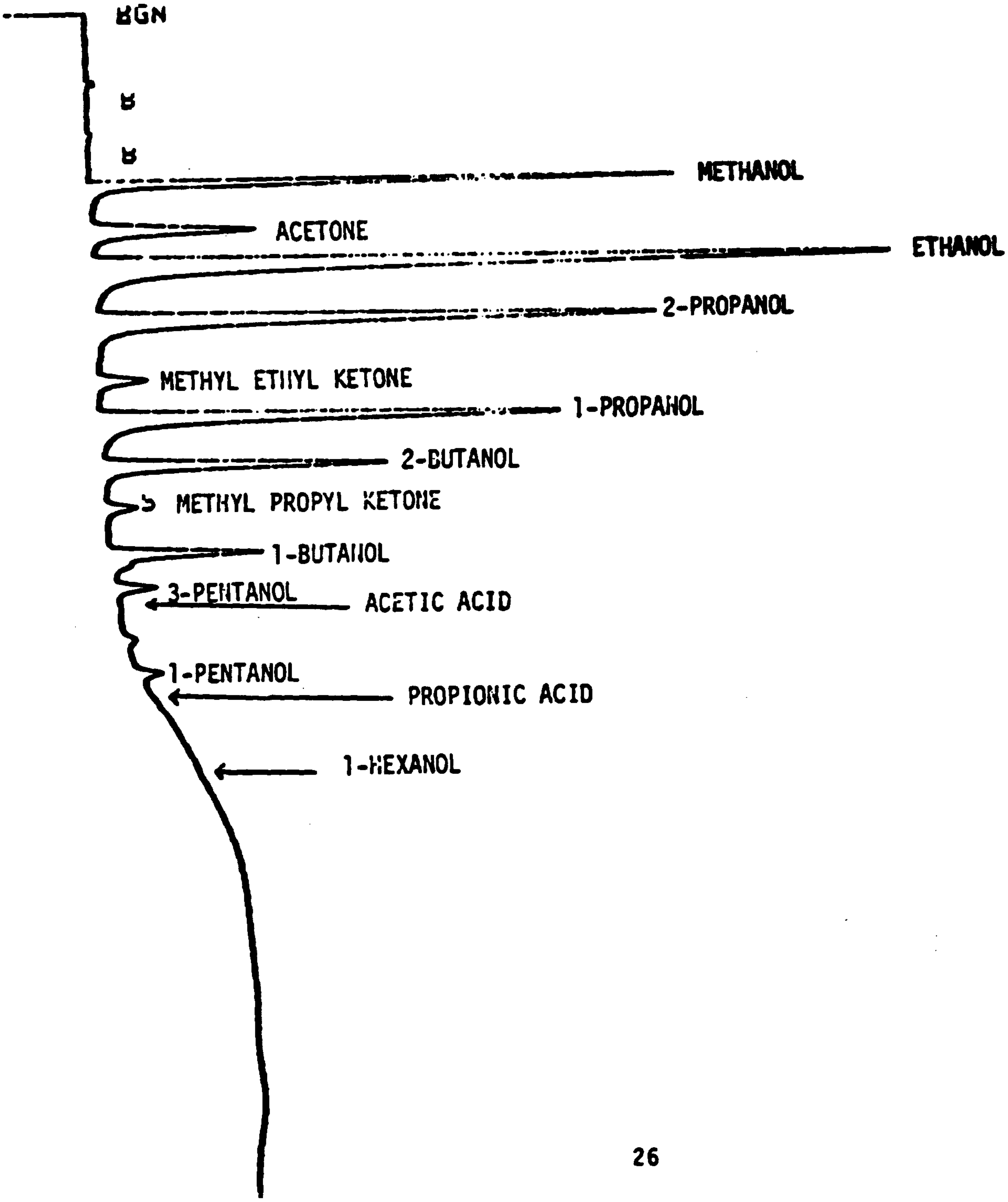
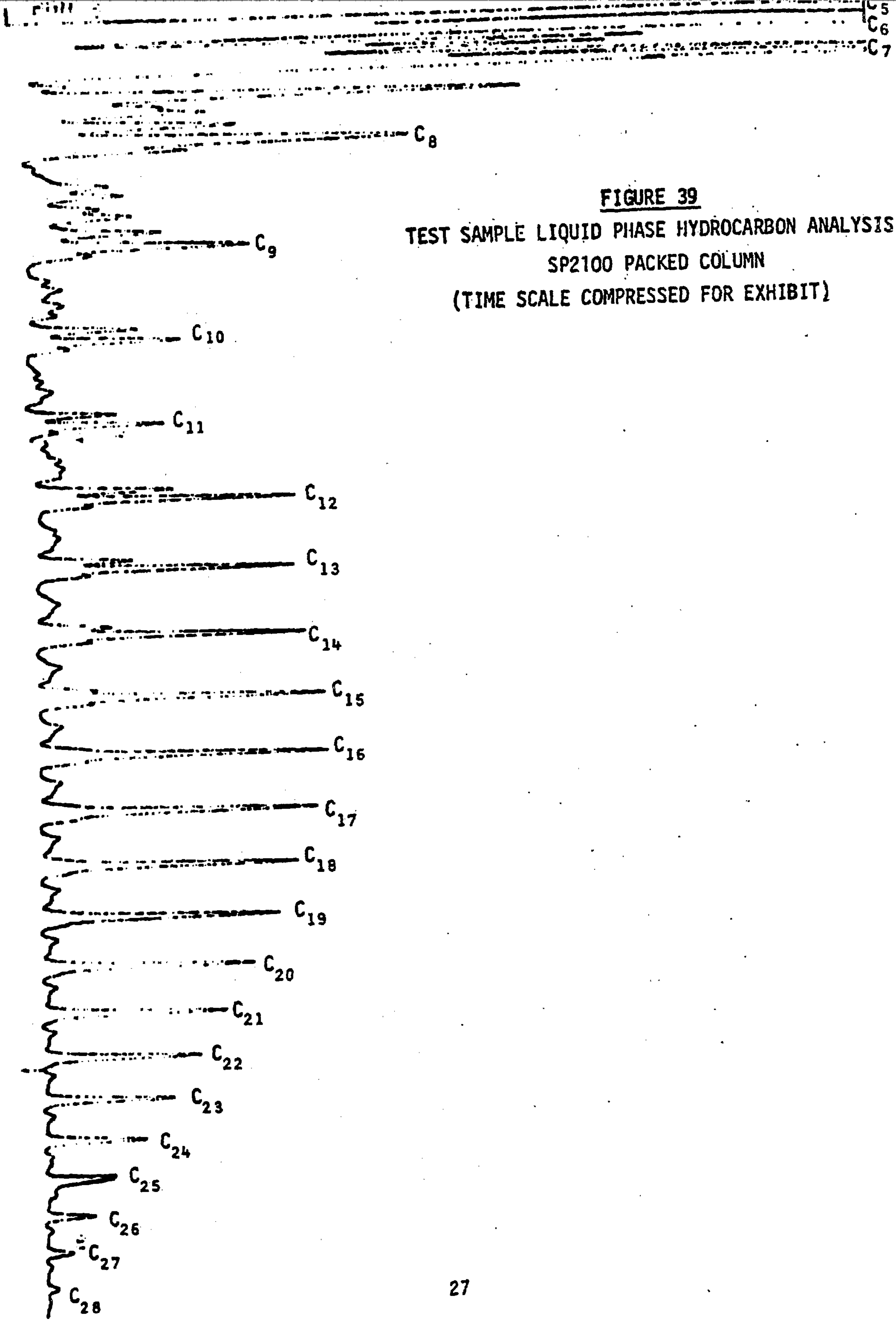


FIGURE 38

TEST SAMPLE AQUEOUS PHASE ANALYSIS



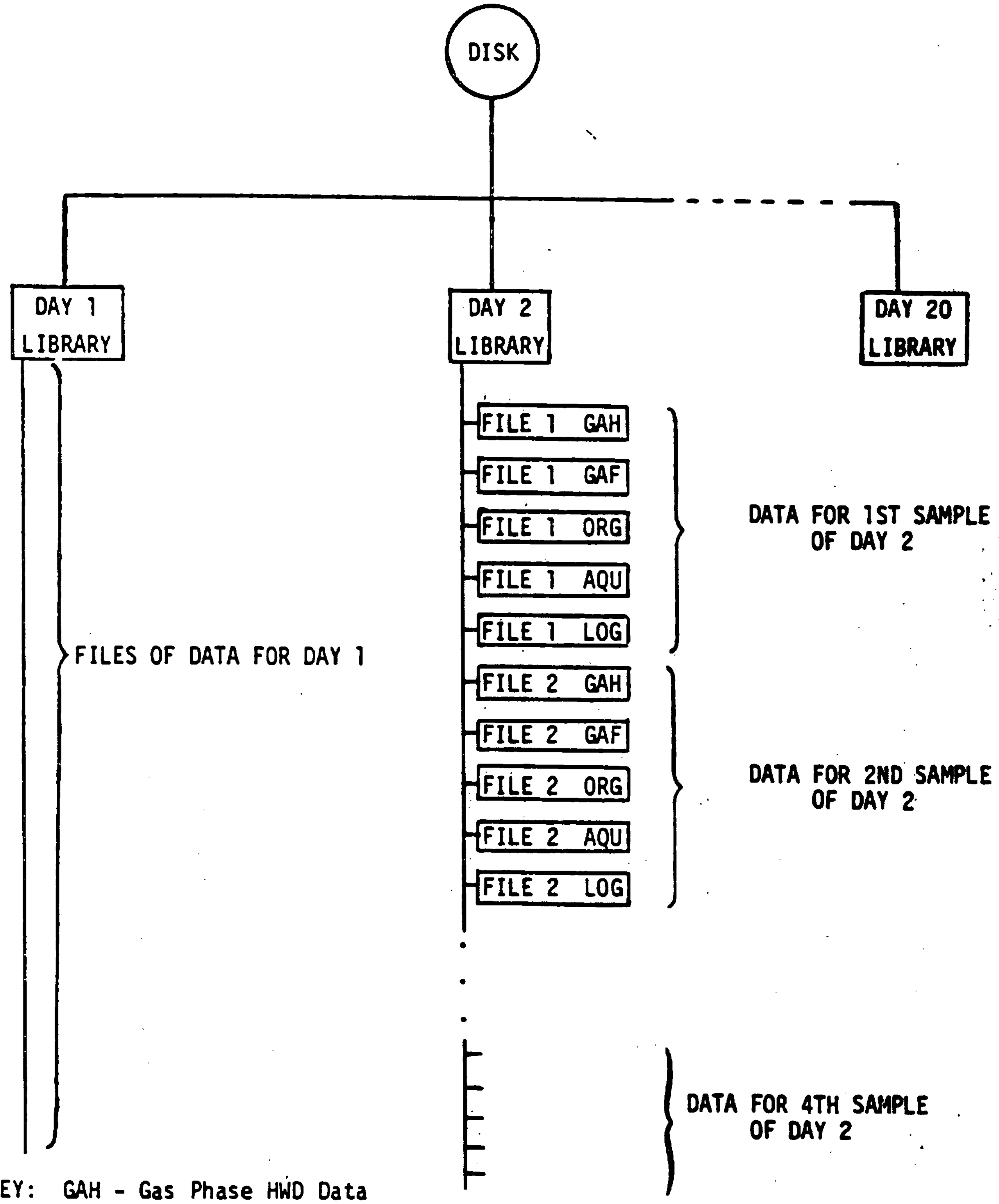


<u>FIGURE 39</u>

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

FIGURE 40

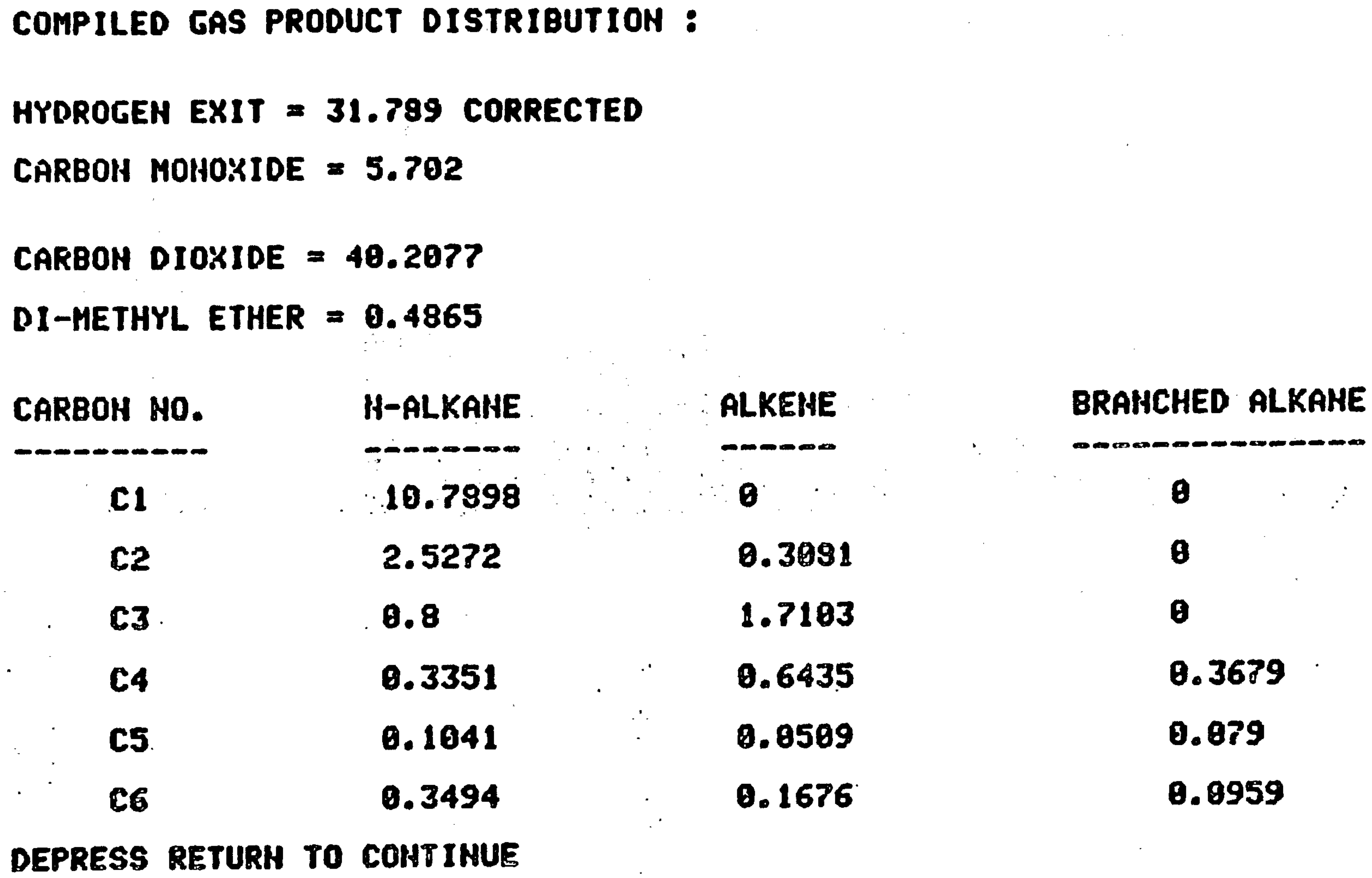
DATA ORGANIZATION ON DISK



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

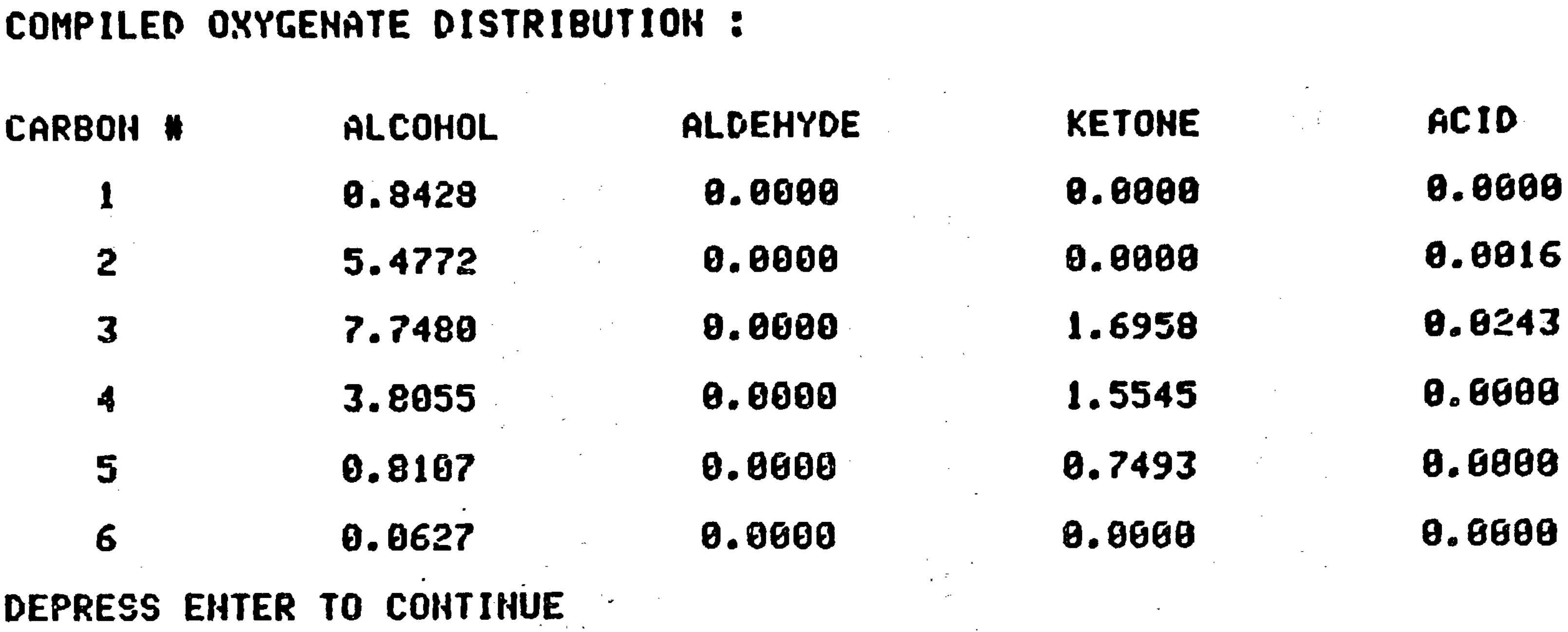
TEST SAMPLE (FROM FIGURE 39)

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	11.6944	2.1710	0.5119
6	11.1421	5.3438	3.0513
7	8.9463	3.2911	5.4485
8	3.9528	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	0.1949
21	0.6979	0.0000	0.1596
22	0.5453	0.0000	0.0892

FIGURE 43

TEST SAMPLE (FROM FIGURE 38)



```
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     2.4493589038      2.59531727119     4.70236862466
C5     5.08268166896     1.7794909738      0.897836390758
C6     7.73166701937     3.66619986071     2.12144950833
C7     3.13327228722     1.165675189       1.92980580965
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    0.305978609955    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                 0.0699962404112
C21    0.247189302787    0                 0.0565287472774
C22    0.19313988653I    0                 0.0315937610097
READY? (YES OR NO)
```

FIGURE 45

TEST SAMPLE (FROM FIGURES 41 and 42)

```
HYDROCARBON DIST IN MOL % IS

C1                51.4852071106       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     0.1106415099
C12               0.0629224673944     0.0389711697742     0.0752496835076
C13               0.0588202865105     0.0281300095571     0.060110876657
C14               0.0585167698755     0.0218425648857     0.0508396623872
C15               0.0608480029768     0.0165595527959     0.0482227543092
C16               0.0799754213199     0                   0.048524279533
C17               0.092740203809      0                   0.0682498582461
C18               0.111830706955      0                   0.100865255055
C19               0.0501509466281     0                   0.0164950458314
C20               0.0413193628605     0                   0.00926771662097
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)

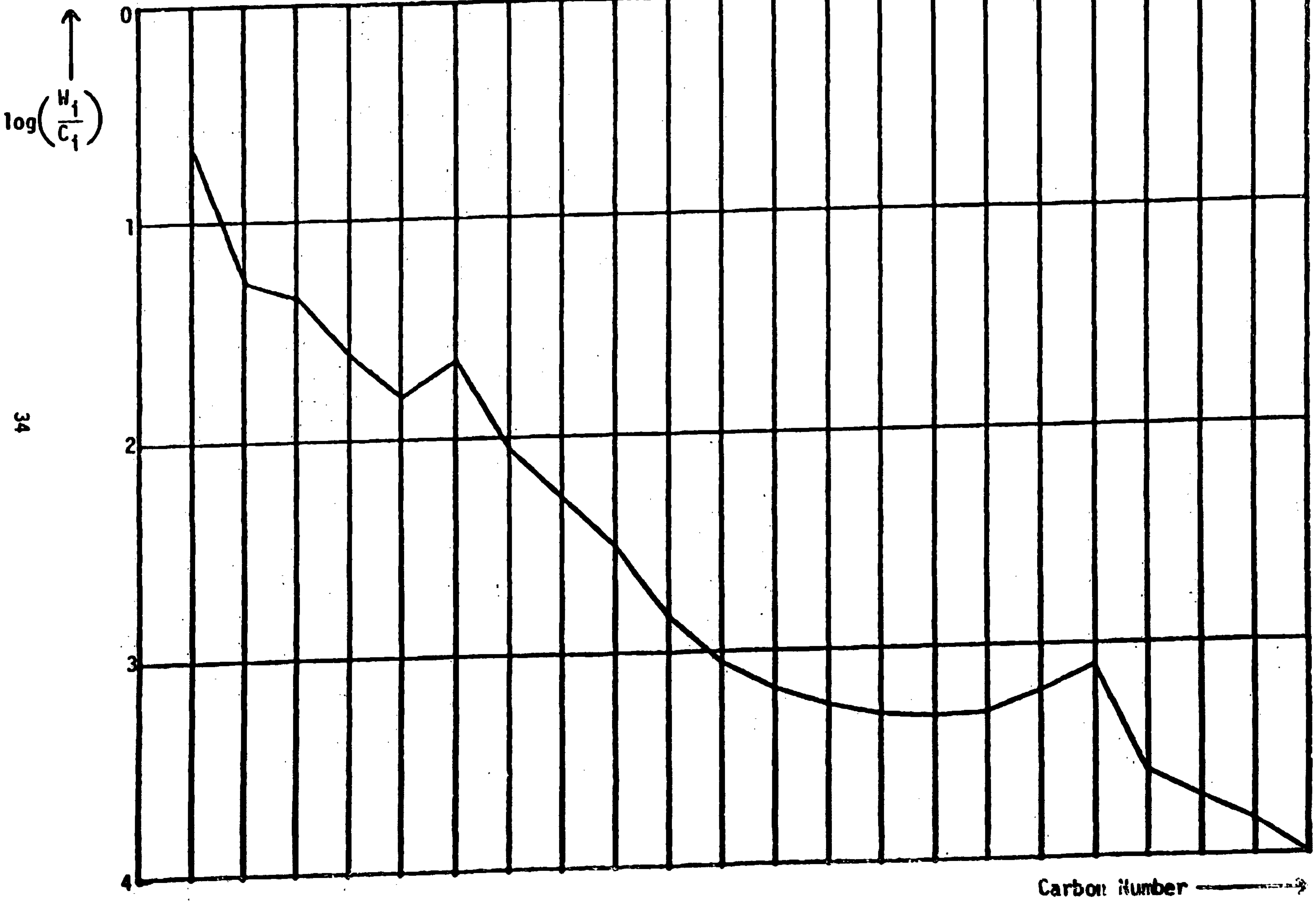
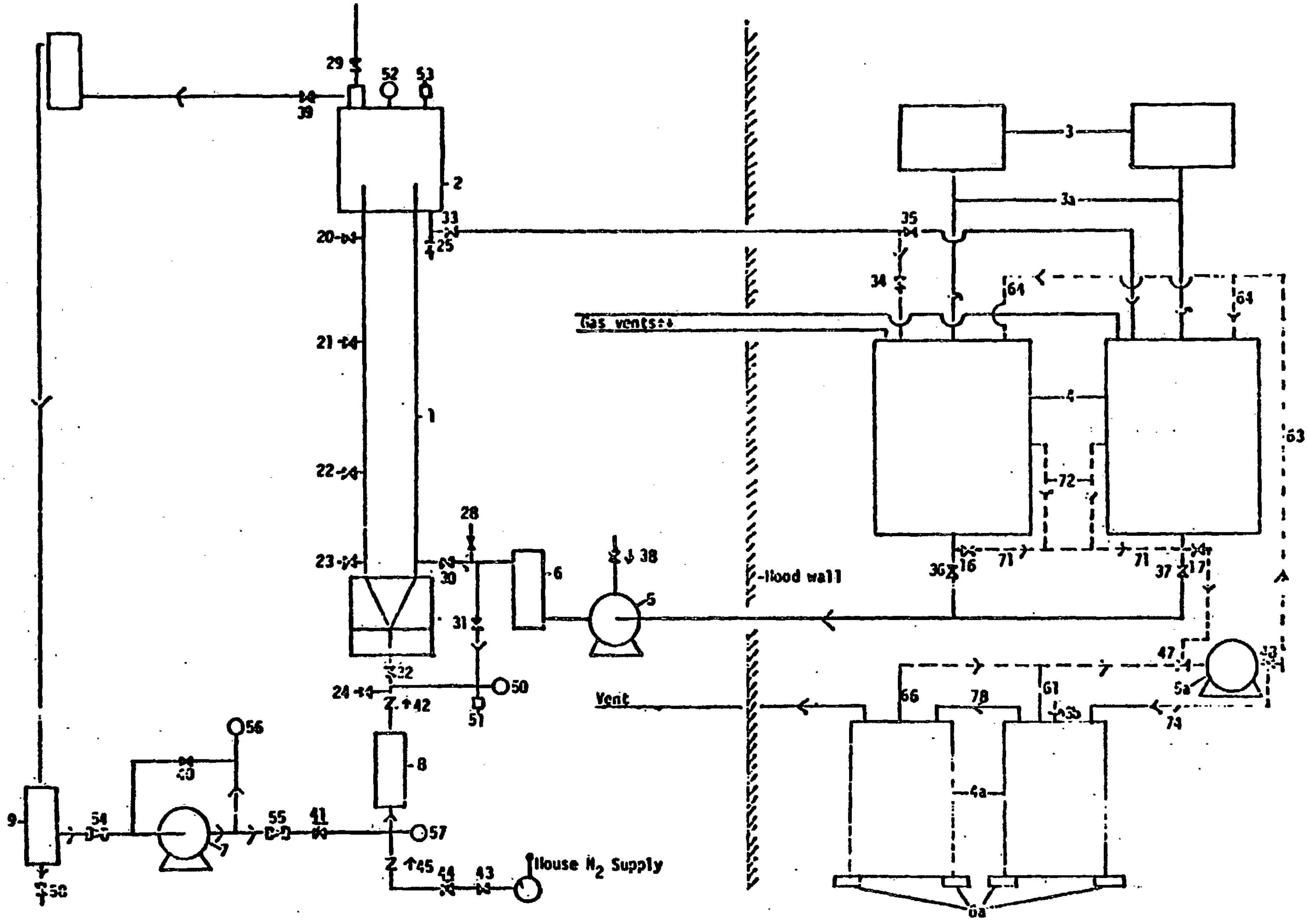


FIGURE 47

PROCESS FLOW DIAGRAM FOR 5" SLURRY COLUMN



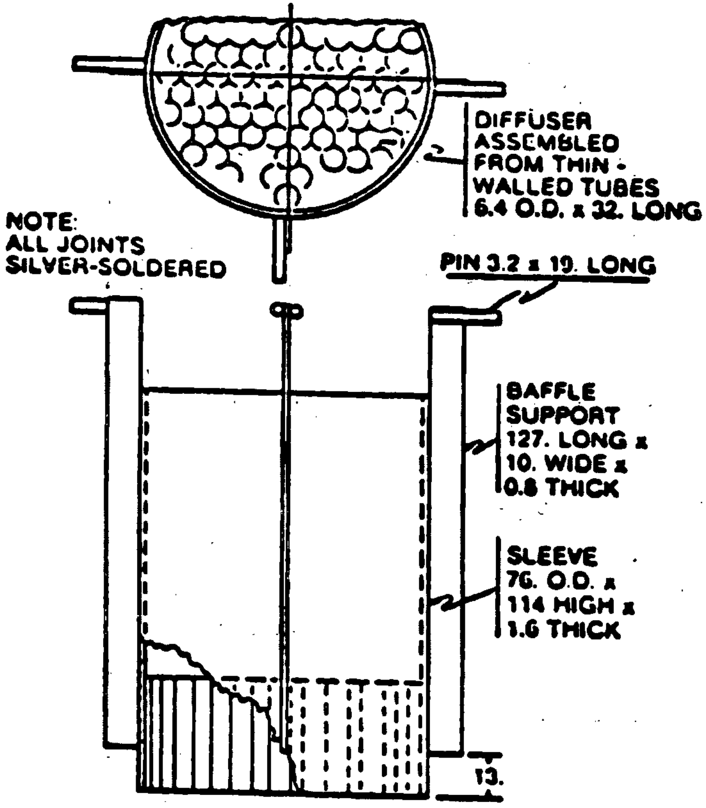


*FIGURE 48 Eddy control basket.

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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-C_3H_7OH	22.5	4.79
CH_3COCH_3	18.4	3.44
n-C_4H_9OH	7.6	2.01
$C_2H_5COCH_3$	5.6	1.44
n-$C_5H_{11}OH$	3.6	1.13
$C_3H_7COCH_3$	3.0	0.87
n-$C_6H_{13}OH$	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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