SLURRY REACTOR HYDRODYNAMIC STUDIES

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Introduction and Summary

Air Products is nearing completion of a 3 year DOE contract[1], in which new diesel fuel selective catalysts and slurry phase bubble column reactor correlations for the Fischer-Tropsch (FT) synthesis were developed. This paper presents results from the reactor studies.

The objective of the slurry reactor modelling studies was to evaluate, through the use of cold flow simulators, the hydrodynamics, flow characteristics and behavior of slurry reactors for the production of hydrocarbons from synthesis gas.

The slurry reactor modelling consisted of three major sub-sections. The first was a hydrodynamic study in a 5" ID x 5' or 12.7 cm ID x 1.52 m tall cold flow simulator. The second phase of the project was to scale up the first hydrodynamic study and to incorporate some additional independent variables in a 12" ID x 15.5', or 30.5 cm ID x 4.75 m column. Finally, in the third section, kinetic data obtained from the catalyst studies, along with the hydrodynamic correlations obtained in the above two sections, was incorporated into a computer model. This computer model was used to predict the conversion rates and space time yields, or production rates/unit volume, to be obtained in actual FT slurry reactor operation. From the model, the heat, mass and momentum mass transfer parameters, which most affect the bubble column design, were better quantified.

Included in Table 1 is a list of the hydrodynamic parameters, or dependent variables, that were investigated in the first two sections of the slurry reactor modelling program. These variables were studied because substantial differences in reactor performance, and thus plant costs, were obtained using existing literature correlations. From a study of these parameters, uncertainty in the optimum reactor design was considerably reduced.

There is some disagreement in the literature on whether the production rates in a FT slurry reactor are limited by mass transfer resistance, i.e. the rate at which reacting gas can transfer into the liquid phase, or kinetic resistance, i.e. the kinetic reaction rate of the catalyst. Gas holdup, or the gas volume fraction in the column, average bubble size, and mass transfer coefficient - all affect the degree in which the overall reaction is limited by mass transfer of reactants. If gas-liquid mass transfer limitations are controlling, then these would be the only parameters needing study. Two parameters, solids dispersion and liquid dispersion, affect the maximum catalyst loaded, and would be the only parameters needed to quantify STY for the kinetic controlled regime. The heat transfer coefficient determines how much heat transfer surface is required inside the reactor, which directly affects how much volume remains for the reaction. It is anticipated in the optimum bubble column design that mass and kinetic resistances, and possibly heat transfer resistances, may be controlling. Thus, it is necessary to quantify all of the above mentioned parameters.

Experimental

Apparatus

Experiments were conducted in a 12.7 cm id x 1.52 m Plexiglass and 30.5 cm id x 475 cm borosilicate glass column[1] (see Figure 1). Four ports to sample the solid concentration were mounted at approximately 9, 38, 76 and 114 cm above the perforated plate distributor in the 12.7 cm column, and 2, 15, 302, and 453 cm in the 30.5 cm column.

Table 1 shows the size ranges and concentrations of the slurries of silica and iron oxide in isoparaffin[2] and water, that were utilized in the tests. From the stirred, baffled reservoir tank, which was approximately the same volume as the columns, slurry was pumped with a diaphragm pump, using a tranquilizer to even out the flow, into the bottom of the 12.7 cm column, and above the distributor for the 30.5 cm column. In the 12.7 cm column, therefore, slurry passed with the gas through the distributor plate for $V_L > 0$. At the top of the column, the slurry was separated from the gas, and returned by gravity to either the reservoir tank, or to a calibrated volume used for slurry flow measurement.

Nitrogen or air was metered with a rotometer in the 12.7 cm column, and with a differential pressure cell in the 30.5 cm column, and entered the columns beneath the distributor plate.

With the highest slurry loadings, a small gas sidestream was also used in the slurry feed to facilitate pumping from the reservoir to the column.

For the 12.7 cm column, the gas and slurry distributor was 1.25 mm thick, with a 10% to 13% open area of 0.9 mm holes. The 30.5 cm column used different 0.3% open area, distributor plates, with 0.9, 3.2 and 12.7 mm diameter holes. The gas traveled with the slurry, separated at the column top, and passed through a demister pad, liquid trap, and rotometer before being vented. All metal parts were grounded to prevent electric arcing during experiments with the non-conducting hydrocarbon liquid.

Independent Variables Studied

The independent variables, shown in Table 1, were chosen to amply bracket the range of conditions anticipated in a slurry phase FT process. The operating conditions used for the Rheinpreussen slurry phase FT pilot plant[10] were considered typical. In that work, a 20 wt% slurry, 50 µm average particle size, precipitated iron oxide catalyst was used. The gas operated from 6.1 to 9.1 cm/sec superficial velocity. With heat transfer internals, circulation of slurry to an external cooler was unnecessary. However, as it was unknown whether internal or external cooling would be optimal in this work, a sufficiently high slurry velocity was studied to allow only a 10°C temperature raise of the slurry in the reactor in the event of external cooling.

Various perforated plate gas distributor hole sizes were investigated. Perforated plates were chosen because distributor plate fouling did not appear to be a problem at Rheinpreussen.

Two liquids used were water and isoparaffin, a C_9-C_{11} branched hydrocarbon. Water was chosen to relate the bulk of the literature data to this study. Isoparaffin was chosen to simulate the Rheinpreussen type paraffinic oil because they both 1) were hydrocarbons, 2) did not exhibit foaming, and 3) had nearly the same density and surface tension. The relative importance of each hydrodynamic parameter studied upon space time yield (STY), and thus anticipated economic cost of the process is discussed in subsequent sections.

Results

Gas Holdup

Gas holdup was studied because of the large differences, as much as 300%, in the values of gas holdup reported in the literature[3, 4]. The actual value that is used to predict column performance would have a large effect on production rates. Therefore, it was important to obtain as accurate numbers as possible on a system as close to the actual system as possible. Gas holdup was measured by, at steady state, shutting off both the gas and liquid flows and then measuring the settled liquid height.

Separate empirical gas holdup correlations were obtained for each of the four solid/liquid pairs studied in the 5" cold flow simulator:

Silicon Oxide/Aqueous

$$\alpha/(1-\alpha)^4 = 0.36\, V_G^{0.96}\, d_p^{0.10}/W^{0.27} \qquad R^2 = 0.94 \qquad 1)$$

Silicon Oxide/Isoparaffin

$$\alpha/(1-\alpha)^4 = 1.26\, V_G^{0.99}/d_p^{0.035} \qquad R^2 = 0.80 \qquad 2)$$

Iron Oxide/Aqueous

$$\alpha/(1-\alpha)^4 = 1.29\, V_G^{1.02} \qquad R^2 = 0.621 \qquad 3)$$

Iron Oxide/Isoparaffin

$$\alpha/(1-\alpha)^4 = 1.50\, V_G^{0.972}/W^{0.035} \qquad R^2 = 0.812 \qquad 4)$$

Gas holdup was found to be mostly a function of gas velocity. Each correlation has gas velocity varying to the first power in agreement with Akita and Yoshida. For silicon oxide, particle diameter is seen to have the opposite effect in an isoparaffin slurry than in an aqueous slurry.

The results for a 20 weight loading, 49 μm particle size are plotted for the four solid/liquid types in Figure 2. As gas velocity increases from 1.52 to 15.24 cm/sec, gas holdup reached a limiting value of about 25%. The largest gas holdups were seen for the isoparaffin/iron oxide system. The smallest holdups were seen in the silica/water system. Isoparaffin is expected to yield a larger gas holdup because of its lower surface tension, producing smaller bubbles at the distributor, and its lower density, giving a slightly lower buoyancy force. A unified gas holdup correlation is currently being constructed using dimensionless groups that include slurry properties, including surface tension, viscosity and density.

Bubble Diameter

Bubble diameter was measured because this type of information has never been obtained before for a three phase hydrocarbon system. Also, the predicted values reported in the literature based on gas-liquid studies do vary by a factor of three[3, 4]. It, along with gas holdup, has a considerable effect on the extent of mass transfer resistance on the overall reaction. Because of the differences in gas holdup between two and three phase systems, there is a reason to suspect that there are also differences between two and three phase bubble diameters.

The procedure that was used for obtaining a bubble diameter measurement in a three phase system is shown schematically in Figure 2. For each bubble, the probe of a double hot film conical probe recorded a bubble trace. These impulses were fed through an electrical bridge, similar to a Wheatstone bridge, into an A-D converter and stored by the computer. The computer then determined whether both probes detected the same bubble. By measuring the difference in initial contact time between probes, the bubble rise velocity was obtained. Multiplying the time a bubble takes to pass a probe by the rise velocity yielded the actual chord length. Since the probe could be transcending any chord of the bubble, a large number of samples, 1400, must be obtained in order to obtain an accurate bubble diameter distribution to within ±10%[5]. Once 1400 bubble sizes were recorded, that information was then transferred by phone line to the mainframe computer. On the mainframe computer, a statistical analysis to convert those 1400 bubble samples into a two parameter bubble size gamma distribution was performed. Data acquisition is currently underway.

Mass Transfer

Mass transfer, or k_La, was measured also because reported values vary, although to a smaller extent. Thus, more accurate values for this particular parameter are expected to have a smaller effect on reactor design than gas holdup or bubble diameter. k_La was obtained by recording the rate of change of dissolved oxygen once the gas flow was switched over from air to nitrogen.

The mass transfer data obtained in the 5" column yielded the following empirical correlation:

$$k_La = 0.30\alpha^{1.06} d_p^{0.05}/W^{0.08} \qquad R^2 = 0.89 \qquad 5)$$

Interfacial area is related to the gas holdup and mean bubble diameter by

$$a = 6\ \alpha/d_b \qquad 6)$$

Since k_La is linearly proportional to gas holdup, the mean bubble diameter probably varies little with increasing gas holdup. This hypothesis is presently being tested in the bubble diameter work. Substituting the gas holdup correlation into equation 5) also indicates that gas velocity is the primary factor in estimating k_La.

The three hydrodynamic parameters just discussed affect the extent that mass transfer controls bubble column production rates. The next two parameters affect how much catalyst can be added to the system, and hence the extent of kinetic control of the system.

Solid Loading and Concentration Profiles

In a kinetic controlled regime, the maximum solid loading, or weight fraction, has a direct and large impact on the production rate/unit volume in a slurry reactor. The maximum solid loading is reached when solid particles just begin to settle out at the reactor bottom. Any further addition may lead to hot spots within the settled catalyst area. Concentration profiles were obtained by weighing a slurry sample before and after filtration to better quantify this maximum.

The sedimentation diffusion model[6], in which the tendency for solids to settle in a column is offset by the tendency for the gas phase to mix up the solids, was applied to the system[7], with some success. However, the sedimentation diffusion model does have some limitations. As shown in Figure 3, where the solid weight fraction is plotted as a function of height for different particle sizes of iron oxide, in every case, there is a slight rise in concentration at this column height in the 5" CFS. This type of phenomena cannot be predicted by a sedimentation diffusion model. The 1-5 μm silicon or iron oxide gave uniform solid concentration profiles over almost all conditions. This is fortunate, because in actual FT operation, the equilibrium particle size, as a result of catalyst attrition, is expected to be in this size range. The silicon oxide was suspended less than predicted, probably due to agglomeration of particles causing particles to settle more quickly. This shows the importance of carrying out hydrodynamic studies with solid particles and liquids as close to the actual system as possible.

The study did show that solid concentration profiles were mostly affected by the solid particle size and density, as well as slurry velocity. The model also showed the maximum solid loading to be a function of column height.

Liquid Dispersion

Liquid dispersion also relates to how much solid can be suspended. However, the effect of obtaining more precise dispersion data on overall space time yields was expected to be small. This is because bubble column slurry reactors are already known to provide good mixing.

Liquid dispersion coefficients were measured in the aqueous phase using a salt tracer to obtain a residence time distribution function, as outlined by Levinspiel[8]. Typical results are shown in Table 3. It was found that liquid dispersion and solid dispersion coefficients are the same in value, and were found to be mostly affected by gas velocity and column diameter. The correlation obtained in this work agreed with Kato[9] and coworkers:

$$Pe = 13\ Fr/(1 + 8\ Fr^{0.85}) \qquad 7)$$

Heat Transfer

Heat transfer coefficients were measured because this affects the amount of cooling surface required. At Rheinpreussen, the heat transfer surface accounted for about 6% of the reactor volume[10, 11]. Thus, the effect of more precise data on overall production rates should be small. It was found that the results did agree with the correlation by Deckwer[12], although the values themselves were about 64% of Deckwer's values yielding

$$St = 0.064\sqrt{Fr_p Pr \sqrt{Re_{SL}}} \qquad 8)$$

The heat transfer coefficient was mostly a function of gas velocity and heat capacity of the liquid. Also liquid density and to a smaller extent, the thermal conductivity of the liquid were also factors.

Engineering Evaluation

Presently, the gas holdup, solid concentration, liquid dispersion and heat transfer relationships have been incorporated into a bubble column computer model proposed by Deckwer[13], although the k_La correlation has not yet been incorporated.

The substitution of the cold flow correlations for those in the original Deckwer model caused some changes in predicted column performance. While the effect at low gas velocities was negligible, at 9 cm/sec, the space time yield doubled (see Table 3 vs. Table 4), primarily due to the lower predicted gas hyoldup. The Rheinpreussen base case was not simulated with the new gas holdup correlation because it's conversion and space time yield were measured[10] quantities, while the reaction kinetics were calculated assuming the Deckwer[12] gas holdup correlation. Thus, any change to the gas holdup correlation would necessitate a change of the inferred reaction kinetics in order to yield the same hydrogen conversion and space time yield.

The lower gas holdup predictions had a desirable effect on reactor space time yield because the mass transfer resistance was not predicted to be limiting. Mass transfer resistance will increase when the cold flow model mass transfer correlation is substituted for the Deckwer correlation. However, it is still not expected to markedly change the results.

Compared to Rheinpreussen, overall STY using these catalysts is lower, although catalyst improvements are anticipated. However, the operating conditions used in the simulations in Tables 3 and 4 are optimized for the

Rheinpreussen case and not for the new catalysts. Comparing fuel fraction yields (see Figure 5), it is seen that catalysts A and B produce several times more diesel fuel than was produced at Rheinpreussen. If shift activity can be added to catalyst B as anticipated, the diesel fraction will be almost five times that obtained at Rheinpreussen, reducing the size of downstream refining equipment.

Conclusion

In summary, the hydrodynamic parameters that, along with the kinetic parameters, are necessary to accurately predict how bubble column reactors will perform in the FT synthesis have been measured and correlated. These correlations, some of which agree with previous literature, and others which expand upon previous literature knowledge, have been incorporated into a computer model to better predict bubble column performance.

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Legend of Symbols

d	diameter, cm
Fr	$V_G/\sqrt{g\ d_C}$ Froude number
Fr_p	$V_G/\sqrt{gd_p}$ particle Froude number
g	gravitational acceleration constant, cm^2/s
k_{SL}	$k_L(2k_L + k_S - 2V_S(K_L-k_S))/(2k_L + k_S + V_S(k_L-k_S))$ slurry thermal conductivity
L	column length, cm
Pe	$V_G\ d_C/E_Z$ Peclet number
Pr	$(\mu c_p/k)_{SL}$ Prandtl number
Rep	$V_p d_S \rho_L/\mu_L$ Particle Reynolds number based on liquid properties
Re_{SL}	$V_{ST} d_S \rho_{SL}/\mu_{SL}$ Particle Reynolds number based on slurry properties
V	velocity, cm/s

v	volume fraction
W	weight fraction
α	gas volume fraction, holdup
ρ	density, g/cm^3
μ	viscosity, g/cm.s

Subscripts

G	gas
L	liquid
P	particle
S	solid
SL	slurry

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TABLE 1

SLURRY REACTOR DESIGN STUDIES

- **DEPENDENT VARIABLES**
  - GAS HOLD-UP
  - BUBBLE SIZE
  - SOLIDS DISPERSION
  - MASS TRANSFER
  - LIQUID DISPERSION
  - HEAT TRANSFER (30.5CM COLUMN)

- **INDEPENDENT VARIABLES**
  - SLURRY MEDIUM : PARAFFIN, WATER
  - SUPERFICIAL GAS VELOCITY : 1.52 - 15.2 CM/SEC
  - SUPERFICIAL SLURRY VELOCITY : 0 - 3.0 CM/SEC
  - SOLID : SILICA, IRON OXIDE
  - SOLID SIZE : 1-5μm, 45-53μm, 90-106μm
  - SOLID CONCENTRATION : 0, 10, 20, 30 WT %
  - ADDITIONAL 30.5cm COLUMN VARIABLES
    - DISTRIBUTOR HOLE SIZE : 0.9, 3.2, 12.8 mm
  - HEAT TRANSFER INTERNALS : NONE, PLAIN

TABLE 2

PHYSICAL PROPERTIES OF LIQUIDS

LIQUID	TEMP. °C	SURFACE TENSION DYNES/CM	VISCOSITY CP	DENSITY G/CM^3	GAS DIFFUSIVITY CM^2/SEC
WATER	20	72.7	1.00	1.00	2.5×10^{-5} (O_2)
ISOPARAFFIN	20	22	1.20	0.73	1.2×10^{-5} (O_2)*
RHEINPREUSSEN TYPE PARAFFINIC OIL*	260	11	0.33	0.67	8×10^{-5} (CO)

*ESTIMATED

TABLE 3

RHEINPREUSSEN SIMULATION
USING DECKWER CORRELATIONS

Regime	Churn Turbulent		
Catalyst	Base Case	Catalyst A	Catalyst B
Inlet gas velocity, cm/sec	9.00	9.00	9.00
Gas holdup	0.385	0.512	0.526
Interfacial area, cm^2/cm^3	32.66	43.44	44.66
Temperature, °C	260.2	259.7	260.2
Rate Constants:			
Pre-exponential factor (sec wt% in slurry)	1.12×10^5	9.03×10^6	1.15×10^7
Activation energy, kJ/mol	70	94.7	94.7
Inlet ratio, mol CO/mol H_2	1.5	1.5	1.98
Us ratio, mol CO/mol H_2	1.5	1.5	0.65
Hydrogen conversion, %	0.804	0.349	0.498
Rel. mass transfer resistance	0.106	0.021	0.035
Space time yield, mol CH_2/hm^3	2937	1065	1002
Constants in Case Study			
Reactor length, ft (cm)	26.25 (800)	→	→
Reactor diameter, in (cm)	59 (150)	→	→
Contraction factor	-0.5	→	→
Particle diameter, μm	50	→	→
Reactor pressure, psig (bar)	174 (12)	→	→
Weight fraction catalyst in slurry	0.20	→	→
Specific heat transfer area, cm^2/cm^3	0.10	→	→

TABLE 4

RHEINPREUSSEN SIMULATION

Regime	Churn Turbulent			
Catalyst	Base*	Catalyst A	Catalyst B†	Catalyst B† with shift
Inlet gas velocity, cm/sec	9.0	9.0	9.0	9.0
Gas holdup	0.385	0.149	0.171	0.146
Interfacial area, cm^2/cm^3	32.66	36.06	41.43	35.39
Temperature, °C	260.2	260.4	260.4	261.1
Rate Constants:				
Pre-exponential factor (sec wt% in slurry)	1.12×10^5	9.03×10^6	1.15×10^7	1.15×10^7
Activation energy, kJ/mol	70	94.7	94.7	94.7
Inlet ratio, mol CO/mol H_2	1.5	1.5	1.98	1.98
Usage ratio, mol CO/mol H_2	1.5	1.5	0.65	1.98
Hydrogen conversion, %	80.4	55.9	62.9	58.5
Rel. mass transfer resistance	0.106	0.043	0.069	0.048
Space time yield, mol CH_2/hm^3	2937	2042	1273	2135
Constants in Case Study				
Reactor length, ft (cm)	26.3 (800)	→	→	→
Reactor diameter, in (cm)	59 (150)	→	→	→
Contraction factor	-0.5	→	→	→
Particle diameter, µm	50	→	→	→
Reactor pressure, psig (bar)	174 (12)	→	→	→
Weight fraction catalyst in slurry	0.20	→	→	→
Specific heat transfer area, cm^2/cm^3	0.10	→	→	→

* Operating conditions at Rheinpreussen

† Cold flow model gas holdup correlation

FIGURE 1
12.7 AND 30.5 CM COLUMN SCHEMATIC

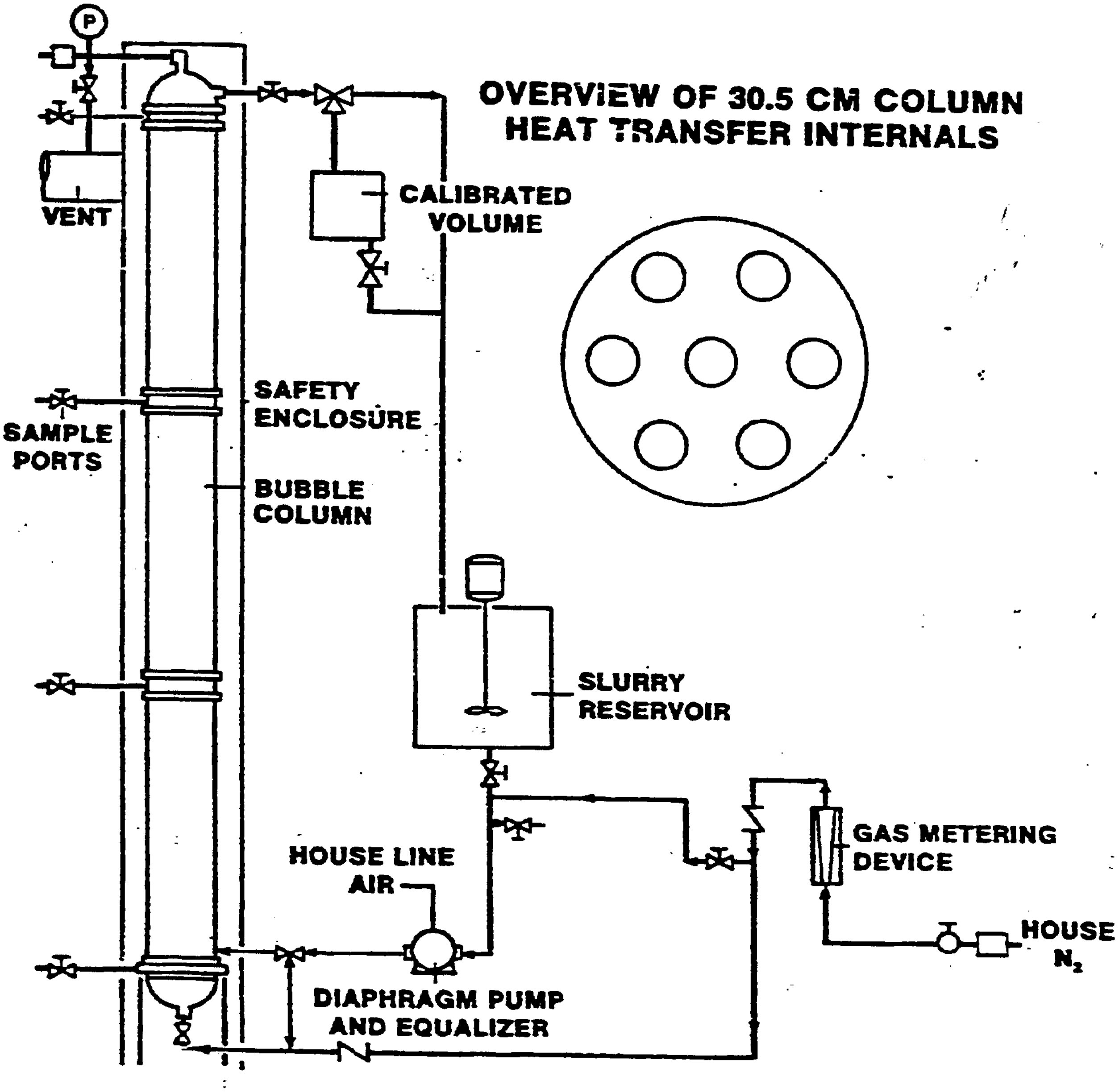

FIGURE 2

GAS HOLDUP VS GAS VELOCITY FOR DIFFERENT SOLID/LIQUIDS

12.7 CM COLD FLOW SIMULATOR

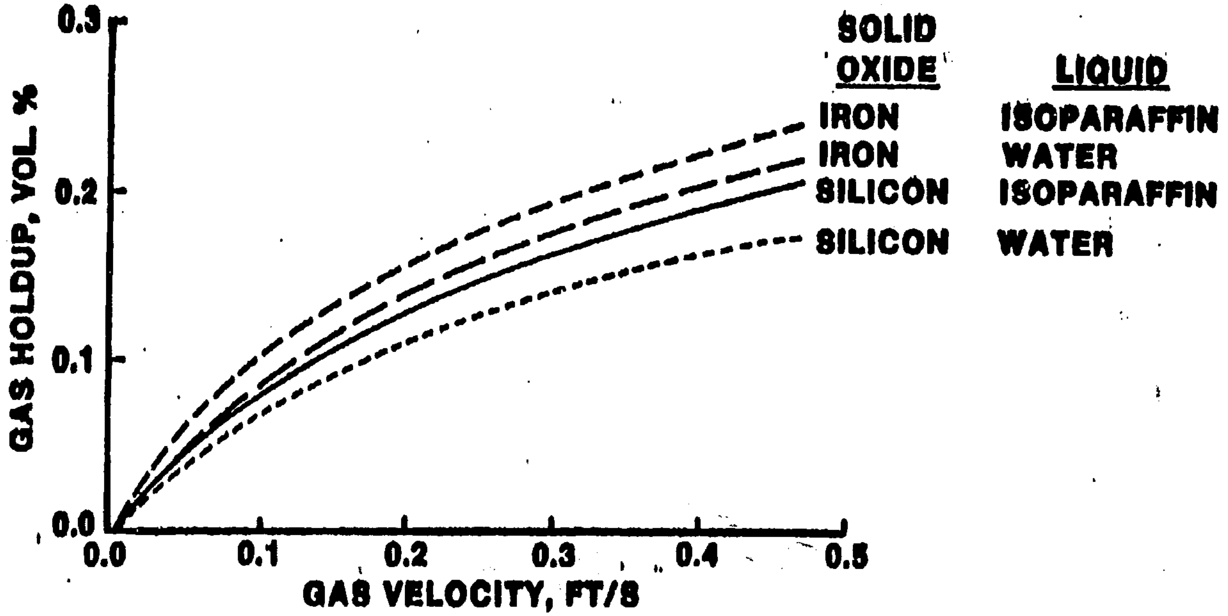

FIGURE 3

BUBBLE SIZE ANALYSIS SYSTEM

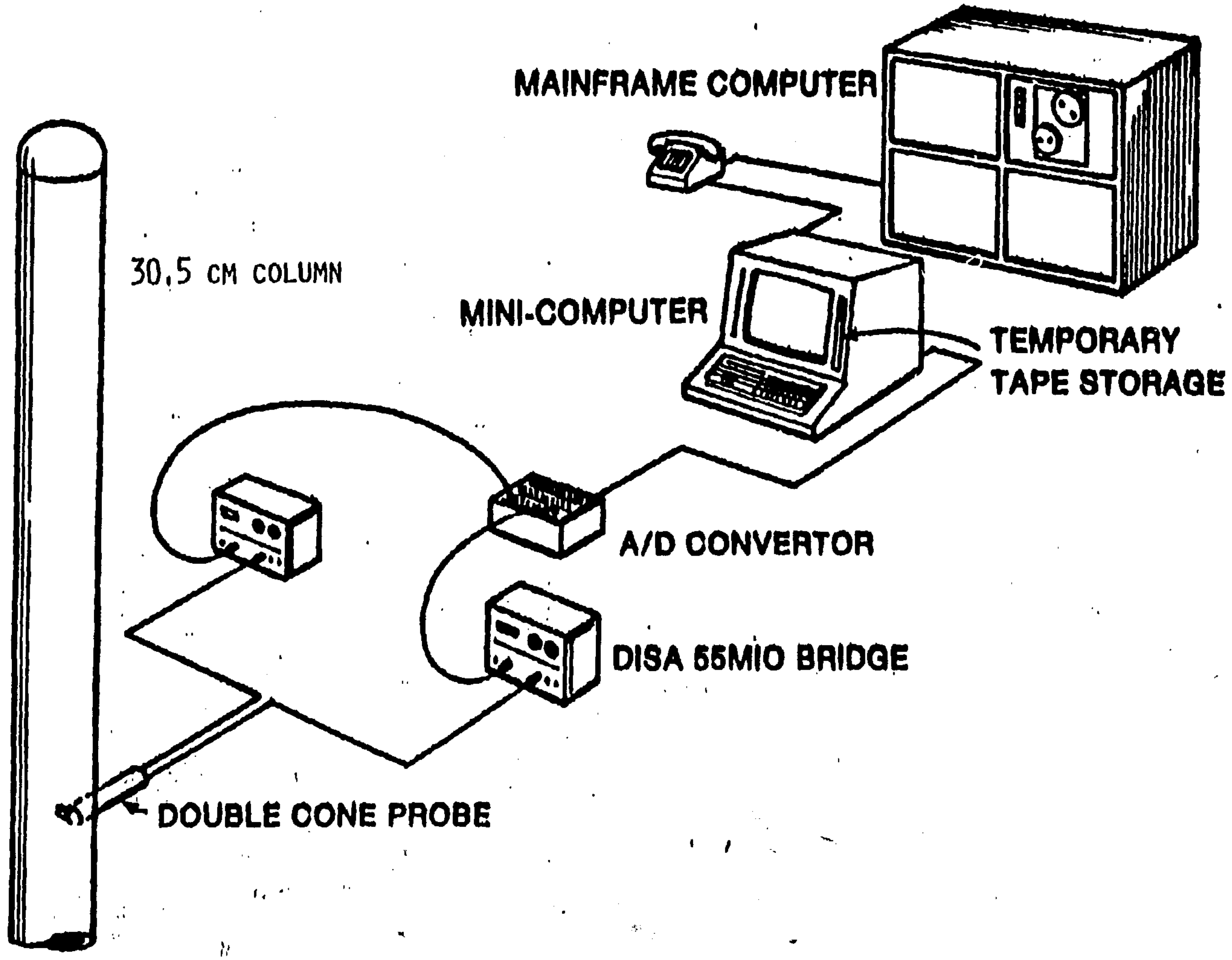

FIGURE 4

Particle Size Effect on Solid Profiles
Continuous System, Positive Liquid Velocity
Isoparaffin, Iron Oxide, N_2

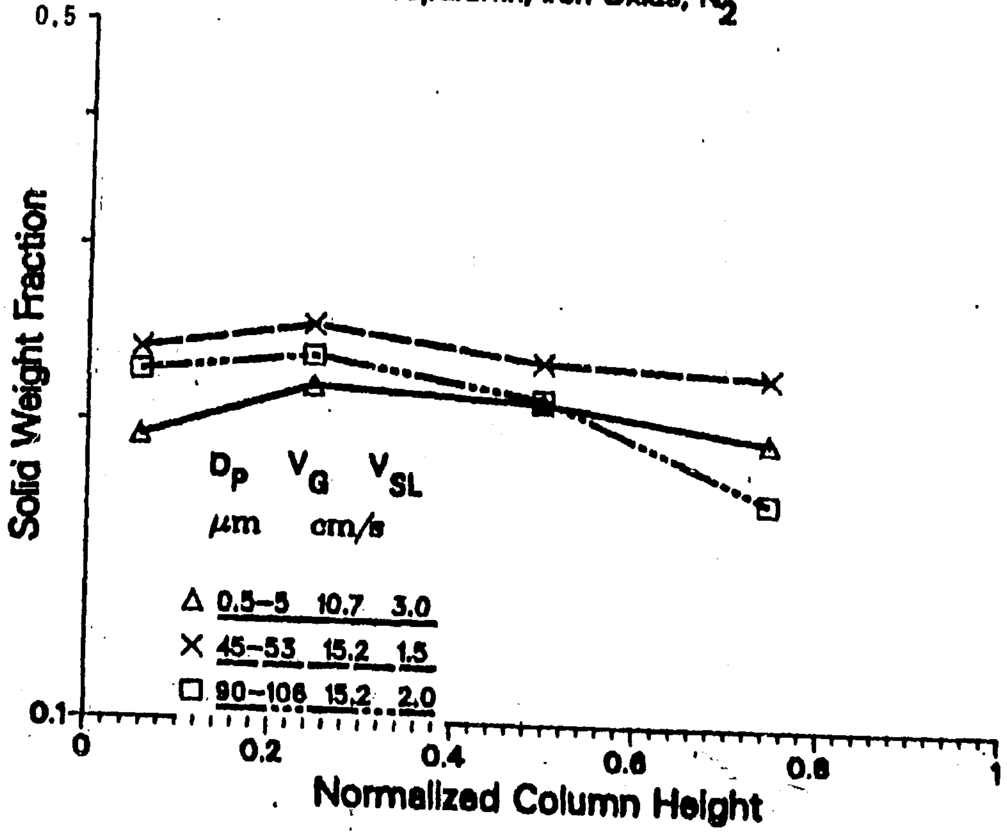

FIGURE 5

SPACE-TIME YIELD
AT RHEINPREUSSEN CONDITIONS