"FISCHER-TROPSCH BUBBLE-COLUMN HYDRODYNAMICS"

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Abstract

In an effort to better understand the hydrodynamics in Fischer-Tropsch (F-T) bubble-column reactors, limited experiments were carried out to measure the average gas holdup in two short hot-flow columns (3.2 and 5.3 cm ID x 215 cm L). In addition, gas holdup and catalyst concentration profiles were measured in a tall bubble-column reactor (5.2 cm ID x 762 cm L). Preliminary results show that the type of liquid, gas distributor design, static liquid height and gas superficial velocity have major effects on gas holdup. For instance, F-T waxes have significantly higher gas holdups than hexadecane although they have similar viscosity and surface tension. Sintered plate gas distributors produce markedly higher gas holdups than single-orifice distributors; also, significant foaming is observed with sintered plates, while little or no foaming is present with single orifices. Decreasing static liquid height and/or increasing gas superficial velocity result in increased gas holdup. In the reactor, gas holdup profiles were shown to follow a three-zone pattern; this pattern was observed before only in cold flow experiments. Lastly, gas holdups were shown to be stable and at acceptable levels during an 86 day synthesis run.

To further study these hydrodynamic phenomena, experiments are planned in two tall hot-flow columns (5.1 and 10.2 cm ID x 915 cm L) currently under construction, and in the bubble-column reactor.

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I. INTRODUCTION

The title of the presentation is "Fischer-Tropsch Bubble-Column Hydrodynamics". The work described here was partly performed under the previous contract which ended on April 30, 1983, and partly under the current contract, "Two-Stage Process For Converting Synthesis Gas to High Quality Transportation Fuels", which began on June 8, 1983, and will end on March 7, 1985. The overall objective is to obtain Fischer-Tropsch Bubble-Column Hydrodynamic data for improved pilot plant operation, and eventually for reactor scale-up (Slide #1). To achieve this objective, limited hydrodynamic studies were initiated to measure the gas holdup in existing short hot flow models and in the bubble-column reactor of the two-stage BSU. In addition, bubble flow patterns were visually observed in the hot flow models. Specifically, we wish to quantify the dependence of the gas holdup and bubble size on the type of liquid medium, gas distributor design, static liquid height, column diameter and operating conditions.

II. EQUIPMENT AND EXPERIMENTAL CONDITIONS

Slide #2 summarizes the equipment and the range of experimental conditions. Two short hot flow columns and the tall bubble-column reactor of the two-stage Bench Scale Unit (BSU) were used. To evaluate the effect of the gas distributor design, sintered plates with different pore sizes, and single orifices with different diameters were tested. To estimate the effect of liquid medium, Fischer-Tropsch (F-T) derived waxes, such as reactor-wax (product of the bubble-column reactor operation) and FT-200 (a Sasol derived F-T product wax) were contrasted with hexadecane. Operating conditions, i.e. temperature, superficial gas velocity and catalyst loading, were also varied.

In the hot flow models, the average gas holdup was measured by visual observation of the static and expanded slurry heights. In addition, bubble flow patterns were visually observed. In the bubble-column reactor, local gas holdups were measured at reaction conditions along the column, using a N_2-purged DP-cell system. Also, the expanded slurry level could occasionally be observed at the viewports located at 305, 610, and 762 cm levels. The extent of catalyst settling was also estimated by slurry sampling at the 30, 157, 305 and 610 cm levels.

III. MAJOR CONCLUSIONS

The major conclusions are presented in Slide #3. The results show that the type of liquid, gas distributor design, static liquid height and superficial gas velocity have major effect on gas holdup. For instance, F-T waxes have significantly higher gas holdups than hexadecane, although they have similar viscosity and surface tension. Also, the bubbles are smaller in F-T wax than in hexadecane. Sintered plate gas distributors produce markedly higher gas holdups than single-orifice distributors; also, significant foaming is observed with sintered plates, while little or no foaming is present with single orifices. Here as well, high gas holdups seem to correlate with small bubbles.

Decreasing static liquid height and/or increasing superficial gas velocity result in increased gas holdup. In the reactor, gas holdup profiles were shown to follow a three-zone pattern; this pattern was observed before only in cold flow experiments, and it provides a plausible explanation to the effect of static liquid height on gas holdup. Column diameter, temperature and catalyst loading have little effect on gas holdup. Lastly, gas holdups were shown to be stable and at acceptable levels during an 86 day synthesis run.

It should be noted, that due to the limitations on column diameters, all the results of this study were obtained in the homogeneous bubbly (laminar) flow regime. For reactor scale-up, hydrodynamic data in large diameter reactors operating in the churn (turbulent) regime may be required.

IV. EFFECT OF LIQUID MEDIUM

Slide #4 compares the gas holdups obtained with F-T wax and hexadecane in the 5.3 cm ID hot flow model equipped with a 15 micron sintered plate. The F-T wax has significantly higher gas holdup than hexadecane although both have similar surface tension and viscosity. Also, high gas holdups correlate with small bubbles. Foaming in F-T wax may account partly for the high gas holdup; however, even when foam is excluded from the calculation, the gas holdup is still several times larger in F-T wax than in hexadecane. Similar conclusions were obtained by Deckwer et al (1980) and Quicker and Deckwer (1981) who compared FT-300 (another SASOL F-T product wax) with other hydrocarbon liquids. Deckwer et al showed that literature correlations developed for liquids other than F-T waxes fail when applied to F-T bubble-columns.

The above results indicate that hot flow studies with F-T wax are essential for accurate description of the hydrodynamics in F-T bubble-columns.

V. EFFECT OF GAS DISTRIBUTOR DESIGN

Sintered plate gas distributors produce significantly higher gas holdups than single orifices, as illustrated in Slide #5. The bubbles are also smaller with sintered plates confirming a close relation between high gas holdups and small bubbles. The extremely high gas holdups observed with sintered plates are at least partially the result of foaming. Foaming initiates at superficial gas velocities of 0.5-1 cm/s in the 3.2 cm ID hot flow model. As the superficial gas velocity increases, the foam propagates up and down along the columns, until the entire column is foam. On the contrary, little or no foam is present with single orifices. It is interesting to note, that in the hot flow models, foaming occured when either FT-200 or the product reactor-wax from Run 1 of the BSU were used. In the bubble-column reactor, however, foaming occured only at the beginning of Run 1, when FT-200 was used for start-up. As soon as the product reactor-wax replaced the start-up FT-200, the holdup dropped to acceptable levels, and no more foaming was observed.

Slide #5 also shows that decreasing the sintered plate pore size and the orifice diameter increases the gas holdup at a given uperficial gas velocity. For single orifices, this effect may be correlated with an increase in the orifice Weber number (We_o) with decreasing orifice diameter. The orifice Weber number (the ratio of bubble kinetic/surface energy) is a widely used design parameter for perforated plates or orifices (e.g. Mersmann, 1977). The higher We_o, the better the bubble break up.

The above results are supported by some literature data, e.g. Koelbel et al (1968) and Calderbank et al (1963). However, Quicker and Deckwer (1981) obtained lower gas holdup with a 75 micron sintered plate (correlation curve on slide #5) than with a 0.9 mm single orifice. Further study is required to clarify these results.

VI. EFFECT OF STATIC LIQUID HEIGHT

'n Run 1 of the BSU, the DP cell system was not operational due to slurry plugging. Average gas holdups could still be obtained by visual observation through the 305, 610 and 762 cm level view ports. The expanded slurry level was set at the 762 cm level by varying the superficial gas velocity. Then, at fixed velocity, slurry was withdrawn until the level dropped to 610, 305 and 0 cm. From the amount of slurry withdrawn each time, the average gas holdup for different static liquid heights could be calculated, as shown in Slide #6. The gas holdup was shown to increase significantly with decreasing static liquid height. Slide #6 also shows that Deckwer's correlation (Deckwer et al, 1980) which does not account for static liquid height, significantly underpredicts the gas holdup.

In Run 3 of the BSU, the plugging problems with the DP-cell system were corrected, and gas holdup profiles could be obtained, as illustrated in Slide #7. The DP legs are located at 30, 152, 305, 458, 610 cm and on the reactor effluent line. Since the expanded slurry level was maintained above the 610 cm level, but below the 762 cm viewport, the average gas holdups for the locations shown in Slide #7 (solid lines) could be accurately measured. The dotted lines show a tentative gas holdup profile, in agreement with a three zone mechanism postulated by Langemann and Koelbel (1967) and illustrated by them in a cold flow model. To the best of our knowledge, this is the first time that such a profile was observed in an F-T bubble-column.

The three zones are: a bottom dynamic zone (0-100 cm) in which bubbles form and eventually attain an equilibrium bubble size distribution; a middle stable equilibrium zone (100-450 cm) where the gas holdup decreases along the column because of syngas conversion; a top high gas holdup zone (450 cm to top of expanded slurry) in which the bubbles disengage from the slurry. When the static liquid height is low, the top high gas holdup zone occupies a significant portion of the column, producing a high average gas holdup, while the opposite is true for large static liquid height. Hence, this three zone mechanism gives a plausible rationale to the effect of static liquid height. Furthermore, it emphasizes the need for studies in tall hot flow models to simulate reactor hydrodynamics.

Note that the change in gas holdup profiles from 9.2 to 80.8 DOS in Slide #7 is due to change in superficial gas velocity.

VII. EFFECT OF LONG TERM OPERATION

Assuming a gas holdup for the top section (between 610 and 762 cm) and using the DP-cell data below 610 cm, enables calculation of the average gas holdup in the reactor. Slide #8 shows, that the average gas holdup was stable and at acceptable levels for the 86 day Run 3 of the BSU (the decrease in gas holdup between 9.2 and 75.5 DOS is due to decreased superficial gas velocity). This stable gas holdup is in agreement with invariant reactor-wax composition and physical properties during most of the 86 day run. This is reassuring when compared with data by Farley and Ray (1964), which show a sharp decrease in gas holdup with time due to increase in reactor-wax viscosity.

VIII. CATALAYST SETTLING

In addition to gas holdup, catalyst concentration profiles were also measured in the F-T bubble-column reactor. This was achieved by determining the solids content of slurry samples from the 30, 152, 305 and 610 cm levels. The catalyst concentration profiles follow an exponential settling mechanism, as shown by the straight lines on the semilog plot of Slide #9. This profile is significantly steeper at 81.8 and 83.0 DOS than at 1.6 and 9.6 DOS, due to lower superficial gas velocity, which in turn results in greater settling.

The especially steep catalyst concentration profile at 81.8 DOS was measured during a "Hydrodynamic" upset which eventually caused the termination of Run 3 at 86 DOS. During the upset, the H_2 + CO conversion dropped and the temperature increased in the bottom section of the reactor. The upset disappeared and the catalyst concentration was flatter (83 DOS on Slide #9) after eight hours of high gas velocity operation, but reappeared after the velocity was returned to its original level. No explanation is yet available as to what triggered the catalyst settling indicated by the steep concentration profile.

Note that the catalyst concentration profile is flatter at 9.6 DOS than at 1.6 DOS; this is due to production of reactor-wax which accumulated in the reactor between 1.6 and 9.6 DOS, thus increasing the expanded slurry height and decreasing the average catalyst loading in the slurry.

IX. FUTURE WORK

My last Slide (#10) shows the remaining hydrodynamic work for the current contract. Exploratory hydrodynamic studies are in progress using the short hot flow models and a short bubble-column reactor. The objective is to estimate the effect of gas distributor design on gas holdup and bubble flow patterns. Design and construction of two tall hot flow models is also in progress. In view of the results of the preliminary hydrodynamic studies, it makes sense to use tall hot flow models for future hydrodynamic studies.

Although the current contract does not provide funds for this, it would be desirable to perform hydrodynamic studies in a larger diameter reactor (>25cm ID) operating in the churn (turbulent) flow regime. This would constitute a further step in reactor scale-up.

APPENDIX A - NOMENCLATURE

DOS	Days on Stream
L	Height (cm)
P	Pressure (MPa)
T	Temperature (°C)
u^i_g	Inlet Superficial Gas Velocity (cm/s)
u_{gm}	Mean Superficial Gas Velocity (cm/s)
w_c	Catalyst Loading (wt% of slurry)
ε_g	Gas Holdup (vol.%)

APPENDIX B - LITERATURE

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SLIDE #1

FISCHER-TROPSCH BUBBLE-COLUMN HYDRODYNAMICS

CONTRACTS DE-AC22-80 PC 30022
DE-AC22-83 PC 30019

OVERALL OBJECTIVES

Obtain Fischer-Tropsch bubble-column hydrodynamic data for improved pilot plant operation, and eventually for reactor scale-up

SLIDE #2

EQUIPMENT AND EXPERIMENTAL CONDITIONS

	Hot-Flow	Reactor
Column Dimensions		
Diameter, cm	3.2, 5.3	5.2
Height, cm	215	762
Gas Distributor	15-60 μm Sintered Plate .24-.57 mm Single-Orifice	10-20 μm Sintered Plate
Gas	N_2	N_2, H_2 + CO
Liquid	FT-200, Reactor- Wax, Hexadecane	FT-200, Reactor-Wax
Conditions		
Pressure, MPa	.1	1.1-2.5
Temperature, °C	200-225	260-270
Superficial Gas Velocity, cm/s	0-4	0-4
Catalyst Loading, wt %	0-15	2-20
Measured	Avg. Gas Holdup	Avg. and Local Gas Holdup, Catalyst Concentration Profiles
Technique	Visual	Visual, DP, Slurry Sampling

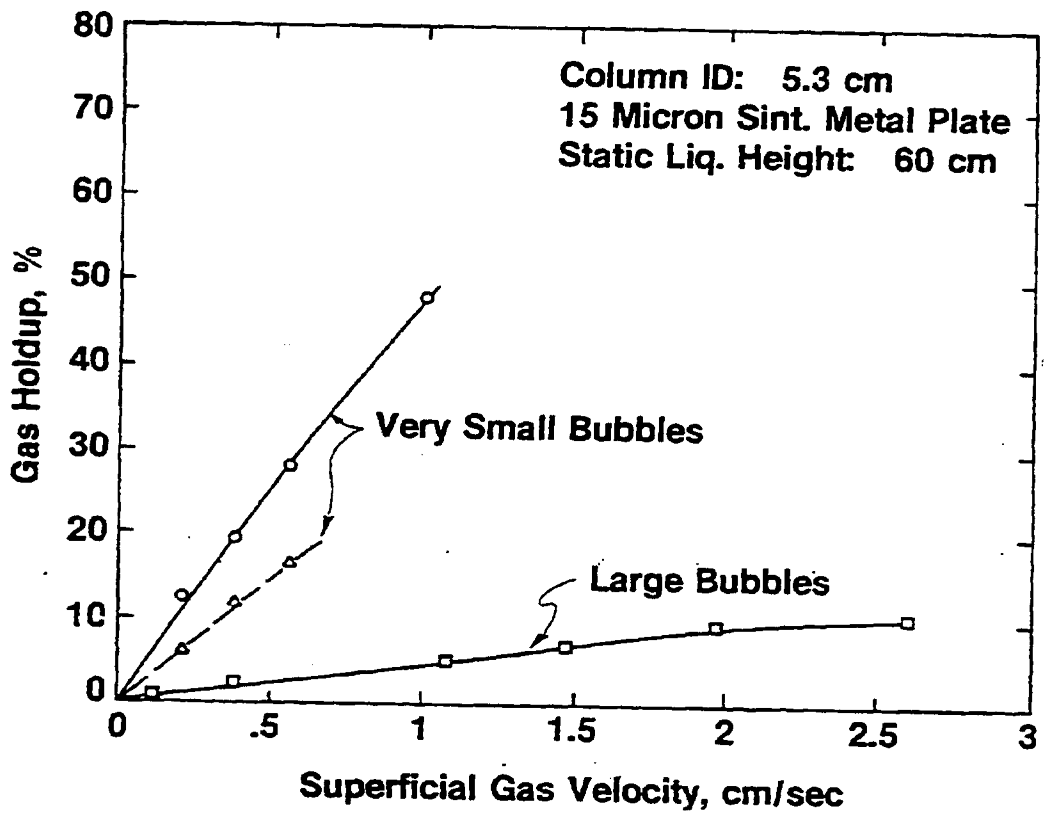
SLIDE #3

MAJOR CONCLUSIONS

- Fischer-Tropsch waxes have significantly larger gas holdups than hexadecane, although they have similar viscosity and surface tension
- Sintered plate gas distributors produce markedly higher gas holdups than single-orifice distributors; also, significant foaming is present with sintered plates while little or no foaming occurs with single orifices
- Decreasing static liquid height and/or increasing gas superficial velocity result in increased gas holdup
- Column diameter, temperature, and catalyst loading have small effect on gas holdup
- Gas holdup profiles in the reactor follow a three-zone pattern, previously observed only in cold flow experiments. Also, catalyst concentration profiles follow an exponential settling mechanism
- Gas holdups were shown to be stable and at acceptable levels during an 86-day synthesis run

SLIDE #4

EFFECT OF LIQUID MEDIUM ON GAS HOLDUP

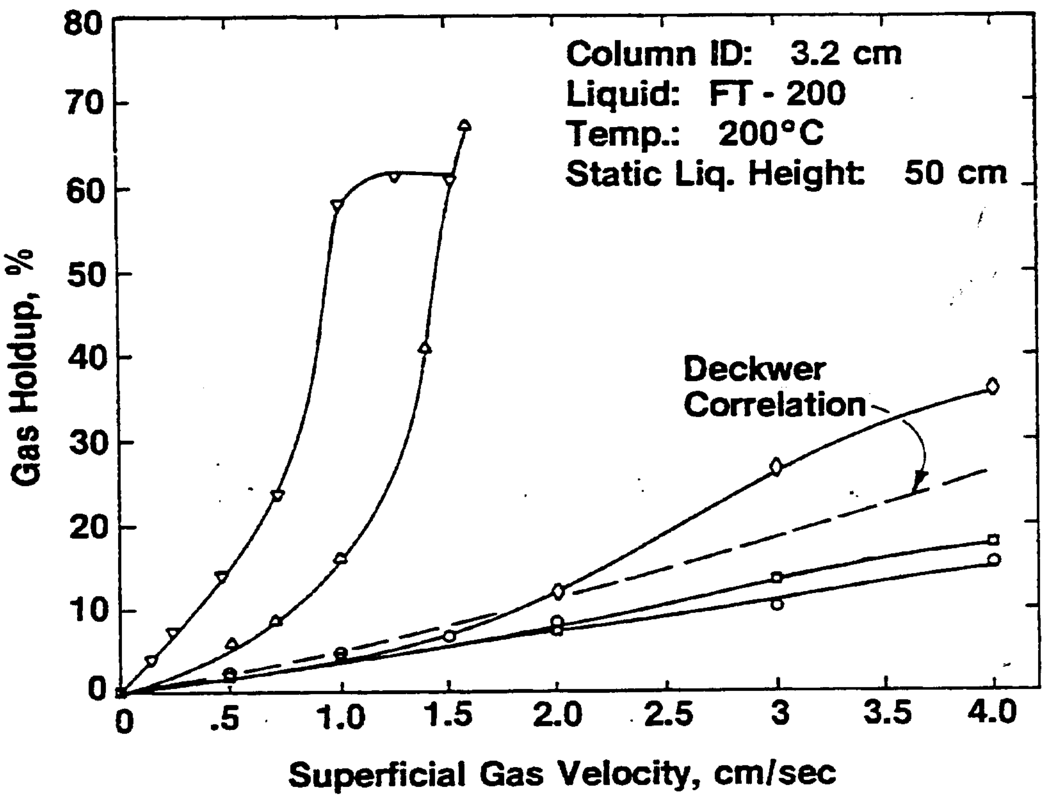


△ FT-200 Excluding Foam

	○	□
Liquid	FT - 200	Hexadecane
Temp., °C	200	20
Visc., cpoise	2.1	3.5
Surf. Tension, Dynes/cm	26.0	27.5

SLIDE #5

EFFECT OF DISTRIBUTOR TYPE ON GAS HOLDUP



Sintered Metal Plates	Single Orifices
▽ 15 Micron	◇ 0.24 mm*
△ 60 Micron	□ 0.39 mm
	○ 0.57 mm

(*Static Liq. Height 100 cm)

SLIDE #6

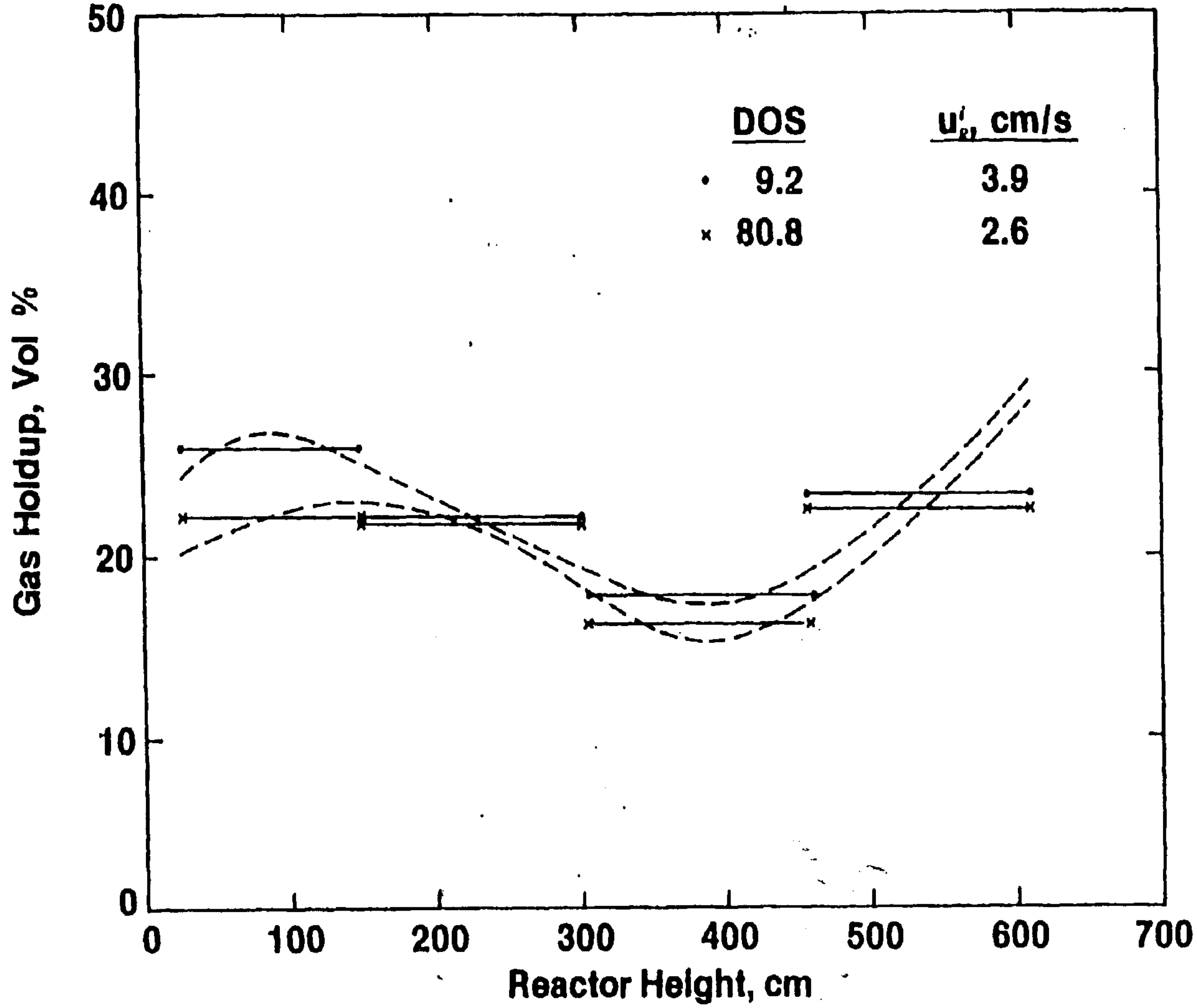
EFFECT OF STATIC LIQUID HEIGHT
(Run 1 of Two-Stage BSU)

DOS	u_{gm} cm/s	W_C wt %	L cm	Avg. ϵ_{g}, Vol % This Study	Avg. ϵ_{g}, Vol % Deckwer, et al (1980)
60.8	1.8	2.5	541	29	10
61.1	2.2	2.5	415	32	13
61.1	2.2	2.6	177	42	13

SLIDE #7

SLURRY FISCHER-TROPSCH BUBBLE-COLUMN GAS HOLDUP PROFILES*

(Run 3 of Two-Stage BSU)



*Estimated expanded slurry heights of ~670-762 cm.

SLIDE #8

SUMMARY OF ESTIMATED GAS HOLDUPS FROM DP-CELL DATA

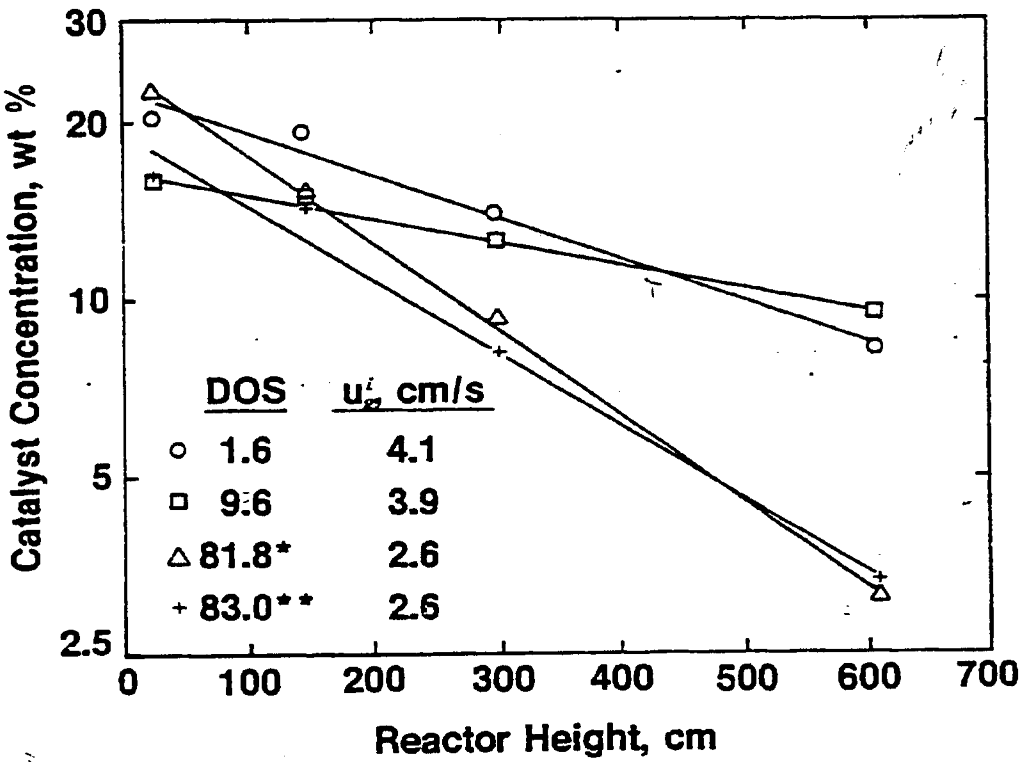
(Run 3 of Two-Stage BSU)

DOS	9.2	75.5	80.8
u_g^l, cm/s	3.9	2.6	2.6
T, °C	260	267	267
P, MPa	1.48	2.51	2.51
W_C, wt %	14.3	13.9	12.0
ϵ_g, vol %	26.6	19.7	19.8

SLIDE #9

SLURRY FISCHER-TROPSCH BUBBLE-COLUMN CATALYST CONCENTRATION PROFILES

(Run 3 of Two-Stage BSU)



Estimated Cat. Load: 10.8-12.9 wt %

Estimated Expanded Slurry Height: 610-762 cm

*During hydrodynamic upset

**After hydrodynamic upset was corrected

SLIDE #10

FUTURE HYDRODYNAMIC STUDIES

- Perform exploratory hydrodrynamic studies in two short hot flow models (3.2 and 5.3 cm ID x 215 cm L) and a short bubble-column reactor (2.7 cm ID x 193 cm L); determine the effect of gas distributor design on gas holdup and flow patterns

- Design and construct two tall hot flow models (5.1 and 10.2 cm ID x 915 cm L)

- Use the tall hot flow models and the bubble-column reactor of the two-stage BSU to determine the effect of gas distributor design, static liquid height, and operating conditions on gas holdup and flow patterns