Report 10

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

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CATALYST AND REACTOR DEVELOPMENT FOR A SLURRY PHASE FISCHER-TROPSCH PROCESS

NON-CONFIDENTIAL VERSION

To be presented at the DOE Contractor's Review on

Indirect Liquefaction in Pittsburgh, 20-21 May 1981

by

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

This work is being undertaken as part of a three year contract between the U. S. Department of Energy and Air Products and Chemicals, Inc. and began 1 October 1980.

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Objective

The objective of the work is to evaluate catalysts and slurry reactor systems for the conversion of synthesis gas into transportation fuels, such as gasoline and/or diesel fuels, via a single stage liquid phase process. Included in this is the development of slurry phase catalysts and the study of the hydrodynamics of a three phase slurry reactor using cold flow modeling techniques.

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Organizational Chart

The overall program manager at APCI for this work is Dr. James W. Brockington. Dr. Paul N. Dyer is the principal investigator. Dr. Ronald Pierantozzi is carrying out the work on supported molecular cluster catalysts. Barry W. Brian is responsible for the cold flow modeling of three phase slurry reactors. Jeffrey V. Bauer has set up the computerized analytical system and the data handling capabilities.

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Advantages of Slurry Phase Fischer-Tropsch Process

Some of the potential advantages of operating the Fischer-Tropsch synthesis in the slurry phase are listed. One of the main advantages lies in the better heat transfer coefficients which are possible with operation in the slurry phase, leading to better control of the exothermic reaction and enabling high conversions per pass to be achieved. Another potential advantage is the ability to use CO rich syngas, such as the 2:1 CO/H_2 ratios which are produced from second generation coal gasifiers, without plugging of the catalyst bed, which can easily occur in gas/solid bed reactors. Both the improvement in heat transfer and the ability to use CO rich syngas should result in a reduction in the yield of methane and should also enable better control to be achieved over the total product selectivity.

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Major Tasks

The contract is divided up into four tasks. The first, Task 1, was completed in the first quarter and involved drawing up an overall Project Work Plan.

Task 2 is the development of a slurry catalyst for the F-T process. Two bench scale slurry reactors are being set up for this task, based on 300 mL and 1 liter stirred autoclaves. In Sub-Task 2c, twenty "modified conventional type" F-T catalysts will be prepared and subjected to testing in the slurry reactors for up to 21 days each. Sub-Task 2d calls for the preparation of 50 supported metal cluster catalysts and their screening for up to 14 days each in a Chem Data Systems tubular gas/solid reactor. The best 10 of the supported molecular cluster catalysts will, in addition, be tested in the slurry phase for periods of up to 21 days.

From the combined results of the slurry phase tests of "modified conventional" catalysts and supported molecular cluster catalysts, the most promising four will be selected and subjected individually to continuous 6 month tests, in the slurry phase.

The objective of Task 3 is to evaluate, using cold flow reactor simulators, the hydrodynamics of slurry reactors for the FT reaction. The correlations of data for gas holdup, solid and liquid dispersion and heat and mass transfer that will be obtained from this work will enable scale up to be made to large scale slurry reactors.

Task 4, the preliminary design of a pilot scale liquid phase reactor for conversion of synthesis gas to transportation fuels, is an optional task that will be decided upon by the DOE in the last 6 month of the contract.

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FT Slurry Reactor

The design of the bench scale slurry reactors for FT synthesis is presented in this diagram in block form. The reactors are capable of 24 hour continuous operation and most of the operating parameters are recorded on a multipoint chart recorder. Operation is possible with continuous slurry feed or recycle from a stirred external reservoir, with the slurry level inside the reactor automatically controlled via a differential pressure gauge which is coupled between the gas inlet and outlet lines. H_2 and CO supplies are manifolded external to the laboratory building and after suitable flow and pressure control and clean-up stages are mixed immediately prior to the slurry reactor itself. The product gas, after partial reflux at 200°C to return most of the vaporized slurry oil back to the reactor, passes to a back pressure regulator and then to a C_5-C_6 splitting column. Overhead from the column, containing unreacted CO and H_2, CO_2, water vapor and C_1-C_5 hydrocarbons, is passed through a calibrated wet test meter to a vent. The bottom products, composed mainly of hydrocarbons of C_6 and above plus a separate aqueous phase, are collected for analysis separately. In addition, samples of the slurry oil can be obtained from the recycle system to monitor the possible build-up of higher molecular weight hydrocarbons in the slurry itself.

A rise in differential pressure between the gas inlet and outlet lines above a set point opens an electrically operated ball valve to allow slurry to transfer back to the glass slurry reservoir via throttling valves. If fresh catalyst needs to be added to the reactor because of deactivation or the addition of slurry oil is required, it can be pumped from the reservoir using a Bran-Lubbe piston metering pump at rates of up to 3.3 vol/v/h. If desired, the slurry feed and withdrawal can operate continuously at a constant set flow.

The reactor is fitted with all necessary monitoring devices and instrumentation to allow unattended operation for 24 hours/day.

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Product Analysis Scheme

Two main requirements were taken into account when setting up the product analysis scheme. The first was that the analysis should be as complete as possible in order to obtain a good overall mass balance for carbon, hydrogen and oxygen. The second was that in view of the large number of samples to be analyzed and the tremendous amount of information that would be generated, the product analysis scheme and subsequent data handling should be fully automated using computerized techniques.

Under computer control, samples of the gas phase from the top of the C_5-C_6 splitting column are analyzed by a Carle SX-3978 gas chromatograph equipped with TCD and FID. This resolves all C_1-C_5 isomers, in addition to analyzing H_2, CO, CO_2, water and dimethylether. An initial backflush of C_6+ components enables the operation of the splitting column to be optimized. For routine analysis of organic liquid phase samples obtained from the bottom of the C_5-C_6 splitting column, a 1/8" 3% SP-2100/Chromosorb column is used in a PE Sigma 1 GC fitted with an autosampler. For greater resolution, selected organic phase samples are analyzed on a 150' SS OV-101 capillary column in a PE Sigma 2 GC. This gives an isomer distribution in the C_6-C_{10} range, as well as normal and branched isomers in the C_{10}-C_{20} range. In addition, it is planned to analyze representative organic phase samples for PONA by fluorescent indicator column chromatography and refractive index measurements as defined in ASTM D1319 and D2159.

Samples of the aqueous phase from the bottom of the C_5-C_6 splitting column are also auto-sampled on the Sigma 1 using a 10% SP-2100/1% H_3PO_4 on Chromosorb 1/8" columns. This analysis quantifies C_1-C_6 alcohols, aldehydes, ketones and acids.

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Data Handling

Computerized data handling procedures have been set up for this project. Chromatographic data files from the Sigma 10 computing integrator are transferred to disk on a Tektronix 4052 microcomputer. Process variables relating

to the samples are also input to the disk via the 4052 system keyboard by the reactor operator. A complete analysis contains a minimum of 5 files; two from the gas analysis (TCD and FID), and one each from the aqueous phase and organic phase analyses and from the operator's log sheet. Data correlation and reduction programs have been written which automatically compute the weight %, mole % and Schulz-Flory product distribution for the samples as well as information on selectivity and mole % conversion of CO and H_2 into selected product ranges. The Schulz-Flory distribution plot can be immediately examined by the operator on the CRT screen, and the graphics routines of the Tektronix 4052 can be used to produce graphs directly from the computer output. It is planned to store the complete output from each 21 day test run on 1 disk, and this will enable intermediate mass balances and product selectivity and activity changes, etc. to be rapidly obtained. To facilitate calculations involving several tests, e.g. kinetic studies and correlations between catalysts, data will be transmitted regularly from the Tektronix 4052 to a data file storage system in the company's Amdahl V8 mainframe computer.

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Slurry Catalyst Development

Although the F-T synthesis has been studied in the slurry phase in the past, the catalysts used have never been optimized specifically for the slurry phase, apart from the Rheinpreussen-Koppers operation. The development of slurry catalysts to be carried out in Task 2 of this contract has the aims of obtaining a high product selectivity to gasoline or diesel fuel, and a high activity to maximize the space time yield of the slurry reactor.

The standard Schulz-Flory distribution, which correlates so much of previous F-T selectivity data, imposes severe restrictions on the maximum yields of the desired product fractions, e.g. 47 wt% gasoline (C_5-C_{11}) or 40 wt% diesel fuel (C_{12}-C_{17})[1,2]. However, notable exceptions to the standard distribution do exist, and the extended S-F theory of H. H. Nijs and P. A. Jacobs explains these by incorporating into the polymerization theory a limitation due to the catalytic metal particle size distribution[3,4].

The important points in developing and optimizing a slurry catalyst and obtaining high product selectivity can be summarized as follows: 1) It appears to be essential to obtain a uniform and stable metal particle size on a supported type catalyst, whether the support be a conventional metal or a zeolitic support. 2) Shape selectivity and diffusional control imposed by zeolitic type supports is another general method of controlling product selectivity. 3) Support metal interactions, particularly significant in the supported metal cluster type catalysts, have significant effects on product yields. 4) Calcination and activation procedures applied to conventional type F-T catalysts can also fundamentally effect the properties and appear to influence the product selectivity.

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Hydrocarbon Weight Distribution, Baseline Catalyst

The "modified conventional" type catalysts, as well as molecular cluster catalysts, will be initially screened in a gas/solid tubular reactor before slurry phase testing to provide information on activation and pretreatment procedures. As a check on our system and to provide basic information about the difference between gas and slurry operation, initial tests have been carried out using a baseline catalyst; a commercial ammonia synthesis catalyst, fused Fe_2O_3 promoted with 2.5% Al_2O_3, 1.0% CaO, 0.6% K_2O. The results illustrated in this slide were obtained from a 15 mL gas phase screening reactor and at the following conditions: 455 psig, 253°C and a GHSV of 295 h^{-1} using 43% CO/ 57% H_2. The high olefinic content of the hydrocarbon product with 1-alkene/ n-alkane ratios of 2.0 to 5.2 in the C_2-C_5 region is noticeable. The aqueous phase oxygenates, about 1.4 mole % of the total product, were typical of this type of catalyst.

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Hydrocarbon Schulz-Flory Distribution, Baseline Catalyst

Overall, the results obtained with the baseline catalyst were as expected, giving a near linear Schulz-Flory distribution plot with $\alpha = 0.76$. The first slurry phase test, utilizing this catalyst, will be carried out shortly.

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Task 3 - Slurry Reactor Design Studies

The objectives of Task 3 are to use cold flow modeling techniques to define heat, mass and momentum transfer parameters critical to the design of slurry reactors, and to correlate gas holdup, solid and liquid dispersion, and heat and mass transfer. The program falls roughly into three separate sub-tasks. In the initial part of the program, a 5" diameter cold flow simulator is being used to simulate the operation of a 3 phase column with no internal heat transfer surface, i.e. with a positive concurrent liquid flow through column as would be required for external cooling. In the second phase, a 12" diameter simulator with removable internal heat transfer surfaces will be used at a lower range of slurry flow velocities to simulate operation with internal cooling. In the third phase of Task 3, an engineering evaluation of slurry reactors will be carried out using the information obtained in the first 2 phases to define, for example, characteristics of internal vs. external cooling, optimum operating conditions, solid liquid separation techniques, staged reactor systems, and the need for any additional data development.

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Task 3 - Slurry Reactor Design Studies - Dependent and Independent Variables

Both paraffin and water based slurries will be used employing silica and iron oxide in the 3 solid size ranges and the weight % concentrations shown in the Table. For the 5" column, superficial gas velocities in the range .05-0.5'/sec and liquid velocities in the range 0-0.1'/sec will be studied. The range of independent variables was chosen to observe any transitions in flow regimes that may occur between apparent 2 phase and 3 phase flow. Transitions of this type have been observed previously in three phase slurry columns by Prof. Deckwer[5]. Because of the large number of combinations of variables which are possible, the study of the dependent variables has been divided into 2 parts. Gas holdup, gas dispersion and solids dispersion will be measured mainly in paraffin based slurries with some representative measurements made in water slurries. Mass transfer and liquid axial dispersion, however, will be measured in water based slurries with representative measurements in paraffin slurries.

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5" Slurry Column

The 5" cold flow simulator that has been constructed for the first phase of the test is illustrated in this block diagram. The column is made of plexiglass and operates with a closed recycle of both gas and slurry. This increases the safety of operation and minimizes the concentration of the slurry due to evaporative loss of the slurry liquid.

Initial measurements of gas holdup have been made and found to be in good agreement with the correlation derived by Akita and Yoshida[6].

REFERENCES

1) G. Henrici-Olive and S. Olive, Angew. Chem. Int. Edn., 15 136 (76).

2) Catalytica Associates Inc., "Catalysis of CO/H_2 Reactions" (78).

3) H. H. Nijs and P. A. Jacobs, J. Catal., 65 328 (80).

4) H. H. Nijs, P. A. Jacobs, J. J. Verdonds and J. B. Uytterhoeven, "Growth and Properties of Metal Clusters", Elsevier, 479 (80).

5) W. D. Deckwer et. al., Ind. Eng. Chem. Process Des. Dev., 19 699 (80).

6) K. Akita and F. Yoshida, Ind. Eng. Chem. Process Des. Dev., 12 76 (73).

SLIDE 1

CATALYST AND REACTOR DEVELOPMENT FOR A SLURRY PHASE FISCHER-TROPSCH PROCESS

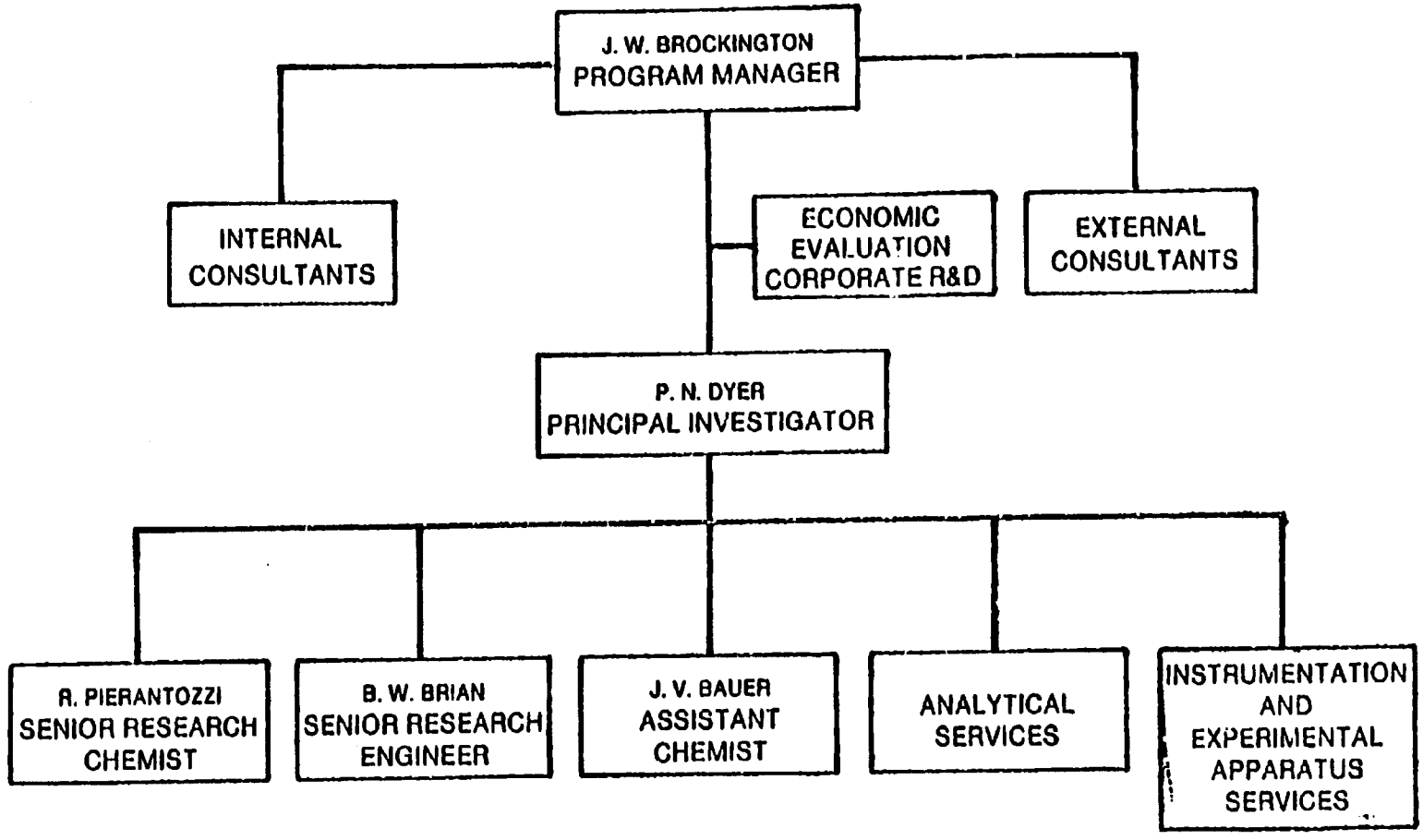
DOE CONTRACT PE-AC22-80PC30021

SLIDE 2

OBJECTIVE

TO EVALUATE CATALYSTS AND SLURRY REACTOR SYSTEMS FOR THE SELECTIVE CONVERSION OF SYNTHESIS GAS INTO TRANSPORTATION FUELS VIA A SINGLE STAGE, LIQUID PHASE PROCESS.

SLIDE 3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SLIDE 4

ADVANTAGES OF SLURRY PHASE FISCHER-TROPSCH PROCESS

- BETTER HEAT TRANSFER AND CONTROL OF REACTION EXOTHERM.
- HIGH CONVERSION PER PASS.
- USE OF CO RICH SYNGAS WITHOUT PLUGGING.
- REDUCTION IN YIELD OF CH_4.
- CONTROL PRODUCT SELECTIVITY.

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MAJOR TASKS

TASK 1 PROJECT WORK PLAN

TASK 2 SLURRY CATALYST DEVELOPMENT
- 2A BACKGROUND STUDIES
- 2B BENCH-SCALE REACTOR SET-UP
- 2C CATALYST PREPARATION AND SLURRY REACTOR TESTING
- 2D METAL CLUSTER CATALYST PREPARATION AND SCREENING TESTS

TASK 3 SLURRY REACTOR DESIGN STUDIES

TASK 4 PILOT FACILITY DESIGN

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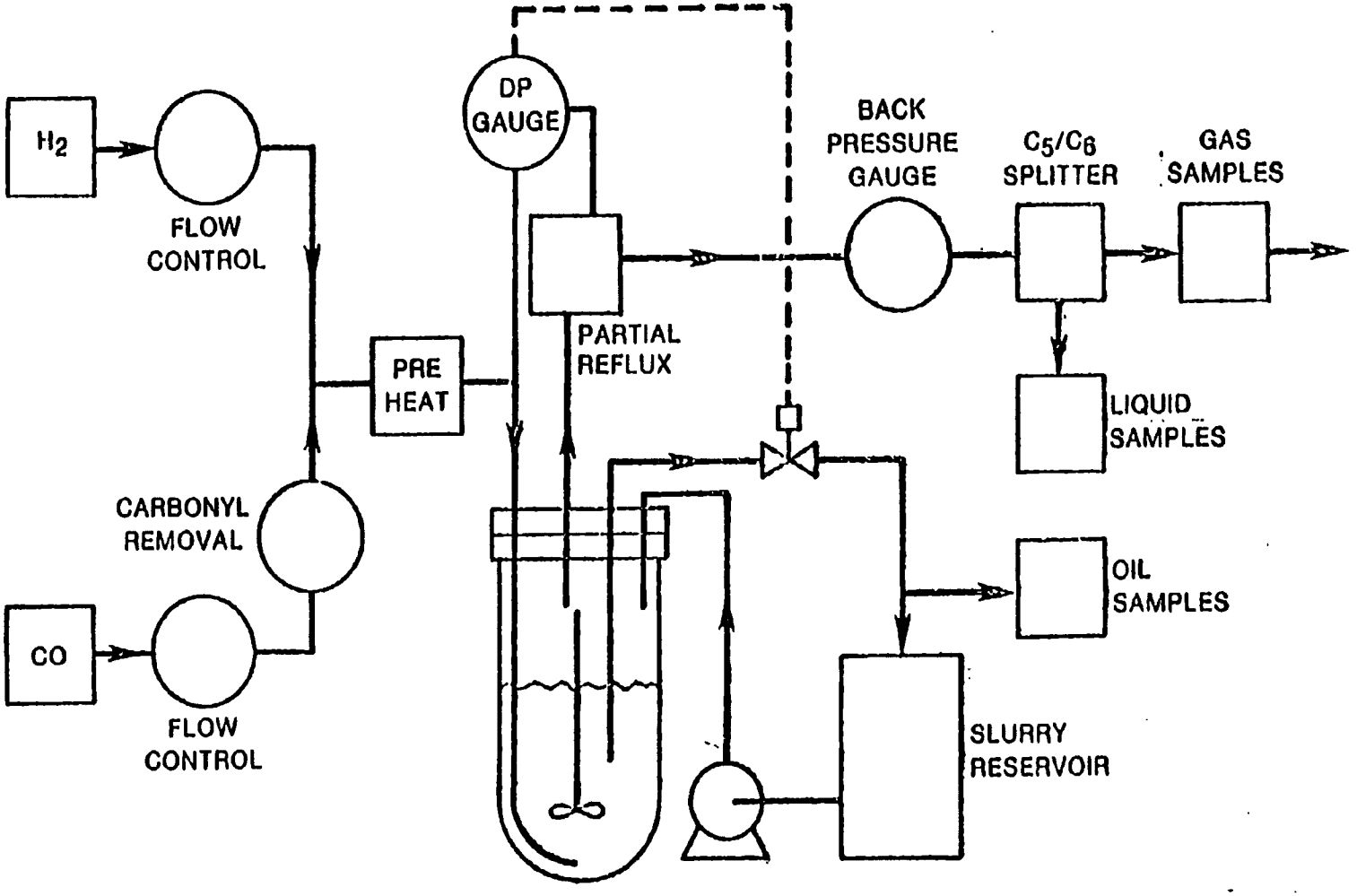
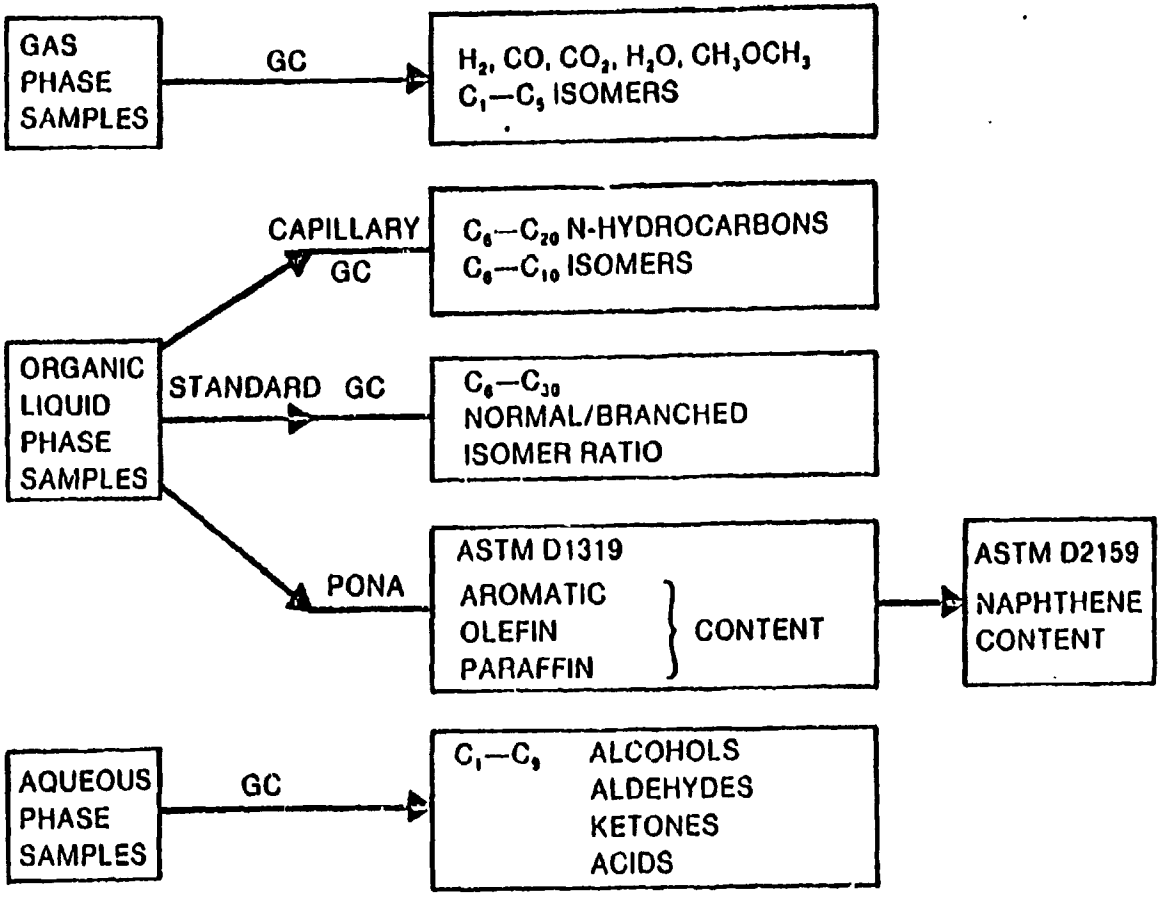
FISCHER-TROPSCH SLURRY REACTOR



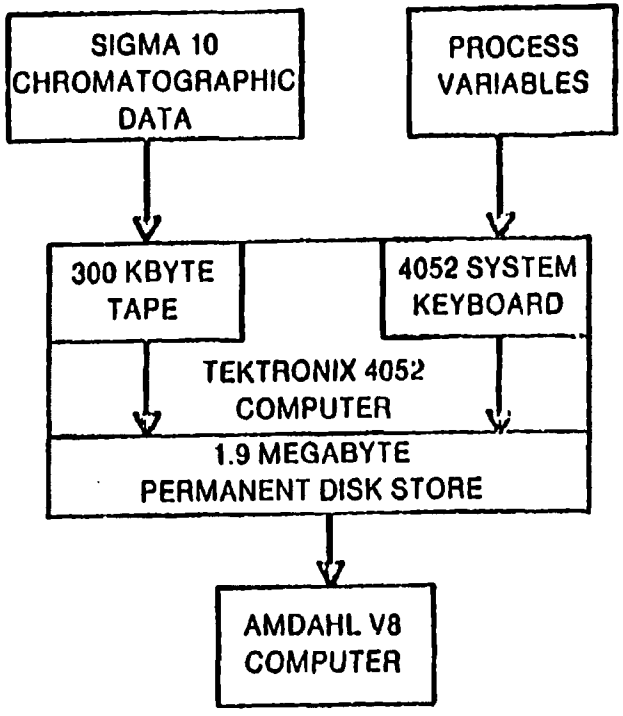
SLIDE 7

PRODUCT ANALYSIS SCHEME



SLIDE 8

DATA HANDLING



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SLURRY CATALYST DEVELOPMENT

AIM

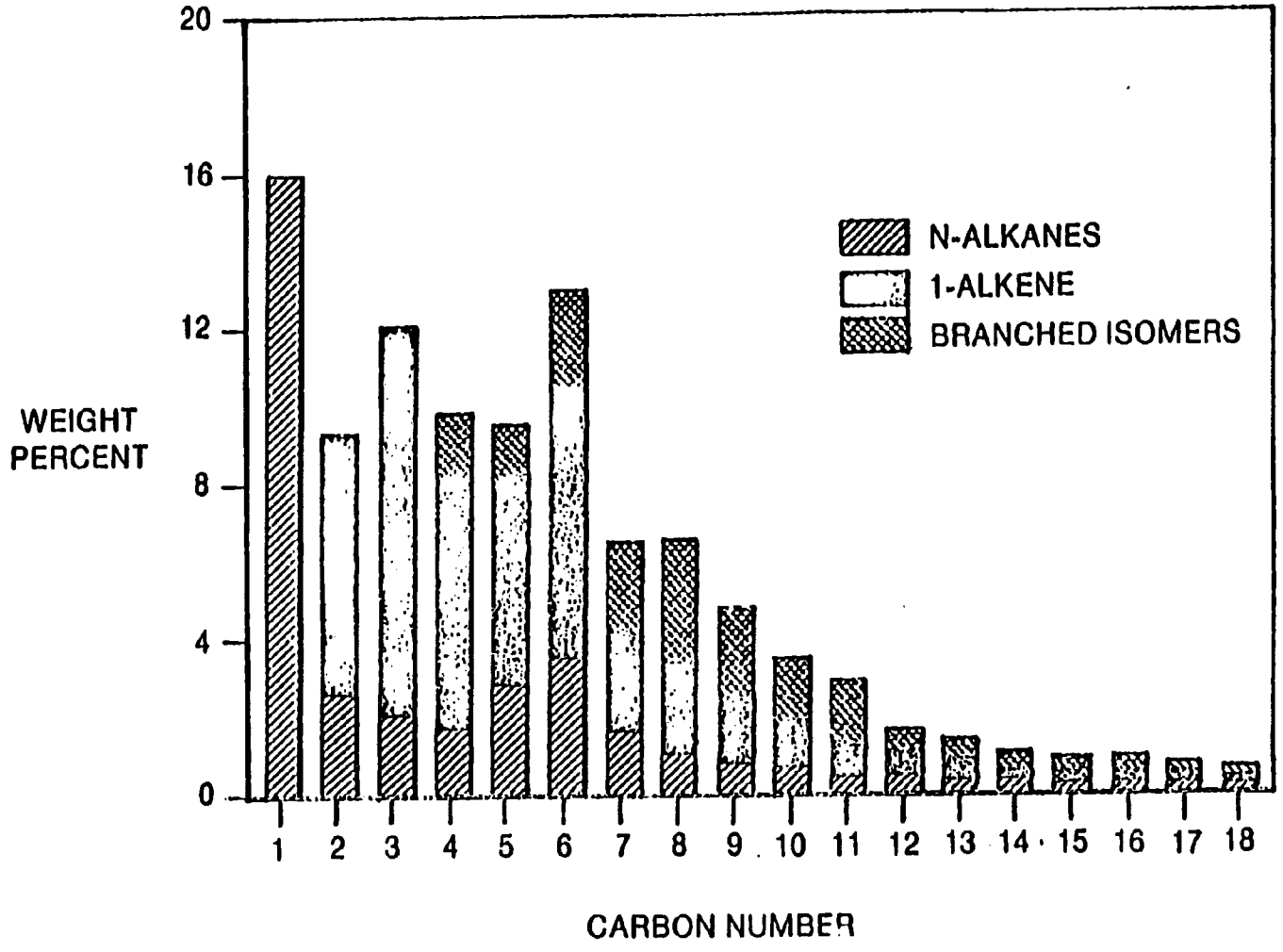
1. HIGH PRODUCT SELECTIVITY TO GASOLINE OR DIESEL FUEL
2. HIGH ACTIVITY TO MAXIMIZE SPACE TIME YIELD

METHOD

1. UNIFORM AND STABLE METAL PARTICLE SIZE
2. SHAPE SELECTIVITY AND DIFFUSIONAL CONTROL
3. SUPPORT - METAL INTERACTIONS
4. CALCINATION AND ACTIVATION PROCEDURES

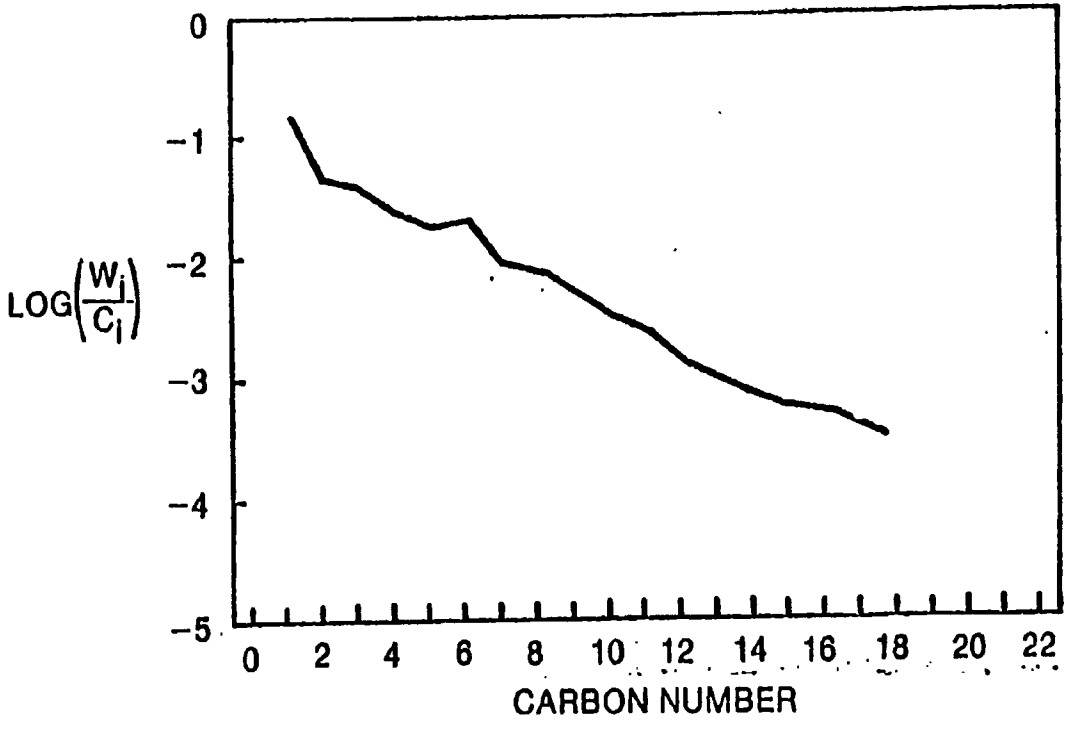
SLIDE 12

HYDROCARBON WEIGHT DISTRIBUTION
BASELINE CATALYST



SLIDE 13

HYDROCARBON SCHULZ-FLORY DISTRIBUTION
BASELINE CATALYST



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TASK 3 - SLURRY REACTOR DESIGN STUDIES

- 5-INCH DIAMETER SIMULATOR
  - — NO INTERNAL HEAT TRANSFER SURFACE
- 12-INCH DIAMETER SIMULATOR
  - — VARIABLE INTERNAL HEAT TRANSFER SURFACE
- ENGINEERING EVALUATION

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TASK 3 - SLURRY REACTOR DESIGN STUDIES

- DEPENDENT VARIABLES

GAS HOLD-UP	MASS TRANSFER
SOLIDS DISPERSION	LIQUID DISPERSION
GAS DISPERSION	HEAT TRANSFER (12" COLUMN)

- INDEPENDENT VARIABLES

SLURRY MEDIUM	: PARAFFIN, WATER
SUPERFICIAL GAS VELOCITY	: 0.05 - 0.5 FT/SEC
SUPERFICIAL LIQUID VELOCITY	: 0 - 0.1 FT/SEC
SOLID	: SILICA, IRON OXIDE
SOLID SIZE	: 1-5μm, 45-53μm, 90-106μm
SOLID CONCENTRATION	: 0, 10, 20, 30 WT %

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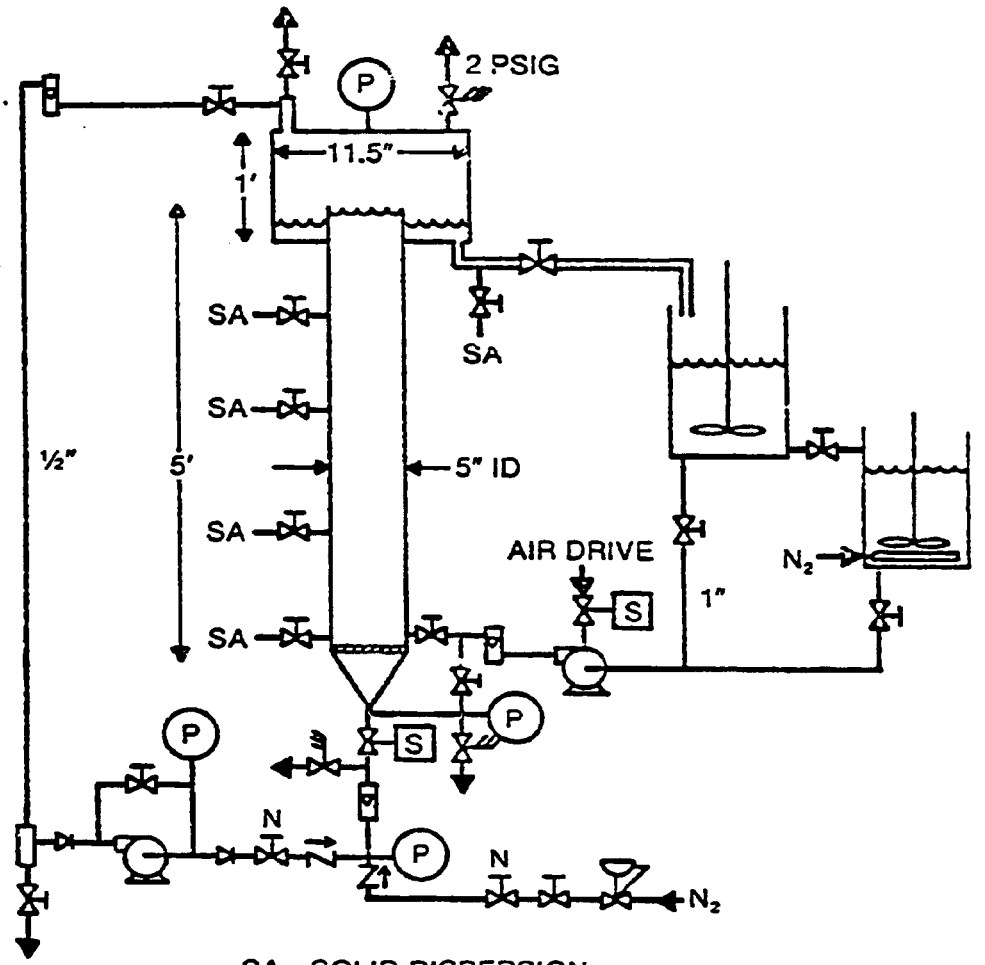
5-INCH SLURRY COLUMN



SA - SOLID DISPERSION
SAMPLING POINT