CATALYST AND REACTOR DEVELOPMENT FOR A LIQUID PHASE FISCHER-TROPSCH PROCESS. QUARTERLY TECHNICAL PROGRESS REPORT, 1 JULY 1983-30 SEPTEMBER 1983

AIR PRODUCTS AND CHEMICALS, INC.
ALLENTOWN, PA

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CATALYST AND REACTOR DEVELOPMENT

FOR A LIQUID PHASE FISCHER-TROPSCH

PROCESS

QUARTERLY TECHNICAL PROGRESS REPORT

FOR PERIOD 1 JULY 1983 - 30 SEPTEMBER 1983

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EXECUTIVE SUMMARY

Two major tasks continued in the twelfth quarter of the Air Products and Chemicals, Inc./U.S. DOE Contract, "Catalyst and Reactor Development for a Liquid Phase Fischer-Tropsch Process": (1) Slurry Catalyst Development, and (2) Slurry Reactor Design Studies.

The second extended slurry test, using a proprietary catalyst was completed. The results were not consistent with a previous short term test of this catalyst where high activity and yields in the diesel fuel region equal to or greater than the Schulz-Flory maximum were observed. The increased methane production and lower bulk activity over the previous test may have been the result of a variation in the surface active species of this catalsyt. The steps in the synthesis procedure combined with surface analysis (ESCA, SIMS, etc.) of the two batches of catalyst are currently underway to determine the causes.

A short term (21 day) slurry test was carried out on another "modified conventional catalyst". Parametric gas phase screening results were concluded for four additional catalysts, and the optimum preparation and activation methods for diesel fuel selectivity were chosen.

In the hydrodynamic studies, work in the 12 inch Cold Flow Simulator continued. The following observations and/or conclusions were obtained:

o Superficial gas velocity is the major factor for determining gas holdup. The results of simulations with water and isoparaffin slurries of both silica and iron oxide fell within a margin of error, in the range predicted by the Akita and Yoshida[1] and Pilhofer and Bach[2] correlations.

o The major determining factor of the solids concentration profile in a slurry bed is particle size. Water and isoparaffin media were studied; the gradient was most pronounced using the 90-115 μm particles with no appreciable gradient using the 0.5-5 μm particles.

o Heat transfer coefficients were obtained for both two and three phase systems. For the two-phase isoparaffin/N_2, the results were 64% of that predicted by Deckwer's correlation. For the three-phase Fe_2O_3/ isoparaffin, the results were better at 71%.

o Bubble diameter measurements were obtained using a double hot film probe. The raw data (uncalibrated) fell within a fairly narrow range size, 0.28 - 0.53 cm with most of the bubble sizes at the lower end. Calibrated bubble profiles are expected to show literature agreement.

o The Air Products gas holdup correlation was incorporated into Deckwer's model of the three phase bubble column. A simulation utilizing kinetic data from an Air Products diesel fuel selective catalyst, under Rheinpreussen conditions, resulted in doubling the space time yield of the Rheinpreussen base case catalyst. Based on the assumption of no mass transfer limitations, the objective of equalling Rheinpreussen space time yields can be achieved with several of the catalysts developed at Air Products.

o Slurry viscosity measurements on some representative slurries used in the cold flow studies are underway.

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1.0 INTRODUCTION

Coal liquefaction will be an important source of transportation fuels in the future, and can be accomplished by both a direct route (hydrogenation of coal in a donor solvent) or by an indirect route (gasification of coal followed by the Fischer-Tropsch reaction).

The 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.

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 previously been developed for producing a narrow range hydrocarbon product, such as gasoline or diesel fuel, without the coproduction of lighter and heavier undesirable products.

The Fischer-Tropsch reaction is exothermic, and improved heat transfer would also be expected to have a major beneficial effect on product selectivity. Slurry phase reactor operation improves heat transfer and temperature control, and results in greater selectivity to liquid products, usually through lower methane production. However, considerable differences have been reported in the space-time yield, catalyst life and ease of operation of slurry phase reactors.

In addition to improved product selectivity, slurry phase operation offers the advantage 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 slurry phase Fischer-Tropsch process has not yet been realized, and its further development is an important part in our country's program to establish viable technology for converting coal to hydrocarbon fuels.

Air Products, under contract to DOE, has undertaken a program in catalyst and reactor development for a slurry phase Fischer-Tropsch process, and this report describes the work accomplished during the eleventh quarter.

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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. This task was completed in the first quarter.

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 bench scale slurry phase Fischer-Tropsch reactor.

3.0   SUMMARY AND CONCLUSIONS

3.1   Task 2 - Slurry Catalyst Development

3.1.1 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.

3.1.2 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   Task 3 - Slurry Reactor Design Studies

Gas holdup experiments were conducted in the 12 inch Cold Flow Simulator (CFS) on water and isoparaffin slurries of both silica and iron oxide, over a range of particle sizes, with and without heat transfer internals. The results follow the same pattern as observed in the 5 inch column, with the iron oxide slurries giving higher gas holdups than silica. Overall, the results straddled the trends predicted by the Akita and Yoshida[1] and Pilhofer and Bach[2] correlations.

In general, gas holdup has been found to be lower in the 12 inch column than in the 5 inch. A test with isoparaffin in the 12 inch column, at 5 and 15 feet of bed height, showed no difference in average gas holdup. Bubble coalescence due to increasing column height is therefore, not a factor. Superficial gas velocity thus remains the major factor for determining gas holdup.

Solid concentration profiles were measured over several particle sizes for silica and iron oxide slurries, in both water and isoparaffin

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media, with and without heat transfer internals. The major determining factor was particle size with the smallest size ranges (0.5-5 µm) showing no concentration gradient and larger sizes (90-115 µm) displaying a considerable gradient.

Heat transfer coefficient measurements were taken for the two-phase isoparaffin/N_2 and for the 90-115 µm Fe_2O_3/ isoparaffin and the 0.5-5 µm SiO_2/isoparaffin systems. For the two-phase system, the results were approximately 64% of that predicted by Deckwer's correlation and for the three-phase iron oxide approximately 71%. The SiO_2 slurry gave an unexpected 30% of the value predicted by the Deckwer correlation; the reason for this result is being explored.

Bubble diameter measurements were successfully obtained using a double hot film probe, located 10 feet above the gas distributor. A radial bubble diameter size was found to be fairly narrow (0.28 to 0.53 cm), with most bubble sizes being at the lower end of the range. The uncalibrated bubble profiles showed larger bubbles at the edge of the column than at the center, contrary to the literature. Calibrated profiles are expected to show literature agreement.

Deckwer's gas holdup correlation is valid only for superficial gas velocities below 4 cm/sec. The Air Products cold flow correlation, while in agreement with Deckwer's in the quiescent regime, does extend into the churn turbulent regime. The Air Products gas holdup correlation was incorporated into Deckwer's model of the three phase bubble column. The simulation of a 1.5 x 8 m column under the Rheinpreussen conditions, i.e. the churn turbulent regime at 0.3 ft/sec, utilizing kinetic data from some of the Air Products diesel fuel selective catalysts, resulted in doubling the space time yield.

Previous computer simulations of the Rheinpreussen slurry reactor have indicated that mass transfer is not limiting. It is, therefore, logical to increase slurry catalyst loading to a practical, suspendable limit. Various weight loadings were simulated to determine which would

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give space time yields close to those achieved at Rheinpreussen. A 60 wt% (22 vol %) slurry of Air Products' catalyst B (with shift) is predicted to have the same space time yield as that achieved at Rheinpreussen. Thus, based on the assumption of no mass transfer limitation, the DOE objective of equalling Rheinpreussen space time yields can be achieved with our existing catalysts.

To try to account for the effect of viscosity in correlating the bubble column hydrodynamics, viscosity measurements were carried out on some representative slurries used in the cold flow modelling, i.e. 30 wt% slurries of 1-5 μm Fe_2O_3 and 90-115 μm SiO_2 in isoparaffin. Shear stress versus shear rate measurements were obtained. To apply this data, an estimate of the shear rate in a three phase bubble column was necessary. Using literature correlations of shear rate versus superficial gas velocity in a bubble column, shear rates of 173-762 sec^{-1} were predicted over the range of linear gas velocities used in the cold flow model columns. The slurry viscosities are estimated to vary by a factor of ~2 over the range of parameters studied in the cold flow modelling experiments. This approach will be used in attempting to correlate further the effect of slurry viscosity.

4.0   ACKNOWLEDGEMENTS

5.0   RESULTS AND DISCUSSION

5.1   Task 2 - Slurry Catalyst Development

5.1.1 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".

5.2   Task 3 - Slurry Reactor Design Studies

5.2.1 12" Cold Flow Simulator

    (i)   Gas Holdup

        Gas holdup measurements were conducted this quarter, to
determine the effects of solids, solid size in the presence and
absence of heat transfer internals and column height, in the 12
inch Cold Flow Simulator (CFS).

        The results of gas holdup measurements for the 0.5 - 5 μm
iron oxide/isoparaffin system with heat transfer internals, are
shown in Table 1 and illustrated in Figure 1. Run 82 is a
repeat of run 81, showing good reproducibility between runs for
all measurements. The addition of solids reduced the gas holdup
to between the Akita and Yoshida [1] and Pilhofer and Bach [2]
correlations.

        Gas holdup measurements were obtained on the 98 μm iron
oxide/isoparaffin, and 2.5 μm silicon oxide/isoparaffin systems
in the presence of heat transfer internals and for the 2.5 μm
silicon oxide/isoparaffin, and 45-53 μm silicon oxide/water
systems with no heat transfer internals. The results are listed
in Table 1 and are illustrated in Figure 2. On a relative
basis, the trends are similar to those obtained in the 5 inch

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CFS. The iron oxide runs gave higher gas holdups than the silicon oxide. However, in spite of the wide range of variables, the results did fall within a 20% band predicted by the Akita and Yoshida[1] and Pilhofer and Bach[2] correlations, Figure 2. These results agree with, or are just slightly lower than, the gas holdup results of the 5 inch CFS.

In the 12 inch CFS, gas holdup has been found, in general, to be lower than in the 5 inch CFS. While column diameter does not appear to affect gas holdup[1], there is some indication that bubble coalescence with increasing height may lower gas holdup in taller columns[3]. Lower gas holdup in the 12 inch column could also be due to the higher concentration of solids found at the lower section of this column. The presence of a greater concentration of solids at the distributor end could result in the formation of larger bubbles and thereby a reduction in gas holdup. To test this hypothesis, three two-phase runs were conducted. The results of these runs are listed in Table 2 and illustrated in Figure 3. A two phase system was chosen to eliminate the effect that a changing solids concentration profile with height would have on gas holdup. Run 78 and 80 have an expanded bed height of 15 feet. Run 79 has an expanded bed height of only 5 feet. There was no observable difference in the average gas holdup measured in these three runs. Thus, it appears that coalescence has no greater influence in a taller bubble column than in a shorter bubble column in the range of 5-15 feet.

The above confirms what has been implied by many empirical correlations that average gas holdup is independent, over a fairly wide range, of column height and diameter, and is mainly a function of superficial gas velocity.

(ii) Solid Concentration Profiles

Solid concentration profiles were measured for the
90-115 μm iron oxide/isoparaffin and 0.5-5 μm silicon oxide/
isoparaffin systems with heat transfer internals and the
0.5-5 μm iron oxide/isoparaffin, 0.5-5 μm silicon oxide/
isoparaffin, and 45-53 μm silicon oxide/water systems without
heat transfer internals and are listed in Table 1 and
illustrated in Figures 4-8. The profiles were similar to those
obtained in the 5 inch CFS, with the major determining factor
being particle size; the smallest particle size range showed no
concentration gradient, the larger size showed a considerable
gradient.

(iii) Heat Transfer Measurements

Heat transfer measurements were conducted for the two phase
isoparaffin/nitrogen system, and the three-phase 90-115 μm iron
oxide/isoparaffin, and the 0.5-5 μm silicon oxide/isoparaffin
systems and are listed in Table 3. Three heat transfer
coefficients are reported. Heater A was located inside the
center heat transfer internal about 10' above the distributor
plate, or about 2/3 of the distance between the distributor and
the top of the bubble column. Two temperatures were measured at
the heater midpoint, 150° circumferentially from each other,
and their number averaged. Heater B, 10' above the distributor,
was located on one of the six outer tubes, with the surface
thermocouple oriented toward the column center. Heater C, 5'
above the distributor, was located on another of the six outer
tubes, also with the surface thermocouple oriented toward the
center column.

For the two phase system, the results were much lower than
those predicted by the Deckwer correlation; about 64% of the
value predicted. The iron oxide gave heat transfer coefficients
approximately 71% of those predicted by the Deckwer correlation

and was in good agreement with the previous results obtained in this study. The 29.4 wt% 0.5-5 μm silicon oxide/isoparaffin system gave an unexpected 30% of the value predicted by the Deckwer correlation. The reason for this unexpected result is being explored.

(iv)   Bubble Diameter

A summary of the results of bubble diameter measurements using a double hot film probe, along with the operating conditions for each system tested, are listed in Table 4. Measurements were taken 10 feet above the gas distributor. The bubble probe was typically located 2 inches from the column center. For runs 86 and 87, a radial bubble diameter profile was also obtained.

The range of operating conditions covered in Table 4 are the possible extremes of bubble column operation in this study. In spite of this wide range of operating conditions, the average uncalibrated bubble diameter size range was fairly narrow, from 0.28 to 0.53 cm, with most of the bubble sizes being at the lower end of the range. The calibrated bubble sizes will be approximately 10-25% smaller, since bubbles tend to be slowed down once they strike the hot film probe.

Run 87 gave unexpectedly large average bubble diameters. In comparison to run 85, it appears that the slightly lower gas velocity may have made a large difference.

The two radial bubble profiles, runs 86 and 87, show that bubble size decreases radially from the center of the column. This profile was steeper for the higher gas velocity case of 0.2 ft/sec. This is expected, since in the bubbly flow regime, at a gas velocity of 0.12 ft/sec, bubbles do not interact, yielding a more uniform radial profile.

(v)   Engineering Evaluation

The cold flow model's gas holdup correlation:

$$\alpha / (1-\alpha)^4 = 0.054 \ V_G^{0.972} / W^{0.035} \qquad (1)$$

was substituted for Deckwer's[4] empirical correlation:

$$\alpha = 0.053 \ V_G^{1.1} \qquad (2)$$

where

α = gas holdup

V_G = gas velocity, cm/sec

W = solid weight fraction

While the effect at low gas velocities was negligible, at 9 cm/sec, the space time yield for an Air Products promising catalyst A doubled (see Table 5 vs. Table 6). The Rheinpreussen base case was not simulated with the new gas holdup correlation because it's conversion and space time yield were measured quantities, and the reaction kinetics were calculated, assuming the Deckwer gas holdup correlation. Thus, any change to the gas holdup correlation would necessitate a change of the reaction kinetics in order to yield the same hydrogen conversion and space time yield.

There are several reasons for considering the cold flow model correlation over the Deckwer one, although the only true test will be that using the actual Fischer-Tropsch catalyst, wax product and correct distributor. Deckwer's empirical gas holdup correlation was obtained in 4.1 cm and 10 cm diameter bubble columns using a porous sintered plate, having a mean pore diameter of 75 μm. While Deckwer used a molten wax, the column

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was only operated at low gas velocities, 0.75 to 4 cm/sec, where there is good agreement between equations (1) and (2). The form of the Deckwer correlation clearly cannot be applied above 14.5 cm, since the gas holdup exceeds unity at that point, a physical impossibility. However, it appears that gas velocities in this higher range would be more economical since the same space time yield would be provided in taller, fewer, vessels. While Farley and Ray[5] did measure a gas holdup of 44% at 6.8 cm/sec in a commercial 24.4 cm column, in agreement with Deckwer, this gas holdup value steadily decreased to as low as 11%, apparently due to free carbon buildup in the slurry. Thus, over the length of the commercial Fischer-Tropsch slurry reactor operation, much lower gas holdup values may be obtained than predicted by the Deckwer correlation.

The lower gas holdup predictions had a desirable effect on reactor space time yield. This is 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. If mass transfer is _not_ limiting, it is logical to increase solid loading up to a practical, suspendable limit. Various weight loadings were simulated to see which would give space time yields close to those achieved at Rheinpreussen. As shown in Table 7 and illustrated in Figure 9, a 60 wt% (22 vol%) slurry was predicted to have the same space time yield as that achieved at Rheinpreussen. Thus, if a 22 vol% iron oxide loading is suspendable, then the objective of equalling the Rheinpreussen space time yield results has been met. Coupled with the diesel fuel selectivity, it appears that the past stated DOE objective of meeting the Rheinpreussen results has been achieved and exceeded.

The fourth entry in Table 6 shows the resulting space time yield that would be expected from adding shift activity to a

catalyst that presently has good diesel fuel selectivity but low shift activity.

6.0 EXPERIMENTAL

6.1 Task 2 - Slurry Catalyst Development

6.1.1 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".

6.2 Task 3 - Slurry Reactor Design Studies

(i) Bubble Diameter Measurements

The following is a description of the bubble diameter data acquisition system now in operation. From the double conical probe (see Figure 10) inserted into the bubble column, voltage versus time curves were obtained (e.g. top curve - Figure 11). The probes detect the different thermal conductivities between the liquid and gas phase. The bubble chord length and velocities are determined. The derivative is taken of the voltage time curve, shown in the bottom half of Figure 11. Locating the maximum point on the derivative curve, point A for the lower probe, single time increments are stepped off until the derivative curve passes through zero. This determines the end of the bubble, T3. In a similar fashion, after finding the minimum of the curve, point B, the program then steps backwards in time until the derivative curve passes through zero again. This establishes the beginning of the bubble, T1. Once the beginning, T2, and end, T4, for the second channel has been determined, four values are calculated, two dwell times, DT, and two lag times, LT.

$$DT1 = (T3-T1)/F \qquad (3)$$

$$DT2 = (T4-T2)/F \qquad (4)$$

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$$LT1 = (T2-T1)/F \qquad (5)$$

$$LT2 = (T4-T3)/F \qquad (6)$$

where

F = digitizing rate, 1/sec

The dwell time is the time that a probe sees a given bubble. The lag time is the time difference of the different probes. From the dwell and lag times, bubble velocities and chord lengths are calculated as follows:

$$V_B = S(LT1) \qquad (7)$$

$$C_B = V_B (DT1) = S(DT1)/(LT1) \qquad (8)$$

where

V_B = bubble velocity, cm/sec

C_B = chord length, cm

S = distance between probes, cm

An arbitrary acceptance tolerance of 50% between dwell times was used. This large tolerance is necessary because 1) bubbles do not necessarily rise vertically; different chord lengths are typically transversed by the two probes, 2) bubbles are not rigid spheres, but pulsate; pulsations give different chord lengths, and 3) bubbles, particularly small ones, are slowed down by the probe. Thus, for small bubbles, LT2 is often greater than LT1. For this reason, LT1 and DT1 are chosen as being more representative for calculating bubble velocity and chord length

than are LT2 and DT2. Using the above 50% criteria, the acquisition system accepted about one out of nine bubble traces analyzed. The system analyzes about one bubble trace/second. Bowen and Davies[6] have estimated that 1400 chord length samples are required to obtain a 10% accuracy of the Sauter mean diameter within a 95% confidence limit, which typically takes about 4 hours.

For run 81, for example, the chord length sizes ranged from 0.02 to 2.3 cm using DT1 and LT1. If average DT and LT's were used instead, the upper range would have been 8 cm. This affect on mean bubble size is very small as only 20 of the 1400 sampled bubbles were above 1 cm in chord length. Fitting the first set of 1400 bubbles to a gamma function gave $\alpha = -13.741$ and $\beta = 3.115$. This corresponds to a mean bubble chord length, CL, of 0.252 cm and a mean bubble diameter, d_B, of 1.57. A comparison between the actual bubble chord lengths and that estimated by the gamma function is shown in Figure 12. Additional work on the gamma distribution function should yield better agreement between observed and calculated distributions.

The calibration procedure between photographic and hot film anemometer techniques is still being finalized. Because, in particular, the smaller bubbles are slowed down when they impinge upon the anemometer, it is expected that the bubble chord lengths will be reduced by as much as 25% for the smaller bubbles, and that no correction will be necessary for the largest bubbles, in order to bring the anemometer readings in line with what is photographically observed.

(ii) Slurry Viscosity

Slurry viscosity affects gas holdup, bubble diameter, and to a lesser extent, heat transfer. As solid loading is increased, viscosity effects can be quite noticeable. For example, at 20 vol%, a 1-5 μm iron oxide slurry has a very high (almost

infinite) viscosity. Several literature correlations [1,2,7] relate viscosity to gas holdup, α :

$$\alpha = k \, \mu_{SL}^{-0.05} \tag{9}$$

Since viscosity can change dramatically, the effect on α can be as much as 30%. From the rheograms of shear stress versus shear rate curves, generated for three cold flow slurry samples and from the literature, the following procedure has been developed for estimating slurry viscosity in the cold flow simulator. This procedure will be extended to a Fischer-Tropsch system at any desired temperature, once rheograms have been received of the actual wax product of the diesel selective catalyst, taken over a range of temperatures.

The data from Tekmar, (Table 8), can be correlated using the Ostwald-de Waele model to yield the following correlations for the 30 wt% 1-5 μm Fe_2O_3, and 98-106 μm Fe_3O_4 systems:

$$\mu_{SL03} = 0.250\gamma^{0.582} \qquad R^2 = 0.987 \tag{10}$$

$$\mu_{SL98} = 0.142\gamma^{0.533} \qquad R^2 = 0.996 \tag{11}$$

where

$$\mu_{SL03}, \mu_{SL98} = \text{slurry viscosity, 1-5 } \mu\text{m } Fe_2O_3 \text{ or}$$
$$90\text{-}106 \ \mu\text{m} Fe_3O_4, \text{ cP}$$
$$\gamma = \text{shear rate, s}^{-1}$$

It is seen from Table 8 that the 90-115 μm SiO_2 measurements yielded identical values to the large size iron oxide. This was quite unexpected, as the SiO_2 density is one half that of Fe_3O_4. These results will be retested. However, for making initial estimates, it will be assumed that the data is correct. Specifically, it was assumed that equations 10 and 11 are also applicable to the 30 wt% silicon oxide systems.

To apply equations 10 and 11 to a bubble column, an estimate of the shear rate in a bubble column is necessary. From the work of Nishikawa, Kato, and Bashimoto[8], who determined bubble column shear rates from deviations from theoretical heat transfer coefficients in two phase Newtonian and Non-Newtonian systems, the following two equations were assumed to apply in the cold flow simulators:

$$\gamma = 100\sqrt{V_G} \qquad V_G < 4 \; cm/sec \qquad (12)$$

$$\gamma = 50\sqrt{V_G} \qquad V_G > 4 \; cm/sec \qquad (13)$$

where

V_G = gas superficial velocity, cm/sec

These equations estimate the range of shear rates from 173 to 762 s^{-1} for gas velocities of 3 to 15.24 cm/sec used in Task 3. This is within the range of shear rates measured by Nishikawa and coworkers[8].

To interpolate to other particle sizes, linear interpolation will be used until other information is obtained. To estimate slurry viscosities at other solid loadings, the work of Sikdar and Ore[8] will be used:

$$\mu_{SL} = \mu_L V_{s\,\infty}/(V_{s\,\infty} - V_s) \qquad (14)$$

where

V_s = solid volume fraction
$V_{s\,\infty}$ = solid volume fraction at infinite viscosity
μ_L = liquid viscosity, cP
μ_{SL} = slurry viscosity, cP

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The value of V_{S_α} is obtained by solving equation (14) for V_{S_α} and inserting the interpolated slurry viscosity value into it:

$$V_{S_\infty} = V_S \mu_{SL}/(\mu_{SL} - \mu_L) \qquad (15)$$

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Table 1

GAS HOLDUP AND SOLID FRACTION: 12" COLD FLOW SIMULATOR

Run No.	Gas	Liq	Solid	Solid Size µM	Solid Avg Wt%	Dist Hole In.	Heat Transfer Internals	Velocity Slurry Ft/Sec	Velocity Gas Cm/Sec	Gas Holdup 1-2	Gas Holdup 2-3 (Vol.%)	Gas Holdup 3-4	Gas Holdup Avg.	Solid Fraction 1	Solid Fraction 2 (Wt%)	Solid Fraction 3	Solid Fraction 4
81	N_2	Isoparaffin	Fe_3O_4	2.5	6.8	0.125	Yes	0.015	0.14	9.9	10.1	10.9	11.4	6.9	6.9	6.9	6.7
82	N_2	Isoparaffin	Fe_3O_4	2.5	6.8	0.125	Yes	0.015	0.14	9.4	10.6	10.6	11.3	6.9	6.9	6.7	6.7
83	N_2	Isoparaffin	Fe_3O_4	2.5	6.7	0.035	Yes	0.0	0.26	13.1	18.0	17.7	18.6	6.8	6.8	6.8	6.4
84	N_2	Isoparaffin	Fe_3O_4	98.0	11.3	0.125	Yes	0.0	0.43	14.2	21.4	23.4	24.0	28.7	8.0	5.4	3.1
85	N_2	Isoparaffin	SiO_2	2.5	29.4	0.125	Yes	0.008	0.16	4.1	6.3	6.3	6.5	29.7	29.5	29.2	29.4
86	N_2	Isoparaffin	--	0.0	0.1	0.500	No	0.008	0.20	11.2	17.8	16.4	16.9	--	--	--	--
87	N_2	Isoparaffin	SiO_2	2.5	24.8	0.035	No	0.008	0.12	5.4	6.5	5.9	6.4	24.8	24.7	24.9	24.7
88	Air	Water	SiO_2	49.0	18.9	0.035	No	0.008	0.40	11.2	15.4	14.8	14.7	22.4	20.8	17.8	14.7
89	Air	Water	SiO_2	49.0	18.4	0.035	No	0.008	0.15	7.9	6.2	7.5	8.1	21.7	19.9	17.6	14.6

TABLE 2

GAS HOLDUP: 12" COLD FLOW SIMULATOR

PLAIN HEAT TRANSFER INTERNALS

SYSTEM: TWO PHASE

GAS- NITROGEN

LIQUID- ISOPARAFFIN

RUN NO.	DIST HOLE IN	VELOCITY SLURRY FT/SEC	VELOCITY GAS FT/SEC	GAS HOLDUP 1-2 VOL %	GAS HOLDUP 2-3 VOL %	GAS HOLDUP 3-4 VOL %	GAS HOLDUP AVG	EXPANDED BED HEIGHT FT
78	0.125	0.0	0.25	15.5	19.4	19.7	20.3	15.63
79	0.125	0.0	0.25	20.2	.	.	20.1	5.13
80	0.125	0.0	0.25	14.8	20.0	19.6	20.2	15.75

Table 3

SHELL-SIDE HEAT TRANSFER COEFFICIENTS: 12" COLD FLOW SIMULATOR

PLAIN HEAT TRANSFER INTERNALS

Run No.	Gas	Liquid	Solid	Size μM	Avg Wt%	Dist Hole In	Velocity Slurry Ft/Sec	Gas Cm/Sec	Heat Transfer Coefficient A	B Btu/Hr/Ft²/F	C	Deckwer
78	N_2	Isoparaffin	-	-	-	0.125	0.0	0.25	137.1	105.7	166.5	211.6
79*	N_2	Isoparaffin	-	-	-	0.125	0.0	0.25	-	-	-	-
80	N_2	Isoparaffin	-	-	-	0.125	0.0	0.25	158.9	121.8	170.9	211.6
81	N_2	Isoparaffin	Fe_3O_4	2.5	6.8	0.125	0.015	0.14	137.4	96.2	136.1	193.5
82	N_2	Isoparaffin	Fe_3O_4	2.5	6.8	0.125	0.015	0.14	134.4	96.9	137.9	195.2
83	N_2	Isoparaffin	Fe_3O_4	2.5	6.7	0.125	0.0	0.26	152.7	110.9	150.1	225.5
84	N_2	Isoparaffin	Fe_3O_4	98.0	11.3	0.125	0.0	0.43	186.4	145.9	192.6	245.7
85	N_2	Isoparaffin	SiO_2	2.5	29.4	0.125	0.008	0.16	99.7	71.7	71.8	270.6

*Heater not submerged for this run.

Table 4

BUBBLE DIAMETER - 12" COLD FLOW SIMULATOR

Run No	Dist Hole in	Internals	Solid Oxide	Solid Size μm	Solid Avg wt%	Liq. Type	Velocity Slurry ft/sec	Velocity Gas ft/sec	Probe Loc.* in	uncorrected** Bubble Diameter Average cm	uncorrected** Bubble Diameter Sauter cm
83	0.035	Y	Fe	2.5	6.7	Iso	0.000	0.26	2	0.320	1.050
84	0.125	Y	Fe	98	11.3	Iso	0.000	0.43	2	0.280	0.941
85	0.125	Y	Si	2.5	29.4	Iso	0.008	0.16	2	0.364	1.09
86	0.500	N	-	-	-	Iso	0.008	0.20	5	0.292	0.765
									3	0.335	0.729
									0	0.374	1.040
87	0.035	N	Si	2.5	24.8	Iso	0.008	0.12	5	0.497	1.261
									3	0.529	1.162
									0	0.530	1.419
88	0.035	N	Si	49	18.9	WA	0.008	0.50	2	0.353	0.888

* Distance from column center

** Diameters not corrected for probe interference. Relative order will be the same. Absolute values will be smaller.

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TABLE 5

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
Usage 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, um	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 6

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	9.03×10^5	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, um	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

Table 7

RHEINPREUSSEN SIMULATION

Regime	Churn Turbulent	
Catalyst	Base*	Catalyst B† with shift
Inlet gas velocity, cm/sec	9.0	9.0
Gas holdup	0.385	0.123
Interfacial area, cm^2/cm^3	32.66	29.89
Temperature, °C	260.2	257.7
Rate Constants:		
Pre-exponential factor (sec wt% in slurry)	1.12×10^5	1.15×10^7
Activation energy, kJ/mol	70	94.7
Inlet ratio, mol CO/mol H_2	1.5	1.98
Usage ratio, mol CO/mol H_2	1.5	1.98
Hydrogen conversion, %	80.4	79.8
Rel. mass transfer resistance	0.106	0.141
Space time yield, mol CH_2/hm^3	2937	2915
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	0.6
Specific heat transfer area, cm^2/cm^3	0.10	→

TABLE 8

SLURRY VISCOSITY MEASUREMENTS

30 Wt% Slurries in Isoparaffin

Shear rate γ s^{-1}	1-5 µm Fe_2O_3		90-106 µm Fe_3O_4		90-115 µm SiO_2	
	Shear stress τ dynes/cm^2	Viscosity μ cP	Shear stress τ dynes/cm^2	Viscosity μ cP	Shear stress τ dynes/cm^2	Viscosity μ cP
167	8797	5.25	3714	2.22	3714	2.22
240	13685	5.71	6256	2.61	6256	2.61
343	25024	7.30	10752	3.14	10752	3.14
492	44574	9.05	18572	3.77	18572	3.77
704	82110	11.68	32257	4.59	32257	4.59
1007	142715	14.16	58650	5.82	58650	5.82

FIGURE 1

12 INCH COLD FLOW SIMULATOR
PLAIN HEAT TRANSFER INTERNALS
ISOPARAFFIN, IRON OXIDE, NITROGEN

Graph with Y-axis labeled "GAS HOLDUP" ranging from 0.00 to 0.30, and X-axis labeled "Vg, ft/sec" ranging from 0.0 to 0.5. Curves labeled Pilhofer & Bach[2], Hikita & Kikukawa[1], and Akita & Yoshida[3].
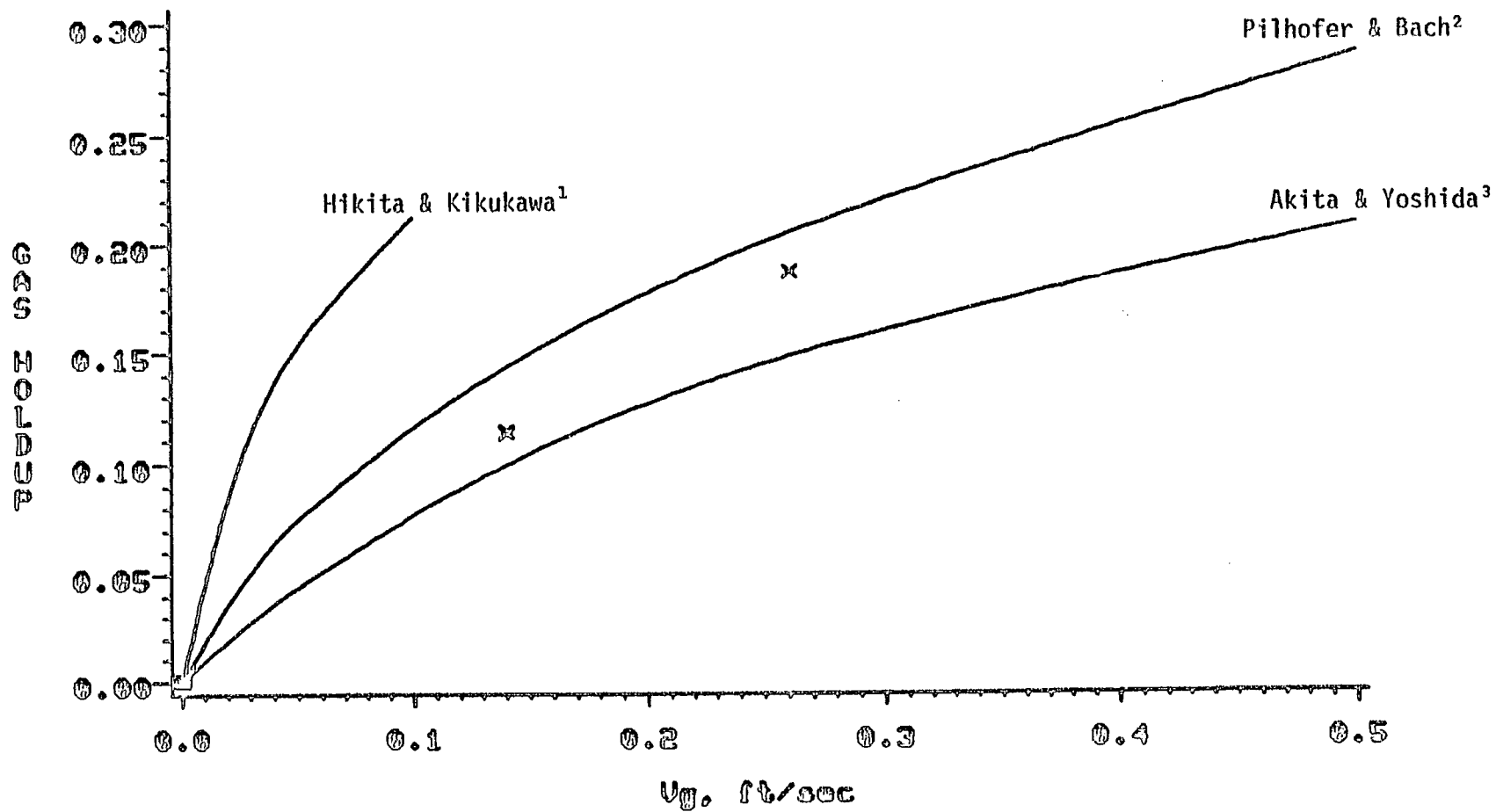
FIGURE 3

12 INCH COLD FLOW SIMULATOR
PLAIN HEAT TRANSFER INTERNALS
ISOPARAFFIN, N2
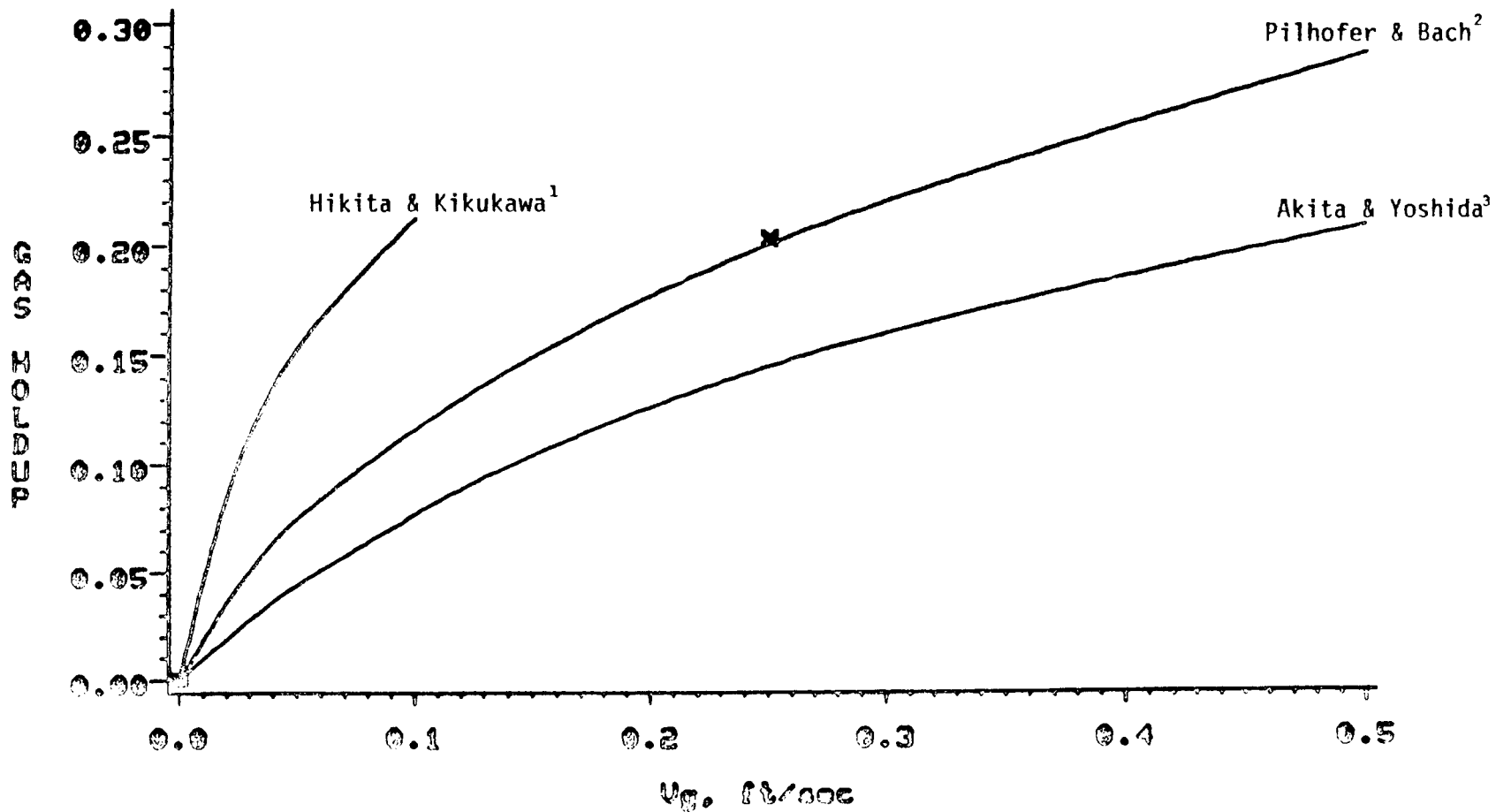
Figure 2

12 INCH COLD FLOW SIMULATOR

GAS HOLDUP MEASUREMENTS

Pilhofer & Bach[2]

Akita & Yoshida[3]

Hikita & Kikukawa[1]

GAS HOLDUP

0.30
0.25
0.20
0.15
0.10
0.05
0.00

Symbol	Solid			Liquid	Internals
	Oxide	Size μm	Avg wt%		
O	-	-	-	ISO	No
*	Si	2.5	29.4	ISO	Yes
+	Si	2.5	24.8	ISO	No
x	Si	49	18.6	WA	No
□	Fe	98	11.3	ISO	Yes

0.0   0.1   0.2   0.3   0.4   0.5

Ug, ft/sec

37
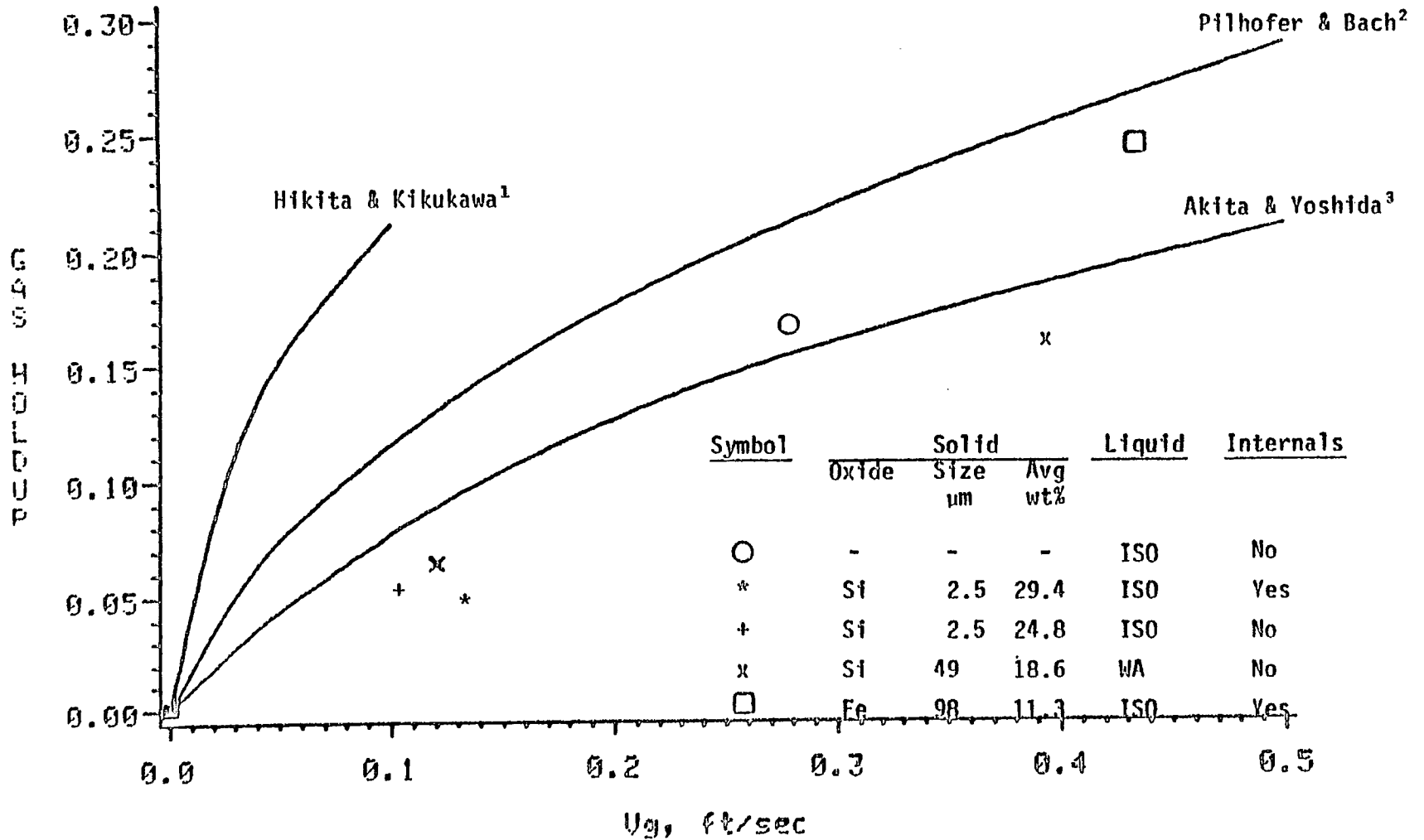
FIGURE 4

12 INCH COLD FLOW SIMULATOR
SOLID CONCENTRATION PROFILES
ISOPARAFFIN, 0.5-5 µM IRON OXIDE, N2
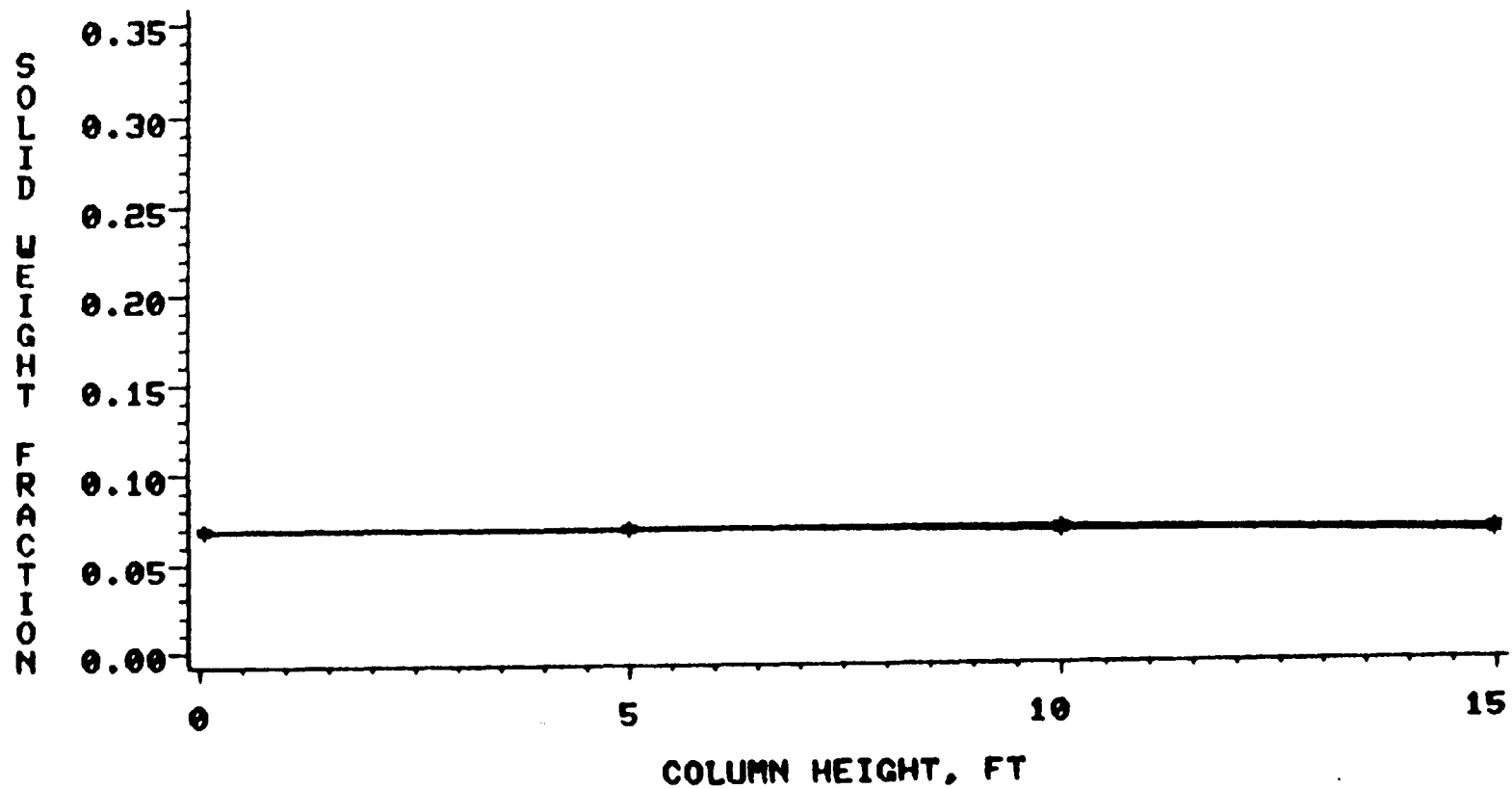
Figure 5

12 INCH COLD FLOW SIMULATOR

PLAIN HEAT TRANSFER INTERNALS
SOLID CONCENTRATION PROFILES
ISOPARAFFIN, 90-115 μM IRON OXIDE, N2
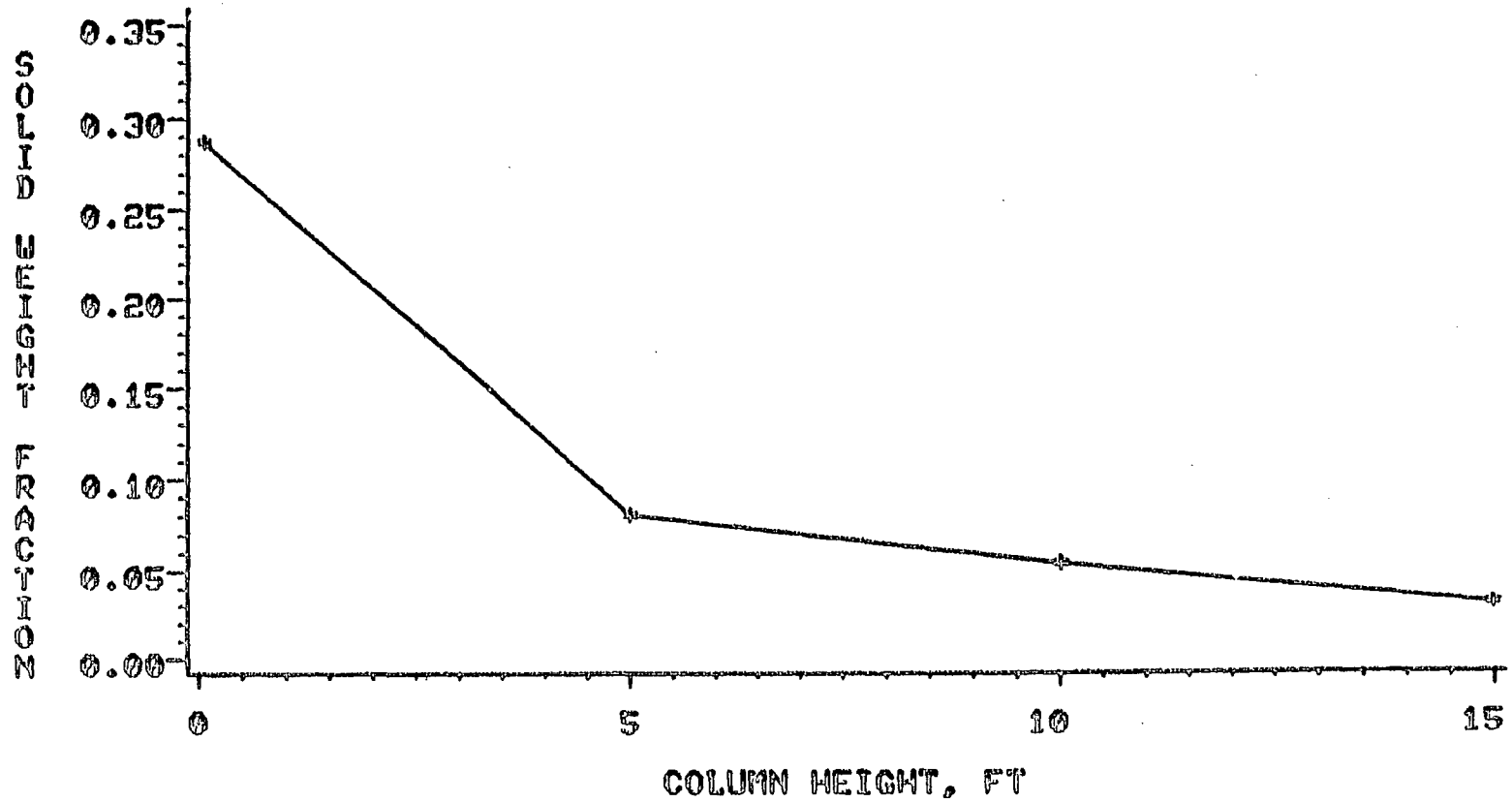
Figure 6

12 INCH COLD FLOW SIMULATOR

SOLID CONCENTRATION PROFILES

ISOPARAFFIN, 0.5–5 uM SILICON OXIDE, N2

PLAIN HEAT TRANSFER INTERNALS
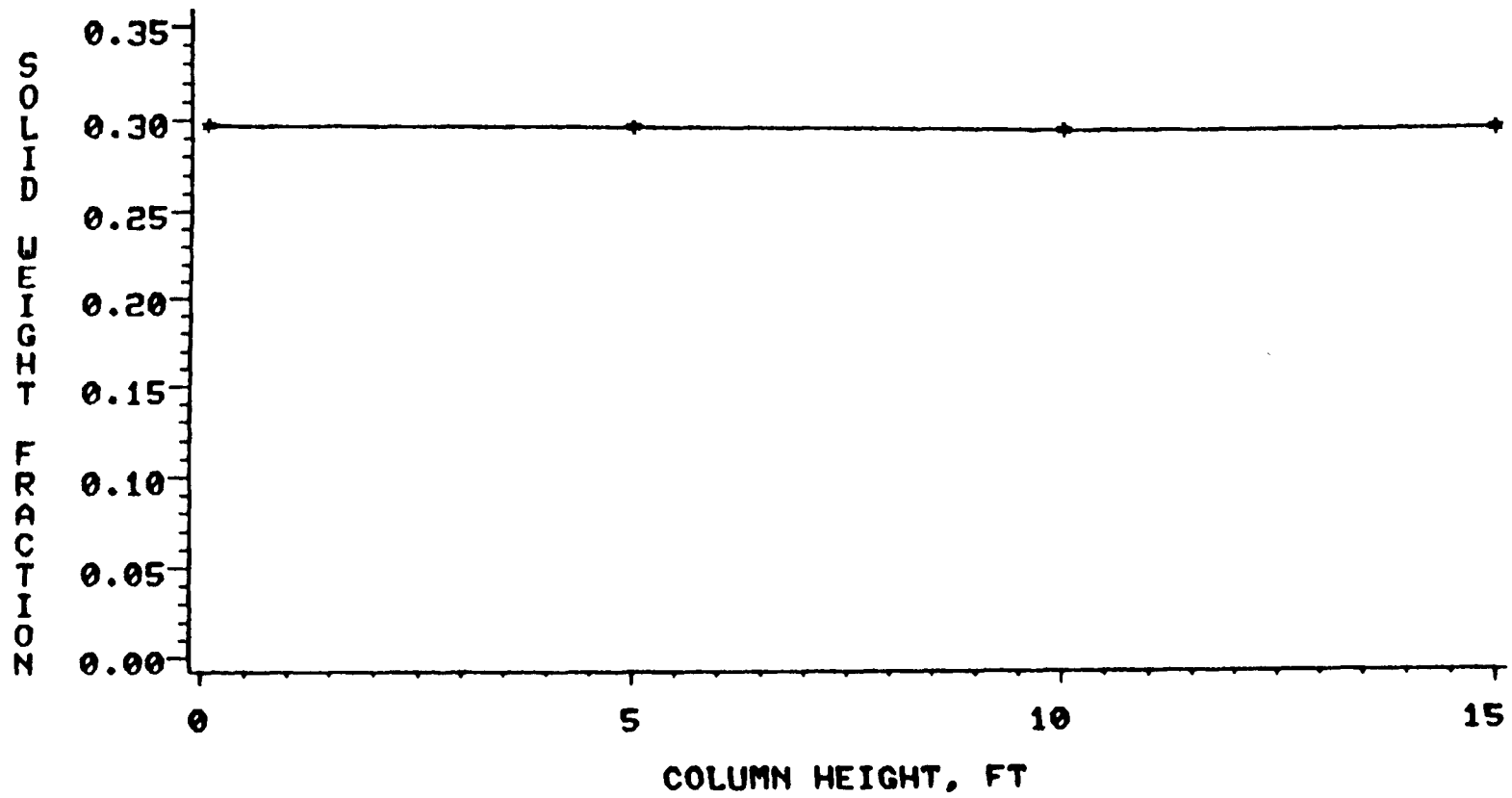
Figure 7

12 INCH COLD FLOW SIMULATOR
NO HEAT TRANSFER INTERNALS
SOLID CONCENTRATION PROFILES
ISOPARAFFIN, 0.5–5 µM SILICON OXIDE, N2
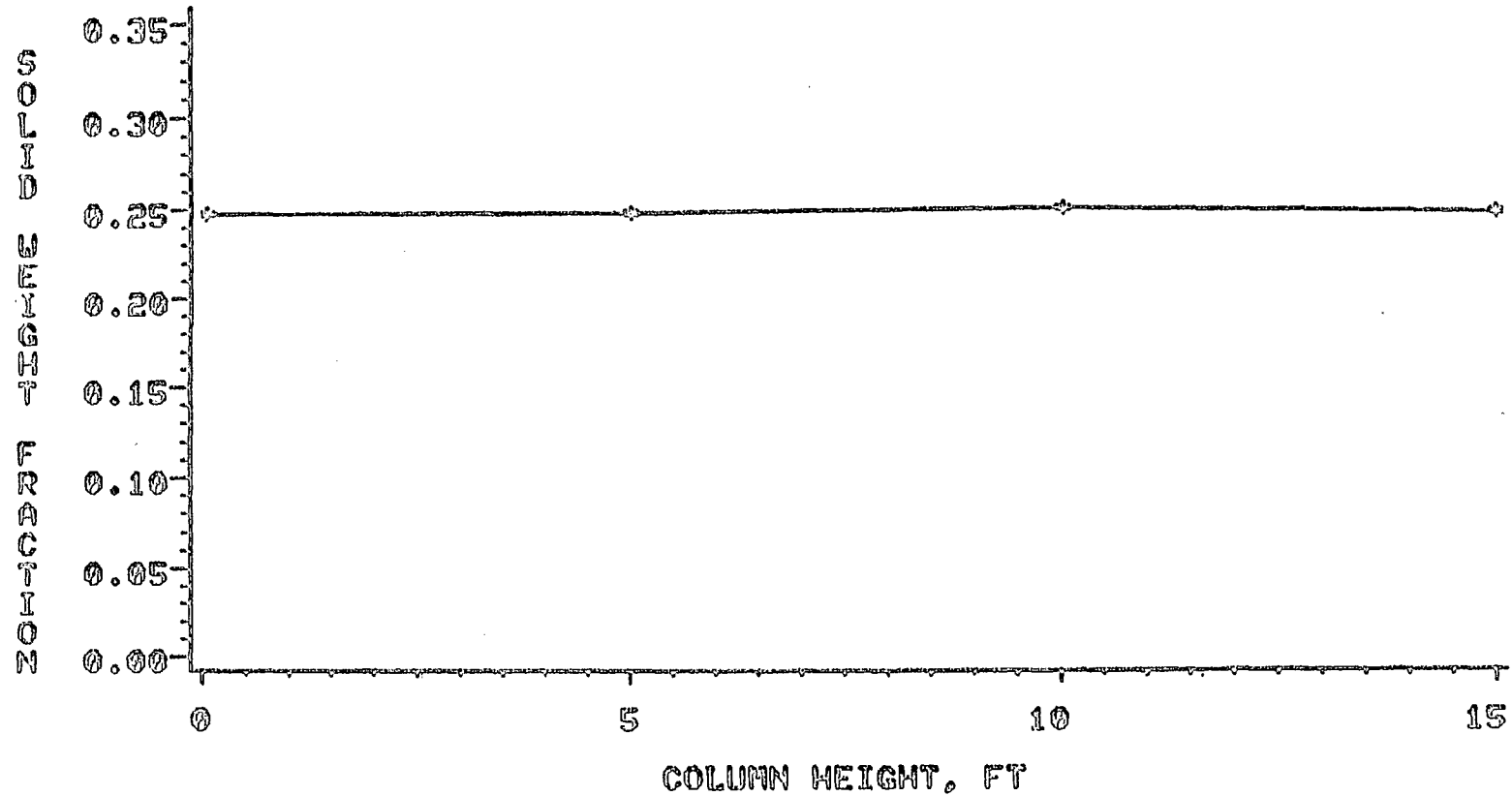
Figure 8

12 INCH COLD FLOW SIMULATOR
NO HEAT TRANSFER INTERNALS
SOLID CONCENTRATION PROFILES
WATER, 45-53 µM SILICON OXIDE, AIR

Figure 9

SPACE-TIME YIELD
AT RHEINPREUSSEN CONDITIONS
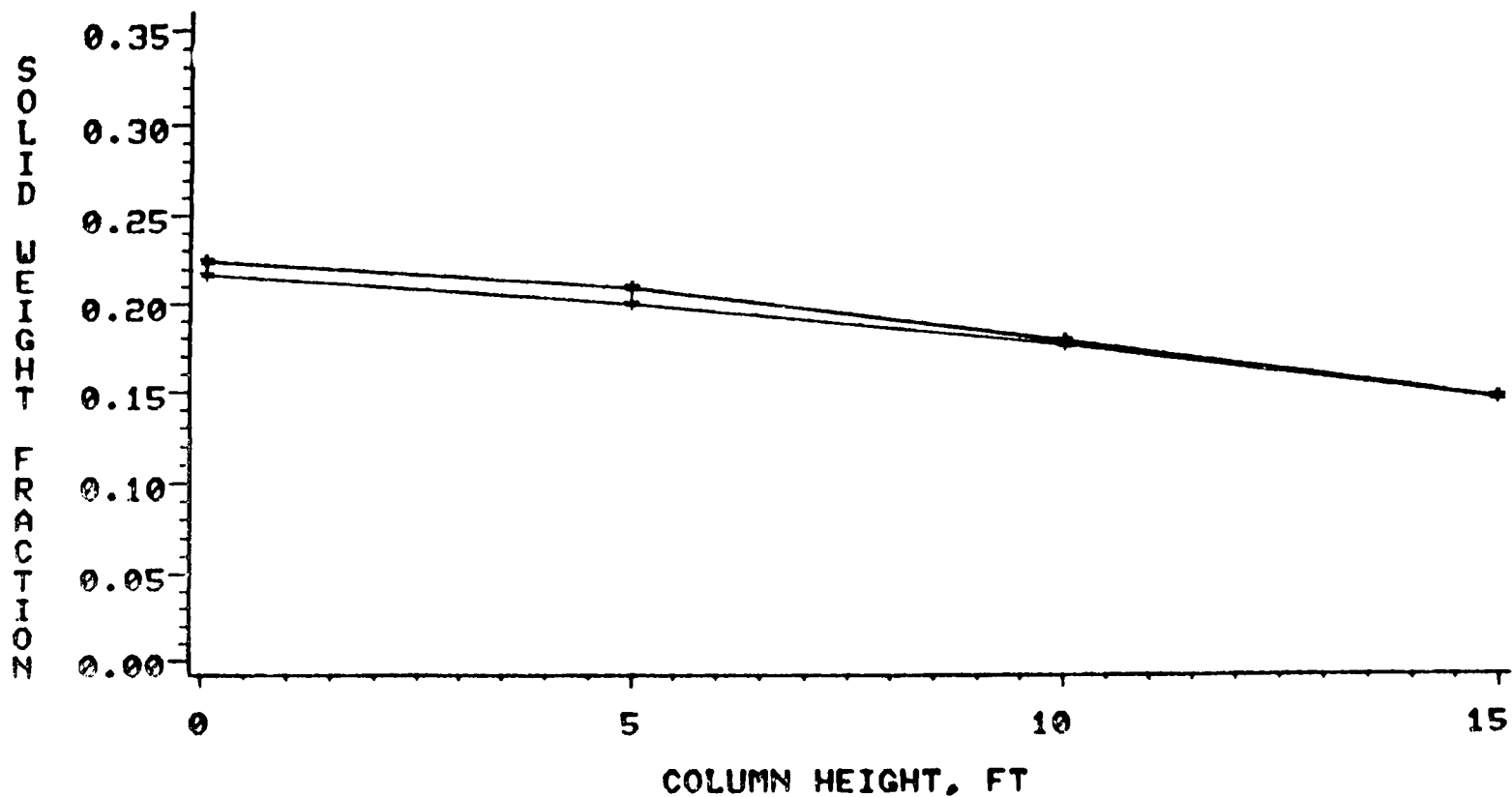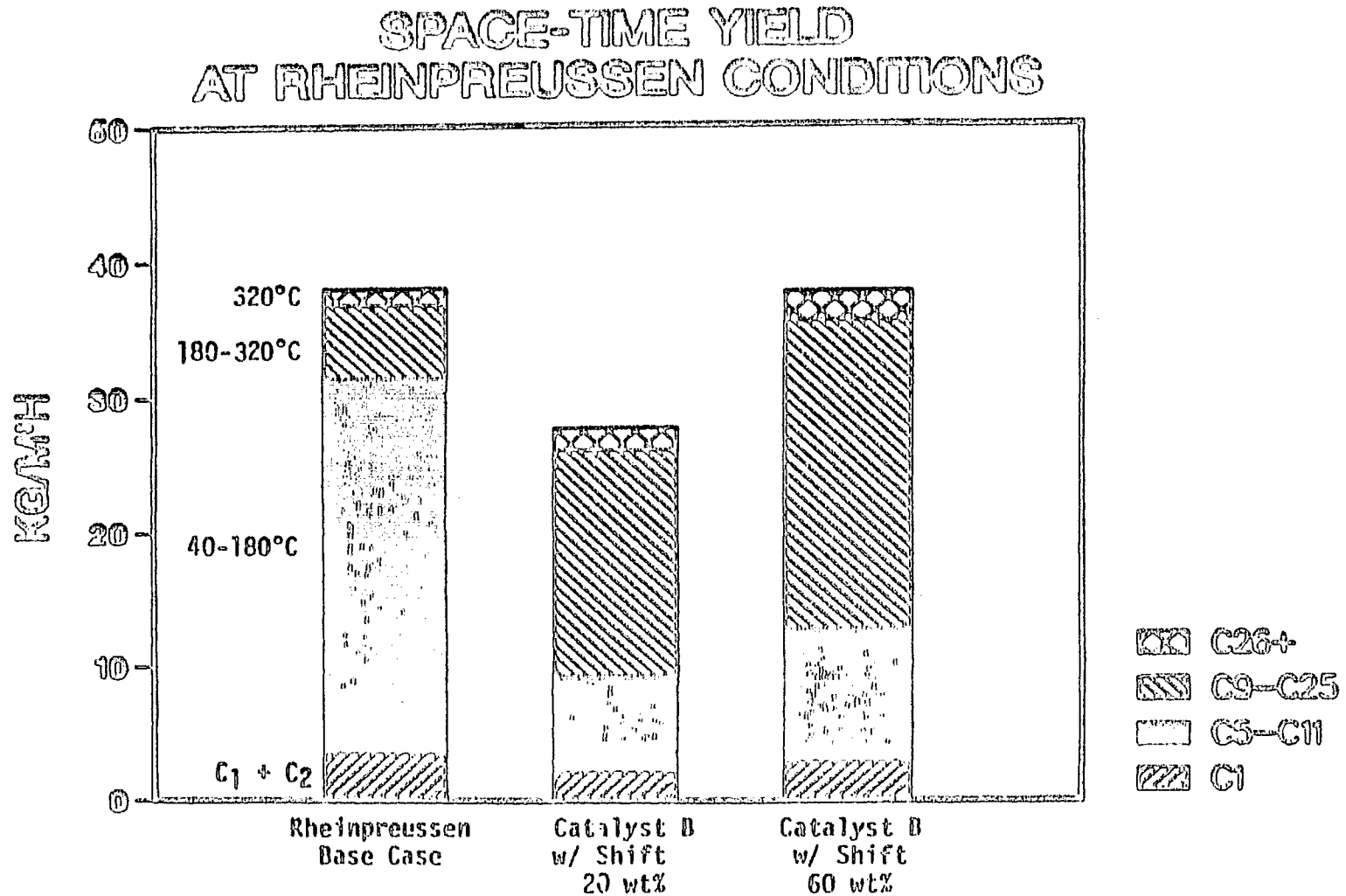
FIGURE 10

BUBBLE DIAMETER
DOUBLE CONE PROBE

Probe 2   Probe 1

→ Gravity
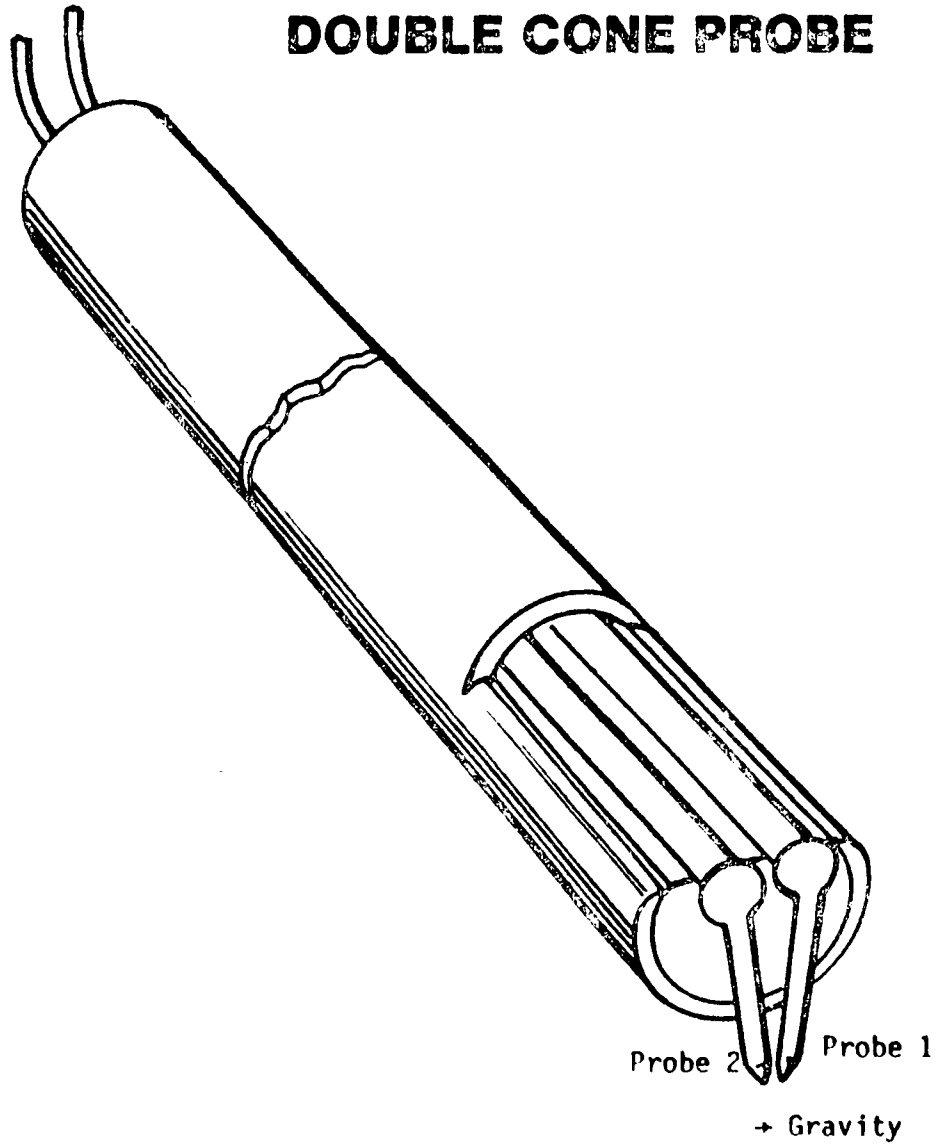
FIGURE 11

BUBBLE TRACE FROM DOUBLE CONE PROBE

39
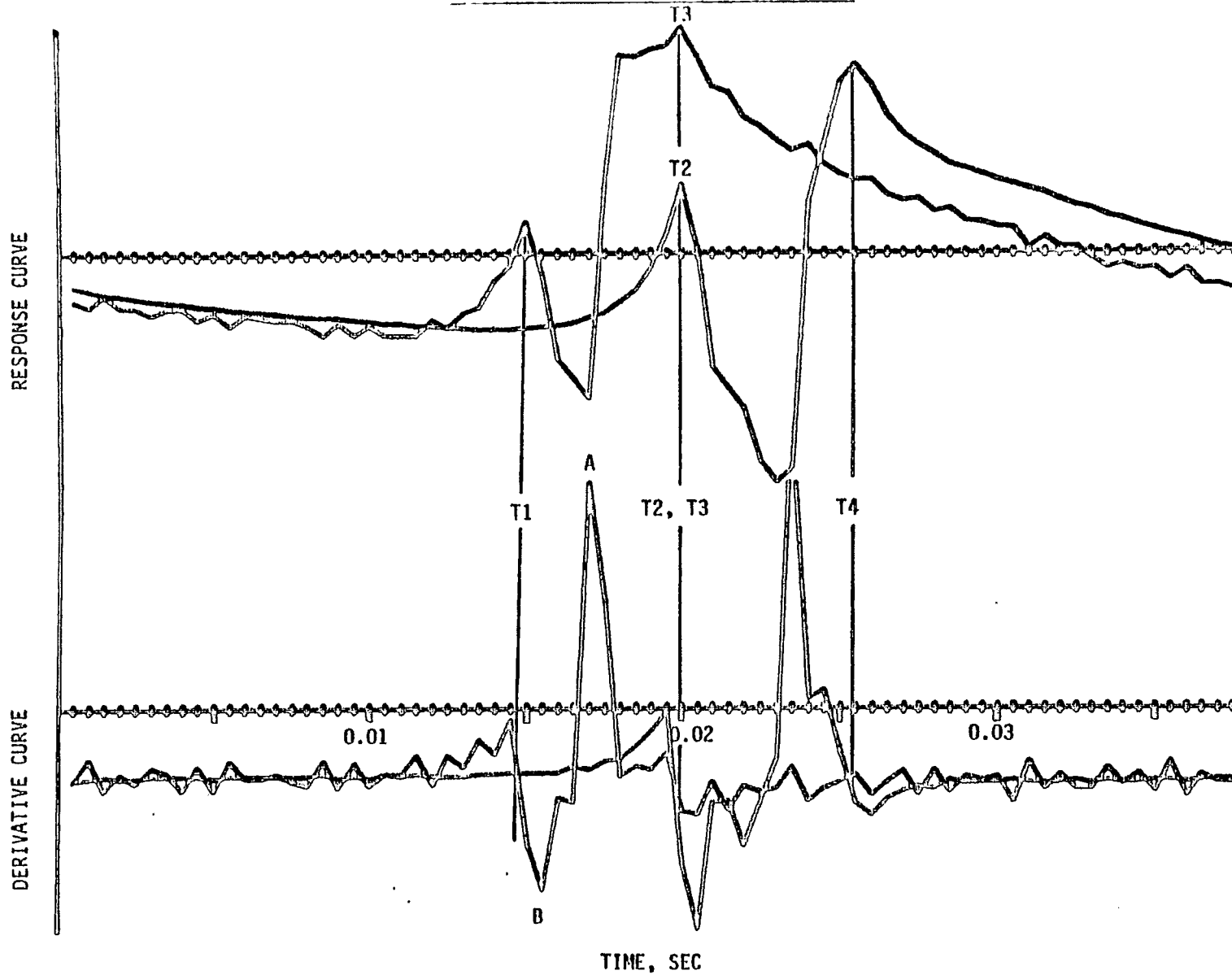
FIGURE 12

12 INCH COLD FLOW SIMULATOR

BUBBLE DIAMTER DISTRIBUTION
ALPHA= -13.741   BETA= 3.115
ISOPARAFFIN, N2
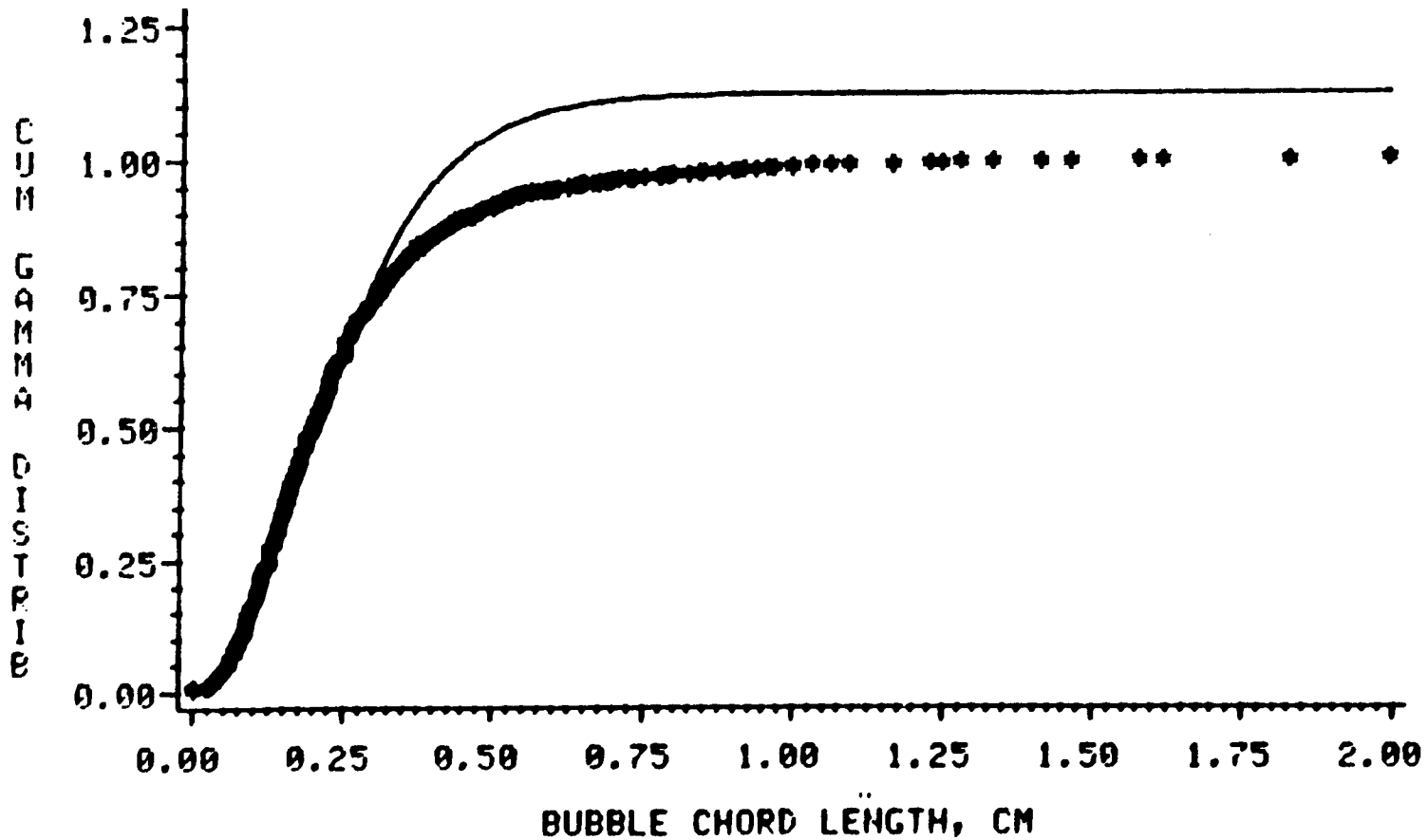
BUBBLE CHORD LENGTH, CM

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