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

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ABSTRACT

In October 1980, Air Products and Chemicals, Inc. began a three year contract with the DOE: "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.

This report describes work on Tasks 2 and 3 carried out in the third quarter of the contract. In Task 2, the computerized search of the Fischer-Tropsch literature was continued, and improvements were made in data processing programs. Shakedown tests were completed on the first 300 ml slurry reactor, and construction of the second and third reactors began. Five modified "conventional" slurry catalysts were prepared, and two batches were tested in the gas phase giving information on selectivity as a function of composition and activation. Four supported cluster catalysts were synthesized, and seven were tested in the gas phase.

In Task 3, the distributor plate for the 5" cold flow column was selected and a computerized multipoint axial dispersion measurement system was designed. Gas holdup measurements were begun in the isoparaffin slurry system. Initial results showed positive deviations from the Akita and Yoshida predictions, and a literature search for a suitable correlation was initiated.

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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 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.

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 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 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 third 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-plant slurry phase Fischer-Tropsch reactor.

3.0 SUMMARY AND CONCLUSIONS

3.1 Task 1 - Project Work Plan

This task was completed in the first 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 three phase slurry reactors was continued.

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

Construction of the 300 ml and 1000 ml slurry reactors ordered for the contract was begun, and the control instrumentation was partially installed.

After several malfunctions of new pieces of equipment, shakedown tests of the first 300 ml slurry, provided by Air Products and Chemicals, Inc., were completed. Mass transfer tests will be carried out shortly.

Development of the automatic analytical data reduction system continued. Improvements were made in programs dealing with data transfer and compilation, and new programs were written for general database servicing.

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

This section contains potentially patentable material and has therefore been issued in 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".

A data processing program was written for the cluster catalyst screening tests.

3.3 Task 3 - Slurry Reactor Design Studies

A 12.2% open area, 1/28" hole size, triangular pitch, perforated plate was selected as the distributor for the 5" column studies. Representative measurements with a 29 wt% 1-5 μm silica-water slurry showed uniform solid dispersion, and a significant effect of liquid velocity upon gas holdup.

Studies were begun on gas holdup in the isoparaffin system. At zero solids loading, discrepancies were observed with the correlation of Akita and Yoshida, which increased at non-zero liquid velocities. A literature search for a suitable correlation is underway. To ensure that observed differences were not due to experimental error, an improved procedure for measuring gas holdup at zero liquid velocity was introduced.

4.0 ACKNOWLEDGEMENTS

The contributions to this program 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 in the first 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, were continued during this quarter.

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

Construction of the 300 ml and 1000 ml slurry reactors ordered for the contract was begun, and part of the control instrumentation was installed.

Shakedown tests for the first 300 ml slurry reactor provided by APCI were delayed by malfunctions in several pieces of new equipment, but have now been completed. Tests will shortly be carried out to establish the gas to liquid mass transfer controlled operating regimes of the reactor, and to check for possible thermal cracking of the slurry oil.

Development of the automatic analytical data reduction system continued, and several improvements were made to streamline operations in the peak data file transfer and data compilation programs. Additional programs were written to correct misidentified peak files, service and maintain the database stored on Tektronix 4052 discs, and reduce the time required for Sigma 10 tape cassette changes.

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

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

a) Data Processing Program for Cluster Catalyst Screening Tests

A program was written to calculate and plot mole percent and Schulz-Flory distributions from a manual entry of weight percent analytical data, for the Chem Data Systems cluster catalyst screening reactor.

5.3 Task 3 - Slurry Reactor Design Studies

5.3.1 5" Cold Flow Simulator

(i) Distributor Selection

Distributors were tested with a 29 wt%, 1-5 micron silica-water slurry to see if plate pressure drop would be acceptable at the highest flow rates. The 12.2% open area, 1/28" hole size, triangular pitch plate was judged the distributor of choice, and will be used for the remaining 5" column studies. At the highest flow rates, distributor pressure drop was 22 psi. At the lowest flow rates with the two-phase air-water system, gas was seen to bubble through only about 1/4 of the distributor holes, although gas holdup results were reproducible and in agreement with Akita and Yoshida(1).

Another question that was considered was, should liquid enter through the gas distributor plate or from a side inlet above it? When liquid entered the column above the plate, the bubble patterns were greatly disturbed in the lower ten to fifteen inches of the column. It was felt that this large end effect would give misleading results, both for gas holdup and liquid dispersion.

Introducing liquid through the gas distributor plate had two major positive effects. First it eliminated the end effect. Secondly, it provided good distribution for all non-stagnant liquid runs. It was therefore decided to introduce liquid through the gas distributor plate.

(ii) Gas Holdup/Solid Dispersion in Water

Representative measurements of gas holdup and solid dispersions were made at selected data points in a 29 wt% 1-5 micron silica-water slurry. Gas holdup results are summarized in Table 1. Solid dispersion measurements with this system showed a uniform concentration profile throughout the column.

It was found that liquid velocity had a definite effect upon the gas holdup and, as a result, the established two-phase stagnant liquid correlations were not in agreement with these results.

A literature search has not yet uncovered a suitable correlation. Once slurry viscosity measurements become available, they will be used instead of the liquid values to determine whether there is an improvement in agreement.

(iii) Gas Holdup in Isoparaffin

Gas holdup results for the isoparaffin system at zero solids loading were consistently intermediate between the Akita and Yoshida(1) and the Kikita and Kikukawa(2) correlations (see Table 2). Figure 1 shows the experimental data at zero liquid velocity plotted against the Akita and Yoshida predicted values.

At a liquid velocity of 0.09 ft/sec, initial results showed a greater discrepancy with the Akita and Yoshida correlation. A literature search for a suitable correlation is underway; and further data, currently being obtained with paraffin based slurries, will be used to fit an established or new correlation.

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

Construction of the 300 mL and 1000 mL slurry reactors ordered for the contract was begun, and part of the control instrumentation was installed. Completion is scheduled for the end of August.

Shakedown tests were completed on the first 300 mL slurry reactor provided by APCI, using Edwards No. 16 oil. The recycle of oil between the reactor and reservoir under automatic level control was successfully demonstrated, with the reactor operating at 500 psig and 230°C.

Startup was delayed by an exceptional number of malfunctions in new equipment, e.g. leakages of in-line and back pressure regulators. However, these now have been resolved and the initial tests under Fischer-Tropsch synthesis conditions, using a slurry of 5% Ru/Al_2O_3 methanation catalyst in No. 16 oil, to establish the gas to liquid mass transfer controlled operating regimes of the reactor and to test for possible oil cracking, will be carried out in July.

b) Data Processing

Development of the automatic data reduction system was continued this quarter and several improvements were made to streamline operations. The following programs were modified or written.

(i) Peak Data File Transfer Processor (Peak Trans)

Peak Trans is used to transfer data files from the Sigma-10 computing integrator to the Tektronix 4052 computer and was reported previously. The tape data storage routines were removed and the program was modified for direct disk storage. The diskette storage structure was changed to allow faster data transfer to and from the disk system. The changes made are transparent to previously transferred data.

(ii) Data Compilation Program (Datacomp)

The program which is run after the transfer of peak file data from the Sigma integrator to the Tektronix unit is Datacomp, which was reported previously. It integrates the two gas phase analyses into a unified data structure and converts an organic phase analysis peak file into a matrix containing weight percentages for n-alkanes, 1-alkenes, and branched alkanes within each carbon number range. Datacomp also identifies aqueous phase components and similarly separates them into a weight percentage for alcohols, aldehydes, ketones and acids.

Datacomp was re-written in a straight-line program to facilitate documentation and future modifications. The program was also modified to scan the data-base for operator log sheet files and wax analysis files. If either or both of these files are missing, the operator is notified automatically.

Wax analysis files have been found to be necessary in the data reduction of tubular gas phase screening reactor tests, and if present can be included in the overall material balances.

(iii) Peak File Editor

A program was written to allow the operator to make changes within a peak file which has already been transfered by the Peak Trans processor. The Sigma-10 integrator occasionally misidentifies peaks and this type of error is more efficiently corrected after transfer to the Tektronix system because of its expanded capabilities. The peak file editor allows changes to be made to the peak name and response factor. Concentration values are recalculated based on the new response factors and the measured peak area. No alteration of the peak area is permitted. This allows the operator to rapidly correct peak matching errors while preserving data integrity.

(iv) Disk Database Maintenance Program

A program was written which performs the utility functions necessary to maintain the disk database. The program is menu driven and allows the operator to erase unwanted files, rename mis-named files, duplicate the entire disk, copy selected files from one diskette to another, display diskette storage status, display a file's status, and selectively list the names of files resident on a diskette. The commands to perform these tasks are complex and demand scrupulous attention to detail. This program allows the operator to safely carry out these functions through interactive prompting and a display of the results of the action before the command is performed. If the potential command should result in error, the operator can cancel it before the database is disrupted.

(v) Tektronix to Sigma-10 Downloading Processor

A program was written which allows down loading of Sigma-10 integrator via the RS-232C serial link. This capability became desirable because if was found that the integrator's tape storage unit required up to 5 minutes to initialize itself after a tape cassette was changed. Since program and data storage are necessarily on different tapes, it was decided that data storage tapes would be allowed to remain mounted and the programs would be down-loaded as necessary from the Tektronix, making cassette changes infrequent.

(vi) Hardware Modifications

A RS-232-C transfer switch was installed to the Tektronix 4052 System. This switch allows transfer of the single Tektronix 4052 RS-232-C serial port between the Sigma-10 integrators and data communications telephone modem. The phone modem is used to access and transfer data to and from the APCI Corporate Computer.

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

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

a) Data Processing Program for Cluster Catalyst Screening Tests

A program was written to allow manual entry of data obtained from the Chem Data Systems' gas phase testing reactor. This program calculates mole percent and Schulz-Flory distributions from the weight percentage input data. The calculated values are then integrated into the same graphical display and storage processors utilized for the slurry phase operations. A separate input and calculation program was needed because the product analysis from a cluster catalyst screening test is entirely gas phase, whereas the analytical method for the slurry phase and conventional catalyst screening reactors performs separate analyses on condensible fractions.

6.3 Task 3 - Slurry Reactor Design Studies

6.3.1 5" Cold Flow Simulator

(i) Experimental Reproducibility Analysis

The system's accuracy and precision were determined so that appropriate measures could be taken to improve accuracy if required. This involved performing a component error analysis and determining the accuracy and precision of each piece of equipment in the system.

Table 3 compiled using a 30 wt%, 1-5 μm silica-water mixture, gives the results of this analysis. From the Table, it appears that all equipment tested is functioning at an acceptable level of accuracy.

(ii) Gas Holdup

Gas holdup results at zero liquid velocity in water were found to diverge from the correlation derived by Akita and Yoshida(1) at higher gas velocities, as described in the previous quarterly report.

To ensure that the observed differences were not due to experimental error, the procedure for measuring gas holdup at zero liquid flow was modified. Originally, liquid was filled to the top of the column and gas was sparged for 30 minutes. The gas flow was then stopped and the settled liquid height, H_L, was used to calculate gas holdup according to the equation

$$\varepsilon_G = 1 - H_L/60 \qquad (3\text{-}1)$$

The results of this procedure deviated increasingly from existing correlations with increasing gas flow rate (see Figure 37, second quarterly report) due to liquid slugging.

To overcome this difficulty, the procedure of Akita and Yoshida was used. Approximately 2/3 of the column was filled initially. Gas was sparged for 30 minutes and the expanded bed height, H_e, was measured. The gas was then turned off and the settled bed height, H_L, measured. The gas holdup was then calculated by the equation

$$\varepsilon_g = 1 - H_L/H_e \tag{3-2}$$

This modified procedure was used to obtain the results reported in Table 2. However, some inaccuracy still remains in determining the top of the expanded bed, especially at high velocities, and this is under continuing investigation. The problem does not exist at non-zero liquid velocities.

(iii) Bubble Diameter

Photographs were taken at each of the experimental conditons in Table 2. An analysis of these will be included in the next monthly report.

(iv) Liquid Dispersion Measurements

An automated data collection and reduction system has been designed to enable the development of a more sophisticated dispersion model and will be provided by Air Products and Chemicals, Inc. It will include (see Figure 2).

1. Six conductivity probes and meters,
2. An A-D converter,
3. A Tektronix 4052 microcomputer,
4. Temporary tape storage, and
5. Permanent disc storage.

In this system, the output from each of the six conductivity probes is sampled in turn and digitized at a rate of up to 60 samples/sec by the computer and stored temporarily on tape. After the experimental run, various dispersion models will be fitted against the digitized values to see which most closely models the system. Among the dispersion models to be tried are a CSTR in series and a back-mixed cell model. After the dispersion coefficients are obtained, the residence time distribution (RTD) curves will be permanently stored on disc to be used later to predict conversions.

The system was successfully demonstrated using an electrolyte solution dispersed in water to simulate a trace pulse in the five inch column.

7.0 REFERENCES

1 K. Akita and F. Yoshida, Ind. Eng. Chem. Proc. Des. Dev. 1973, 12, 76.

2 H. Hikita and Kikukawa, Chem. Engng. J. 1973, 81 74.

8.0 Figures

FIGURE 1

GAS HOLDUP DATA VS. AKITA AND YOSHIDA CORRELATION

System: Isoparaffin-Nitrogen, Zero Liquid Velocity

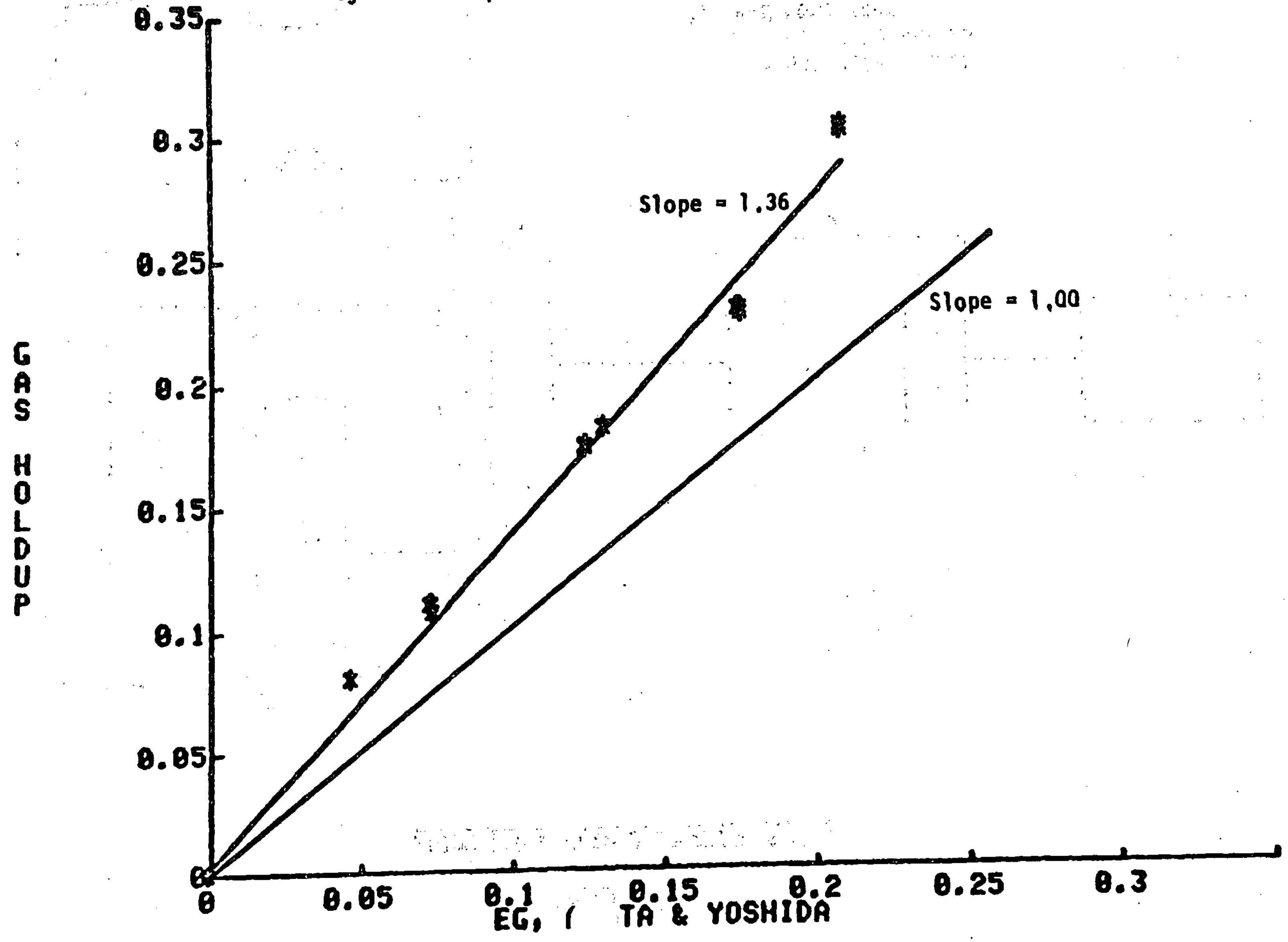
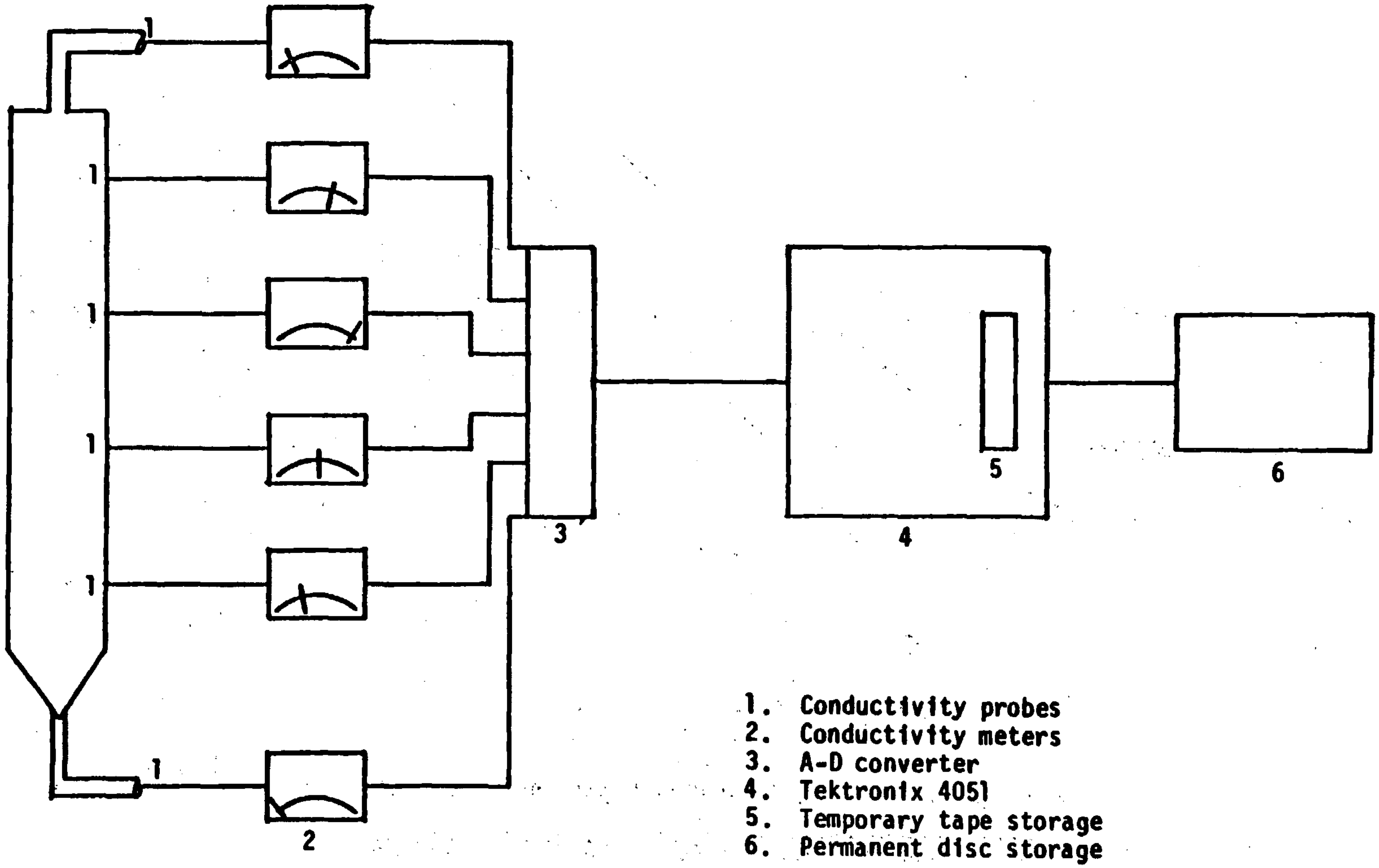


FIGURE 2

AUTOMATED LIQUID DISPERSION SYSTEM



1. Conductivity probes
2. Conductivity meters
3. A-D converter
4. Tektronix 4051
5. Temporary tape storage
6. Permanent disc storage

9.0 TABLES

TABLE 1

Gas Holdup, 5" Cold Flow Simulator

System: Liquid - tap water

Solid - 29 wt%, 1-5 μm, silica

Run	V_G Ft/Sec	V_L Ft/Sec	ϵ_G Measured	ϵ_G Akita & Yoshida[1]	ϵ_G Hikita & Kikukawa[2]
5992-39	0.45	0.072	0.139	0.2174	0.1985
5992-40	0.51	0.083	0.153	0.2284	0.2086
5992-42	0.20	0	0.154	0.1406	0.1356
5992-43	0.05	0	0.021	0.0529	0.0713
5992-44	0.20	0.050	0.081	0.1496	0.1356
5992-45	0.51	0.108	0.140	0.2284	0.2086
5992-46	0.51	0.108	0.151	0.2284	0.2086
5992-47	0.51	0.108	0.149	0.2284	0.2086

References

[1] K. Akita and F. Yoshida, Ind. Eng. Chem. Proc. Des. Dev. 1973, 12, 76

[2] H. Hikita and Kikukawa, Chem. Engng. J. 1973, 81, 74

TABLE 2

Gas Holdup, 5" Cold Flow Simulator

System: Two Phase:

Liquid - Isoparaffin

Gas - Nitrogen

Run	V_G Ft/Sec	V_L Ft/Sec	ε_G Exp.	ε_G Akita & Yoshida[1]	ε_G Hikita & Kikukawa[2]
5992-57-1a	0.353	0.0	0.227	0.174	0.384
-1b	0.356	0.0	0.227	0.174	0.386
-1c	0.358	0.0	0.225	0.175	0.386
5992-57-2a	0.095	0.0	0.107	0.074	0.207
-2b	0.096	0.0	0.110	0.074	0.208
-2c	0.094	0.0	0.110	0.073	0.206
5992-57-3a	0.198	0.0	0.172	0.124	0.292
-3b	0.213	0.0	0.180	0.130	0.302
-3c	0.198	0.0	0.173	0.124	0.292
5992-57-4	0.054	0.0	0.080	0.047	0.149
5992-58-1	0.290	0.094	0.214	0.156	0.350
5992-59-1	0.390	0.094	0.260	0.184	0.402
5992-60-1	0.006	0.096	0.141	0.051	0.167
5992-61-1	0.099	0.096	0.164	0.076	0.211
5992-62-1	0.050	0.101	0.305	0.208	0.452
5993-63-1	0.500	0.0	0.299	0.208	0.452
5992-64-1	0.200	0.100	0.200	0.124	0.294
6000-35-1	0.130	0.094	0.174	0.093	0.240
-2	0.100	0.090	0.140	0.077	0.212
-3	0.290	0.094	0.220	0.156	0.350

References

[1] K. Akita and F. Yoshida, Ind. Eng. Chem. Proc. Des. Dev. 1973, 12, 76

[2] H. Hikita and Kikukawa, Chem. Engng. J. 1973, 81, 74

TABLE 3

COMPONENT ERROR ANALYSIS

EQUIPMENT	TEST	# SAMPLES	MEAN	STANDARD DEVIATION	
				ABSOLUTE	RELATIVE TO MEAN
Slurry Pump	Time Consistency	11 over 2 1/4 hrs	0.966 ft^3/min	1.06×10^{-2} ft /min	1.1%
Slurry Pump	Sample Reproducibility	2 over 2 mins	0.9845 ft^3/min	2.12×10^{-3} ft /min	0.2%
Tank	Sample Reproducibility	10	28.72 wt%	4.14×10^{-1} wt%	1.44%
Tank	Time to steady state in batch mode = 1/2 to 1 hr.				
Scale	Sample Reproducibility	10	142.89g	$.98 \times 10^{-3}$g	6.8×10^{-4}%
Oven	For even heating	6	All samples were dry between 45 minutes and 1 hour		
Column	Solid Concentration Profile (One sample per port)	5	28.88 wt%	.205 wt%	0.710%

Gas rotameter (Fischer-Porter) - accuracy 2% of scale (manufacturer's claim)

Gas rotameter (Brooks) - accuracy 1% of rate (manufacturer's claim)

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