The parameters studied were the superficial gas velocity, Fe-catalyst loading, and feed H_2/CO ratio. Figure 49 shows that the superficial gas velocity has a large effect on the F-T bubble-column performance. The predicted reactor length becomes substantially longer with higher gas velocity. Figure 50 shows that the Fe-catalyst loading also exerts a significant effect on the F-T bubble-column performance. An increase of Fe-loading from 5 to 10 wt % strongly affects the F-T column performance; however, the effect resulting from an increase of the loading from 10 to 15 wt % is considerably less. Figure 51 shows that the effect of varying feed H_2/CO ratios on the F-T bubble-column performance is not significant except in the high H_2/CO conversion region. The varying feed H_2/CO ratio affects the reactor exit H_2/CO ratio in the high H_2+CO conversion region as indicated in Figure 52. This may somewhat affect the catalyst aging and the methane formation rate, both of which vary with the H_2/CO ratio in the gas phase.

E.   Comparison of Fischer-Tropsch Bubble-Column
      Model Predictions and Experimental Data

The predicted effect of the feed H_2/CO ratio on the exit H_2/CO ratio compares well qualitatively with experimental results from the two-stage bench-scale unit. The trends in Figure 52 (model predictions) and Figure 22 (from Run CT-256-3) are very similar.

In another set of calculations, predicted and measured H_2 and CO conversions and H_2/CO usage ratios are compared (Table 36). The multi-component mathematical model was used in those calculations. The data cover Runs CT-256-2, -3, and -4, in which the same F-T catalyst I-B was used. The intrinsic kinetic parameters were estimated using data from the beginning of Run CT-256-3 (9.2 DOS). These data were chosen because the catalyst was at its start-of-cycle activity. In addition, hydrodynamic data, i.e. gas holdup and catalyst concentration profiles were also available at that time. The intrinsic kinetic parameters were estimated to be

$$k_1 = 0.50 \quad cm^3 \text{ liquid/gFe-s}$$
$$k_2 = 1.35 \quad cm^3 \text{ liquid/gFe-s}$$
$$k_3 = 0.20 \quad \text{and}$$
$$k_4 = 37.5$$

(See Equations (29) and (31) for the definition of these parameters). Since catalyst aging is not taken into account in the mathematical model, the calculated results are restricted to the start-of-cycle activity of catalyst I-B.

FIGURE 49

PREDICTED EFFECT OF GAS SUPERFICIAL VELOCITY ON
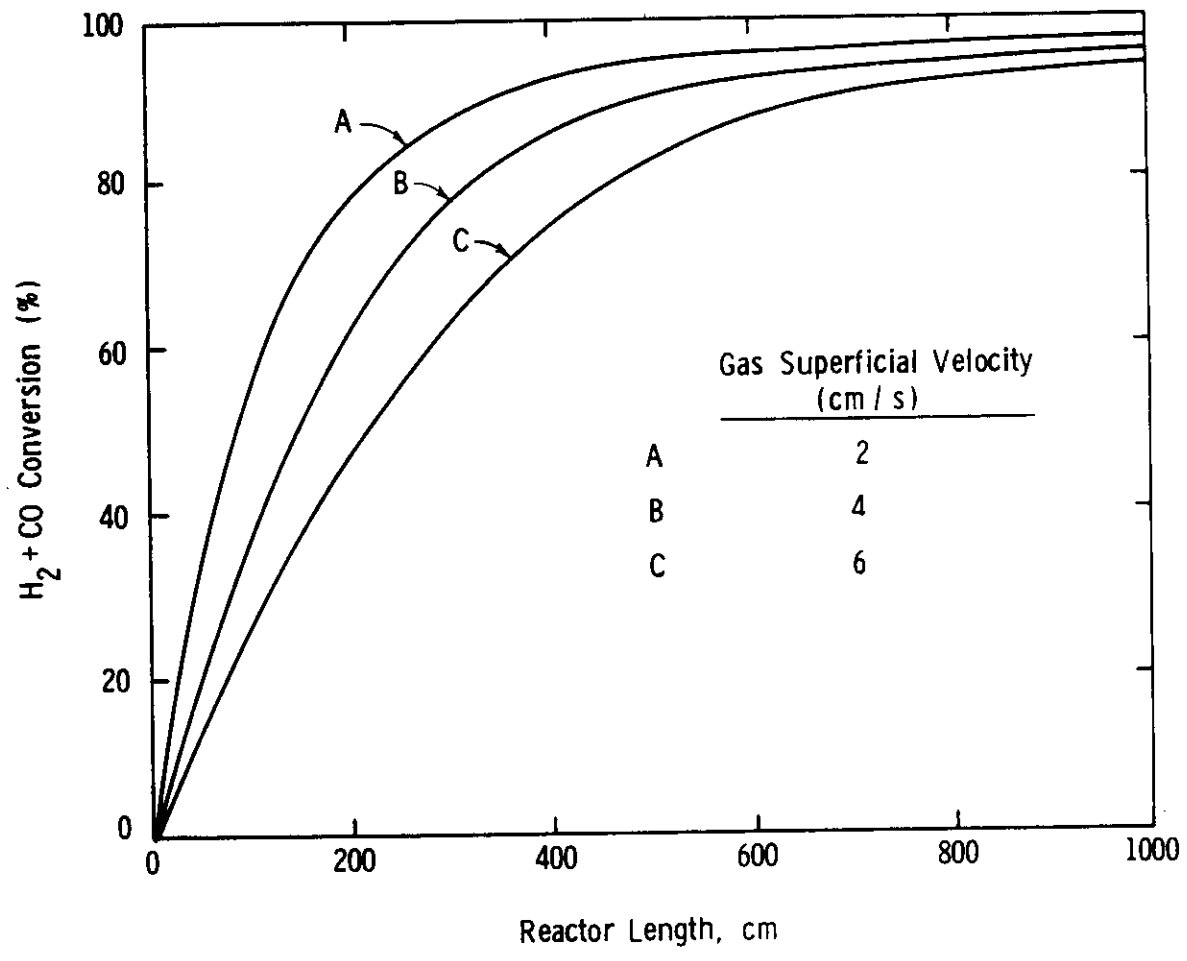H_2 + CO CONVERSION

FIGURE 50

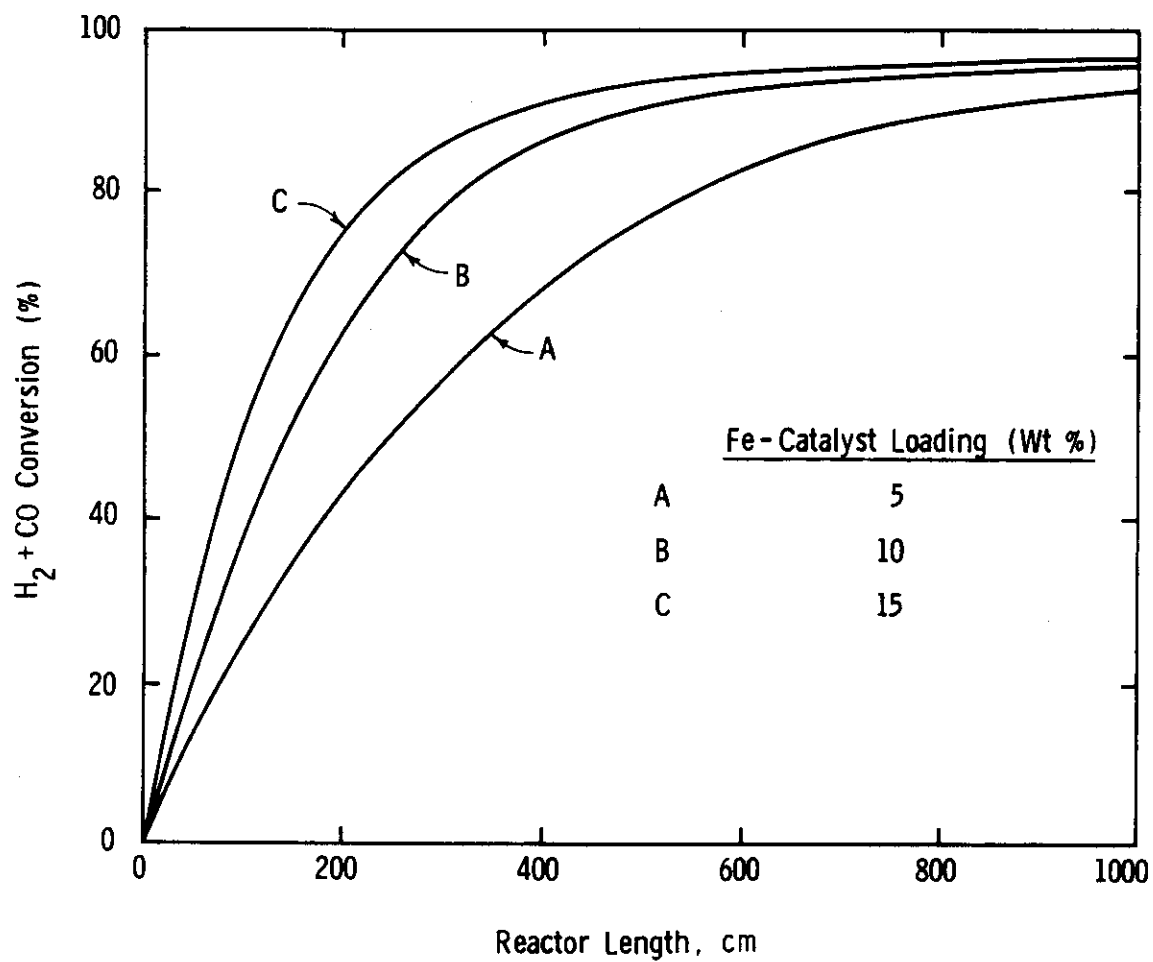## PREDICTED EFFECT OF Fe-CATALYST LOADING ON
H_2 + CO CONVERSION

FIGURE 51

PREDICTED EFFECT OF FEED H_2/CO RATIO ON $H_2 + CO$ CONVERSION

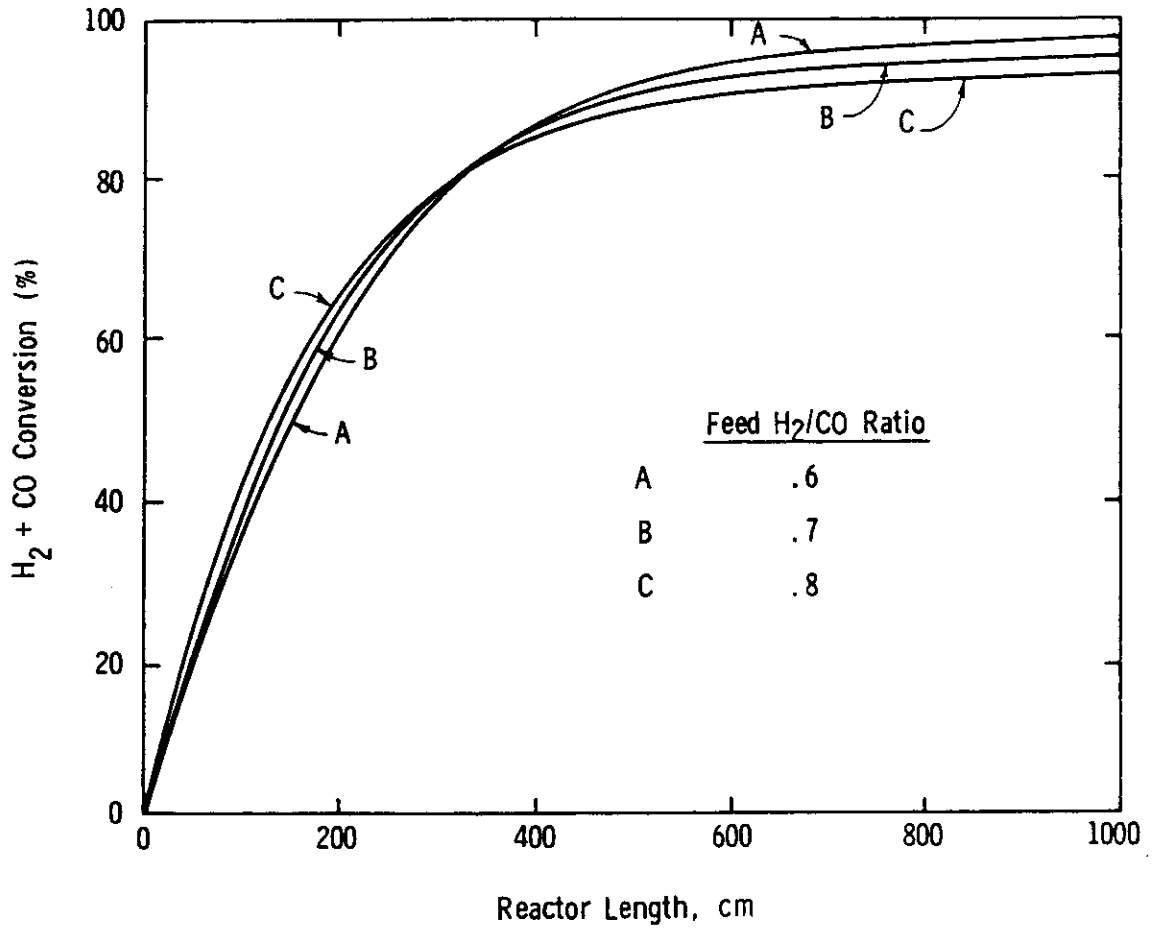|	Feed H_2/CO Ratio
A	.6
B	.7
C	.8

FIGURE 52

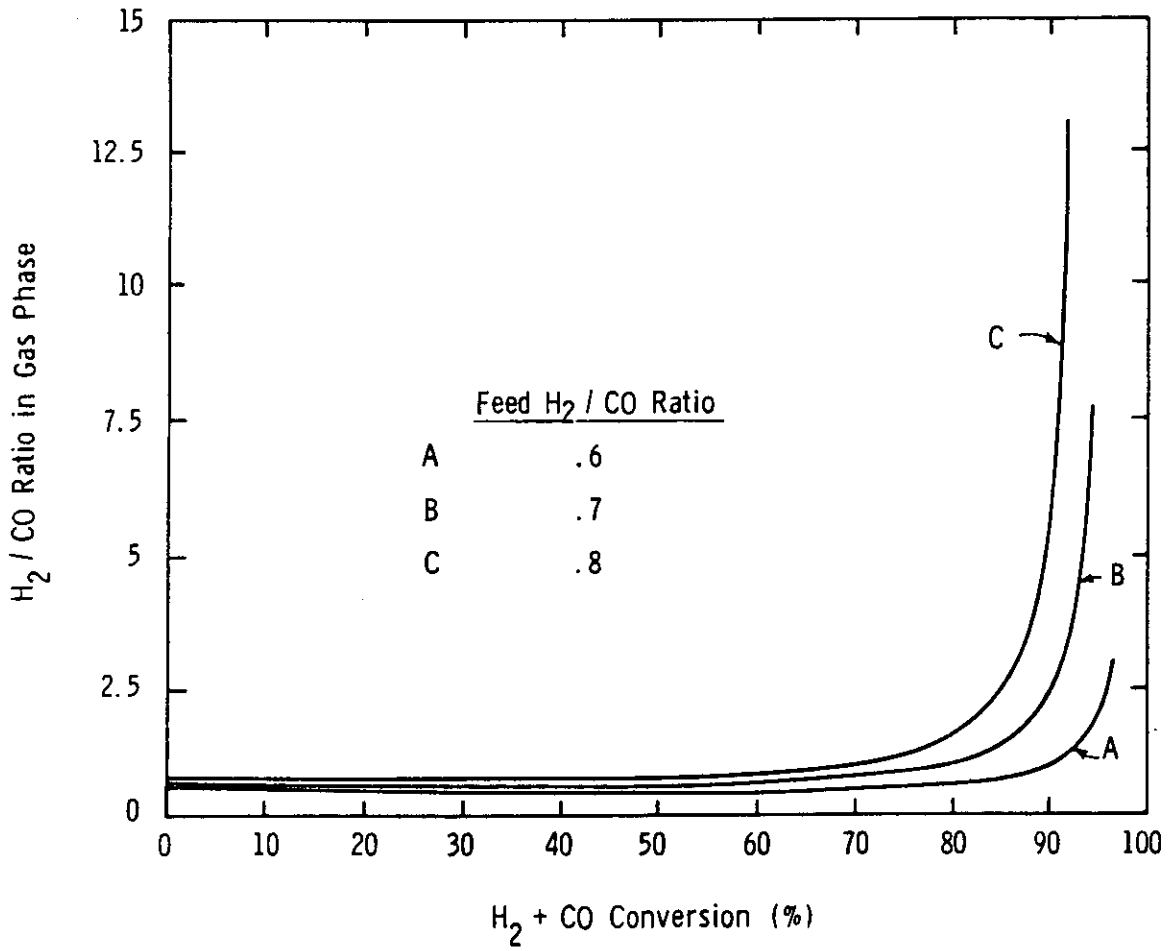PREDICTED EFFECT OF FEED H_2/CO RATIO ON
H_2/CO RATIO IN GAS PHASE

Table 36

Comparison of Multi-Component Slurry F-T Model
Predictions and BSU Bubble-Column Data

Run CT-256-	2	2	3[2]	3	3	3	3	4
DOS	2.9	6.9	9.2	15.8	25.0	35.5	50.5	1.6
Feed H_2/CO, Molar	.68	.68	.67	.67	.69	.70	.68	.70
T, °C	259	258	260	260	260	259	261	256
P, MPa	1.14	1.47	1.48	1.48	1.48	1.48	1.50	1.14
u_g^i, cm/s	4.06	3.61	3.90	4.30	3.73	3.41	3.15	4.00
L, cm	762	762	728	762	713	730	671	782
w_c, Wt %	13.7	12.8	14.3	13.7	13.8	12.9	14.4	17.6
N_2 in Feed, Mol %	4.5	3.9	4.5	12.7	4.5	5.0	6.4	8.3
ϵ_g, Vol %	26.6[1]	23.3[1]	26.6	26.6	21.7	24.7	20.6[1]	20.0
H_2 conv., %[3]	75.8 (76.8)	77.3 (78.4)	78.3 (79.6)	72.6 (74.1)	78.4 (81.4)	79.1 (80.3)	80.0 (88.0)	64.2 (85.3)
CO conv., %[3]	87.3 (87.1)	89.2 (89.3)	91.2 (89.7)	84.4 (82.8)	90.3 (92.7)	92.0 (92.7)	90.4 (97.6)	82.4 (97.1)
H_2/CO Usage Ratio[3]	.59 (.60)	.59 (.60)	.61 (.60)	.61 (.60)	.59 (.60)	.60 (.60)	.60 (.61)	.55 (.61)

(1) Estimated gas holdup.
(2) Data used to estimate the intrinsic kinetic parameters.
(3) Numbers in parenthesis are predicted values.

Since not all the input data for the model were measured, the following assumptions were used:

- The activation energies were 100 kJ/gmol for the F-T reaction rate constant, k_1, and 24 kJ/gmol for the water-gas shift reactor rate constant, k_2. The parameter k_3 was assumed temperature independent, and the temperature dependence of the water-gas shift equilibrium constant, k_4, follows that of Newsome (1980).

- Gas holdups, where noted, were extrapolated from the data at 9.2 DOS of Run CT-256-3 assuming $\epsilon_g \propto u_g^j$.

- Other parameters, such as d_B, K_i, D_{Li}, k_{Li}, and reactor-wax and slurry physical properties were the same as those used in the multi-component model calculations (Tables 28 and 35).

- No backmixing of either the liquid or the gas phase is assumed since this effect on the BSU slurry reactor is expected to be negligible.

The activation energy for k_1 is in line with literature data (Deckwer, et al., 1982a). The activation energy for the water-gas shift reaction is unknown and is estimated from that of the k_1, by assuming that the activation energy is approximately proportional to the heat of reaction.

Table 36 indicates good agreement between predicted and measured results for the two balances of Run CT-256-2 (2.9 and 6.9 DOS), indicating that the kinetics and hydrodynamics at the beginning of this run are similar to those at the beginning of Run CT-256-3. The model is adequate in predicting the effect of varying superficial feed-gas velocity and pressure.

The predicted results from 15.8, 25, and 35.5 DOS of Run CT-256-3 agree well with the experimental results. The model also adequately predicts the effect of superficial feed-gas velocity (all three balances) and N_2 dilution (9.2 and 15.8 DOS). No significant catalyst aging up to 35.5 DOS is detected by comparison of the actual conversion data with the predicted data. The data from 50.5 DOS shows, however, that moderate catalyst aging might have occurred.

The data from the beginning of Run CT-256-4 show that the model significantly overpredicts the H_2 and CO conversions. There are two possible explanations. The first is that catalyst I-B was not activated properly in this run. The other is that the catalyst loading might be much larger than optimum loading. Unfortunately, the concept of optimum catalyst loading is not well understood and is not included in the current model.

VIII. <u>Hydrodynamic Studies Using</u>
       <u>Non-Reacting Bubble-Columns</u>[1]

   A. <u>Introduction and Conclusions</u>

         Hydrodynamic data of bubble-column reactors are essential
   for analyzing the performance of the reactor, for providing
   essential parameters for a slurry reactor mathematical model and
   for characterizing factors of the slurry reactor scale-up.
   Limited work in this area was carried out using existing
   nonreacting bubble-columns. The conclusions obtained from these
   studies shall be interpreted cautiously because of the small size
   equipment used. The physical limitations include the diameter of
   the columns (3.2 cm for a hot column, and 5.1 cm for a cold
   column), the column height (about 216 cm for both columns), and
   the maximum temperature of the hot column (225°C). Further
   studies using larger equipment are strongly recommended.

         There is a vast amount of bubble-column gas holdup data in
   the literature (e.g., a review by Shah, et al., 1982). However,
   most of these data are for air-water systems. The gas holdup is
   generally a function of liquid medium properties, bubble column
   dimensions, operating conditions, type of gas distributors, and
   solids contents. Since none of the gas holdup correlations in
   the literature takes all these into account, it is questionable
   if these data can be applied to F-T bubble-column systems. To
   further complicate the matter, Deckwer, et al. (1982b) and
   Quicker and Deckwer (1981) showed that the gas bubble size in a
   F-T wax was significantly smaller and the gas holdup was
   significantly larger than those for pure hydrocarbon liquids with
   similar density, viscosity, and surface tension. It was
   therefore necessary to study bubble-column hydrodynamics in
   nonreactive flow models using an actual F-T slurry as the liquid
   medium.

         Gas holdup in a bubble-column is an important parameter
   since it closely relates to the gas-liquid interfacial area, the
   residence time of the gas rising through the column, and the
   reactor volume required for achieving a given conversion. In
   general, a large gas holdup goes together with small bubble size
   (Deckwer, et al., 1979). Furthermore, small bubble size implies
   small bubble rising velocity and larger gas-liquid interfacial
   area. A good gas holdup is essential in achieving a satisfactory

   _____

   [1]This work was carried out by a summer employee,
   W. J. Cannella, a graduate student in the Department of Chemical
   Engineering, The University of California at Berkeley (Berkeley,
   California.)

bubble-column performance. However, too high a gas holdup would mean that a much larger reactor volume is needed to hold a given amount of the catalyst. Consequently, a high gas holdup could mean a waste of reactor volume. Based on our experience, the approximate range of desirable gas holdup is 10-35 vol %. The gas holdup is a strong function of the superficial gas velocity and is often very sensitive to the properties of the liquid phase.

The liquid mediums studied include FT-200 Vestowax and used slurry from the end of Run CT-256-1. The gas used was nitrogen. The effects of solid concentration, temperature, and static liquid height on gas holdup were studied in a 3.2 cm diameter hot bubble-column. The column was installed with a 15 μm stainless steel sintered plate as gas distributer and was wrapped on the outside with heating tapes to keep it hot. The effects of column diameter and static liquid height were also studied using n-hexadecane in cold bubble-columns with diameters of 3.2 and 5.1 cm. A comparison of the results with those available in the literature was also made.

The major conclusions obtained from the current studies are summarized in the following:
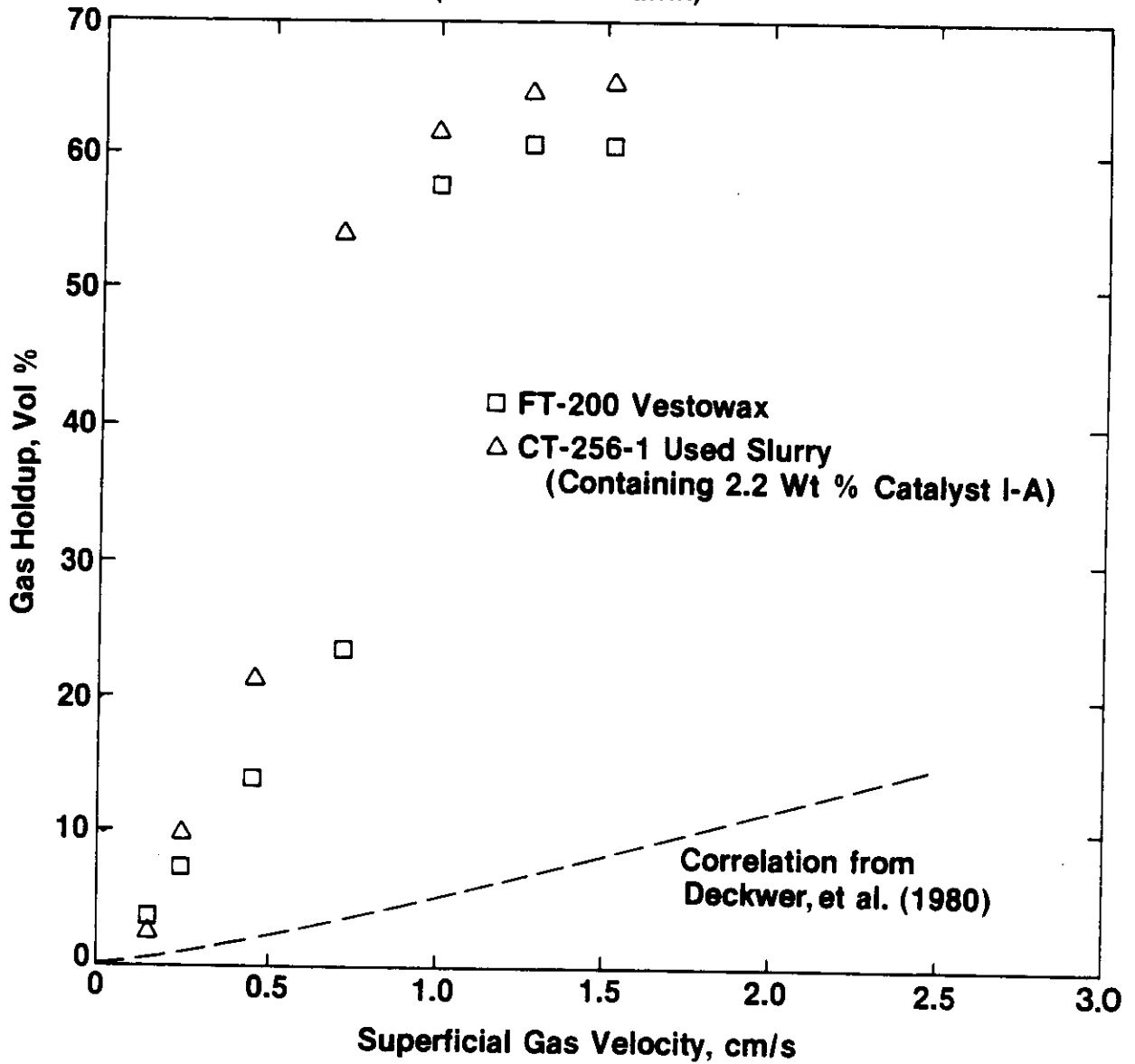
- The bubble-column gas holdup decreased with increasing static liquid height. No significant effect due to temperature variation (over a 25°C variation) was observed.

- The bubble-column gas holdup increased linearly with increasing superficial gas velocity up to about 0.4 cm/s, then quickly reached high holdup (about 60 vol %) at higher gas velocity with excessive foaming observed. Gas bubble slugging was observed at superficial gas velocities above 1.5 cm/s.

- At solid concentrations larger than 6 wt %, the gas holdup increased with solid content.

- Using n-hexadecane as liquid medium in two cold columns, decreasing gas holdup with increasing column diameter was observed. However, the gas holdups observed there were substantially less than those observed for F-T waxes at the same gas velocity.

B.   Hot Bubble-Column Studies

The relationship between gas holdup, ϵ_g, and superficial gas velocity, u_g, for FT-200 Vestowax was studied in a 3.2 cm diameter nonreacting, hot bubble-column at 200°C. The static liquid height studied was 46 cm and the results obtained are presented in Figure 53. The expanded slurry consisted of many

FIGURE 53

HOT, NON-REACTING
BUBBLE-COLUMN GAS HOLDUP
(3.2 cm ID Column)

□ FT-200 Vestowax

△ CT-256-1 Used Slurry
(Containing 2.2 Wt % Catalyst I-A)

Correlation from
Deckwer, et al. (1980)

Gas Holdup, Vol %

Superficial Gas Velocity, cm/s

very small gas bubbles distributed throughout the liquid and was topped by a layer of foam. The liquid was clean and it was possible to see through the column. At low superficial gas velocities (u_g <0.72 cm/s) the foaming was minimal and there was a discernible boundary between the foam and non-foam liquid layers. In this regime the gas holdup appeared to vary linearly with the superficial gas velocity according to the following equation:

$$\epsilon_g = 0.30 \ u_g \qquad (40)$$

As the velocity was further increased to about 1 cm/s, the wax began to foam excessively. The foaming region expanded both up and down, and the boundary layer between the foam and the non-foam liquid could no longer be distinguished. Soon the whole column appeared to be foaming and it was no longer possible to see through the column. The gas holdup values reported included the foam and thus were very high (about 59%).

At higher velocities, the gas holdup increased slightly and then leveled off at a value of about 61%. At a velocity of about 1.5 cm/s, large gas bubbles which extended across the column diameter were observed. Operation in this regime may be highly undesirable since the gas-liquid interfacial area available for mass transfer is greatly reduced.

Since products formed during F-T synthesis may affect the bubble-column hydrodynamics, it was necessary to repeat the study using the slurry actually formed during synthesis. A slurry containing 2.2 wt % of catalyst I-A from sixty-one days on-stream of Run CT-256-1 was used. The results are also presented in Figure 53. Qualitatively the results obtained were similar to those of the FT-200 Vestowax except that the slope of the gas holdup versus the gas velocity at the low velocities is slightly larger than that of the FT-200 Vestowax. Foaming also began to increase with increasing gas velocity, causing a large rise in gas holdup. The gas holdup then leveled off until slugging occurred.

Also depicted in Figure 53 is the gas holdup correlation developed by Deckwer, et al. (1982b), as represented by following equation:

$$\epsilon_g = 0.053 \ u_g^{1.1} \qquad (41)$$

The measured gas holdups were consistently larger than the values predicted by this correlation. However, the conditions under which the gas holdup data were obtained here are somewhat different from the conditions under which the correlation was established. These conditions include the static height, the column diameter, and the temperature.

C.   Effect of Solid Concentration in Slurry

The effects of varying solids content on the gas holdup of the used slurry from Run CT-256-1 was studied. The results are presented in Figure 54 and Table 37. At low velocities (<0.4 cm/s) when there is very little foaming, the addition of solids appears to decrease the gas holdup slightly. This may be due to an increase on the apparent viscosity of the liquid. However, at higher flow rates when the foaming is excessive, the gas holdup is increased. Bikerman (1953) claims that the coalescence of foam bubbles can be prevented or retarded by solid particles immersed in the liquid. Thus, the fine solids may stabilize the foam.

The effect of solids content has also been studied by Deckwer and coworkers in a molten paraffin-wax/N_2 system under nonfoaming conditions. They observed virtually no effect on gas holdup for solids content ranging from 5.5 to 16 wt % and only a slight decrease of gas holdup (about 0.01 to 0.02) from 0 to 5.5 wt %.

Thus it appears that at least up to a solids content of about 15 wt % there is little effect on gas holdup under nonfoaming conditions, but there may be an effect under foaming conditions.

D.   Effects of Temperature

The temperatures frequently used in F-T synthesis range between 200 and 300°C. Thus it is important to determine if there is any effect of temperature on gas holdup. In this study, due to equipment limitation, temperature was maintained below 225°C in the hot bubble-column. A comparison of the results obtained at this temperature and at 200°C using used slurry from Run CT-256-1 is presented in Figure 55 There seems to be no significant effect of temperature over this small range. Extrapolation to temperatures outside this range is not recommended.

The effects of temperature were also studied by Deckwer, et al. (1980). They observed no effect over a temperature range of from 143 to 285°C for a 10 cm diameter column, but did observe a decrease in gas holdup with increasing temperature for a 4 cm diameter column. They attributed this to wall effects in the small column. Further studies on the effects of temperature and the relationship of column diameter are recommended.

FIGURE 54

EFFECT OF SOLID CONCENTRATION
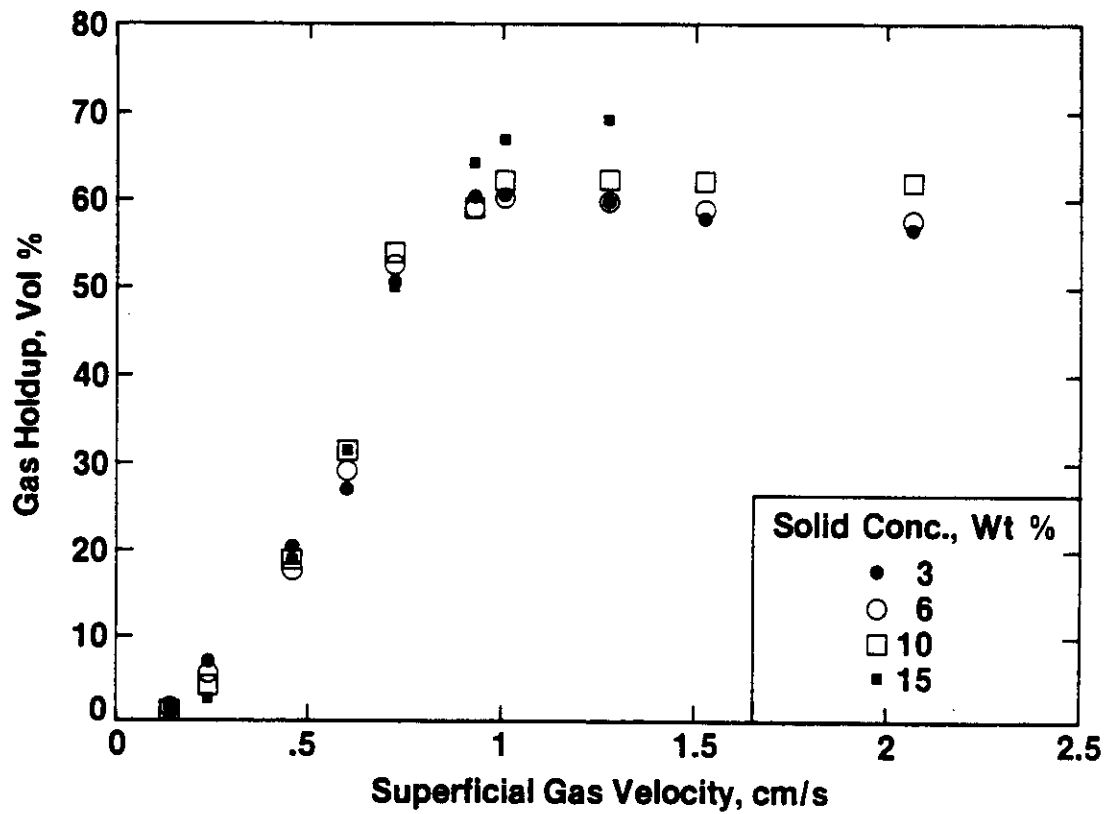## ON GAS HOLDUP

(3.2 cm ID, Hot, Non-Reacting Column)

Table 37

Effect of Solid Concentration on Gas Holdup

(3.2 cm ID column. Gas Holdup in Vol %)

Solid Content, Wt %

u_g cm/s	3	4	5	6	7.5	1	12.5	15
0.14	1.3	2.3	1.9	1.9	2.1	1.5	0.9	1.0
0.24	7.0	7.5	5.6	6.1	6.1	4.4	4.4	3.2
0.46	20.5	20.3	17.9	18.0	21.1	18.8	19.3	19.0
0.60	26.3	25.3	25.7	29.2	30.7	32.0	32.2	31.9
0.72	50	51.7	50.9	52.5	52.6	54.0	54.2	50.4
0.93	60.7	59.5	58.9	59.2	58.8	59.1	61.8	65.4
1.01	60.4	59.9	57.2	60.2	58.5	62.2	66.2	67.1
1.28	59.9	60.7	60.5	59.9	58.5	62.4	69.1	69.5
1.53	58.1	51.9	59.0	59.0	58.3	62.2	(2)	(2)
2.07	56.7	56.7	58.3	57.7	54.3	62.1	(2)	(2)

(1) A used slurry from Run CT-256-1 plus catalyst I-A was used.

(2) Gas holdups were too high for the given static height and column height.

FIGURE 55

EFFECT OF TEMPERATURE ON GAS HOLDUP
(3.2 cm ID, Hot, Non-Reacting Column)

Used Slurry from Run CT-256-1
△ 200°C
▽ 225°C
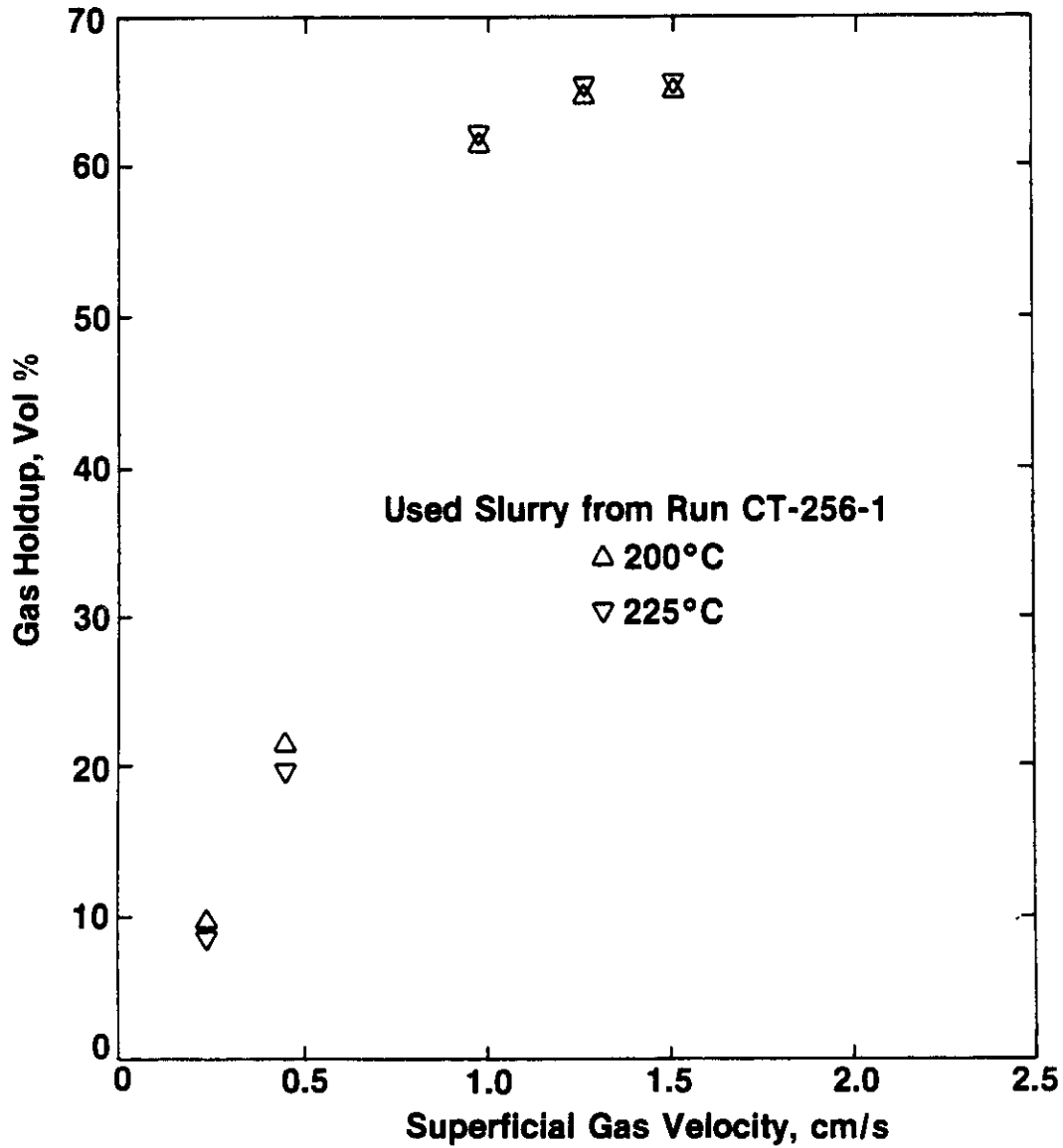
E. Effect of Static Liquid Height and Column Diameter

Since the static liquid heights and column diameters of commercial reactors are expected to be larger than those used in the present hydrodynamic studies, experiments were conducted to determine what effect these parameters have on gas holdup.

The results for the used slurry from Run CT-256-1 in the hot, nonreacting bubble-column are presented in Figure 56 for static heights of 46 and 69 cm. The gas holdup was found to decrease as the liquid height increased. Similar effects were also observed by Langemann and Koelbel (1967). Further studies in taller and larger hot columns are recommended.

The effects of static liquid height and column diameter were also studied in cold flow columns using n-hexadecane. The results are presented in Tables 38 and 39. In general, the gas holdup values measured using n-hexadecane are substantially less than those measured using F-T waxes at the similar gas velocity. For example, at 0.4 cm/s gas velocity, the highest gas holdup ever observed using n-hexadecane was about 6 vol %, while values of 15-20 vol % were observed using F-T waxes. Similarly, the bubble size in n-hexadecane medium seemed to be substantially larger. There was an observed effect of both the static liquid heights and the column diameters. In general, gas holdup increases with decreasing static liquid height and column diameter. However, when the static liquid height was above 64 cm, there seemed to be little observed effect on gas holdup. When the liquid height was large enough, bubble coalescence and slugs occurred at a gas velocity higher than 1.9 cm/s.

Several studies on the effects of static liquid height and diameter on gas holdup have been presented in the literature. Deckwer, et al. (1980) observed no effect in a molten paraffin-wax/N_2 system for liquid heights of 60-100 cm. Likewise Yoshida and Akita (1965) observed no effect for larger liquid heights (larger than 90 cm) and diameters (larger than 7.7cm). On the other hand, Langemann and Koelbel (1967) have observed a significant effect of static liquid height for a mineral oil/CO_2 system. Shulman and Molstad (1950) also observed an effect of column diameter for an air/H_2O system. Columns of 5.1 and 10.2 cm diameters gave the same results, but a column of 2.5 cm diameter gave much higher gas holdup values. In addition, foaming was observed in the 2.5 cm diameter column and a critical velocity was reached at which the whole column seemed to be foaming.

Langemann and Koelbel (1967) suggested that there are three zones of flow which exist within a bubble-column. The first zone is near the gas distributor and is a zone of incident flow. Bubble flow patterns come to the equilibrium state which is

FIGURE 56

EFFECT OF STATIC LIQUID HEIGHT
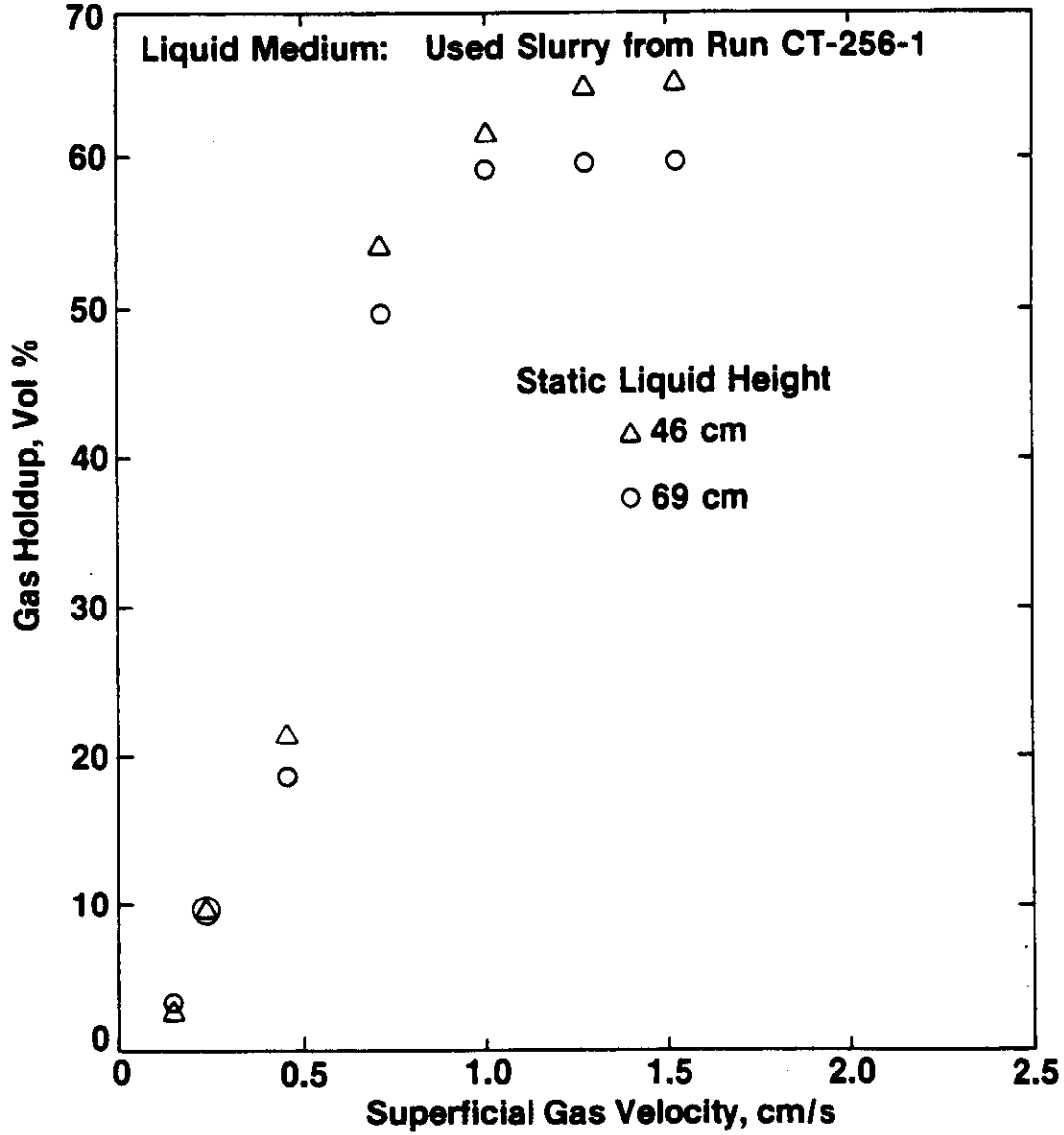## ON GAS HOLDUP

(3.2 cm ID, Hot, Non-Reacting Column)

Table 38

Cold Column Gas Holdup Data Using n-Hexadecane

(3.2 cm ID Column Gas Holdup in Vol %)

	Static Liquid Height, cm					
u_g, cm/s	15	36	45	62	124	172
0.08	3.09	0.87	1.72	1.01	1.01	0.92
0.19	5.05	2.16	2.06	1.75	1.51	1.90
0.29	6.00	3.42	2.72	2.24	1.75	2.48
0.63	6.93	4.23	4.19	3.68	2.74	3.65
0.80	7.84	-	4.98	-	-	4.58
0.96	8.74	6.61	5.92	5.30	-	4.92
1.29	10.04	8.13	7.14	6.43	5.34	6.24
1.61	11.73	8.87	8.33	7.75	7.33	7.52
1.90	12.55	11.02	9.49	9.03	8.65	8.50
2.20	14.54	13.07	10.62	9.45	9.88	9.60
2.45	15.1	14.39	11.18	-	-	10.60
2.76	-	15.03	11.73	-	-	11.60

Table 39

Cold Column Gas Holdup Data Using n-Hexadecane

(5.1 cm ID Column. Gas Holdup in Vol %)

	Static Liquid Height, cm			
u_g, cm/s	15	36	63	169
0.03	1.03	0.44	0.25	-
0.07	2.04	-	-	-
0.12	3.03	0.88	0.75	1.57
0.25	4.00	-	-	-
0.38	4.43	2.16	2.21	2.29
0.64	5.88	3.21	3.16	3.35
0.86	6.80	4.24	4.22	4.39
1.08	7.69	5.04	5.24	5.41
1.29	8.57	6.22	6.13	6.07
1.47	-	-	7.01	-
1.64	-	8.13	7.87	-
1.84	-	8.68	8.71	8.76
1.97	-	9.60	9.54	-
2.29	-	10.31	10.15	-
2.60	-	11.02	10.76	-

determined by a combination of medium properties, column dimensions, and operating conditions. In this zone, the gas holdup rises, peaks, and begins to fall. In the middle zone, bubbles flow upward in an equilibrium pattern. The gas holdup tends to decrease slightly as the bubbles move up the column. The top zone is one of bubble disintegration which occurs due to the requirement of a finite time for bubbles to disengage from the liquid. The gas holdup rises sharply in this zone to its maximum value. The height of the last zone varies little with static liquid height. Consequently, in a short column, the average gas holdup is high because it is dominated by the last zone. Based on this analysis, one expects the average gas holdup to decrease with increasing static liquid height. Thus it is advisable to study bubble-column hydrodynamics in a tall column.