EXTRUDATE CATALYST STUDY

Fluidization characteristics of the following six systems were studied using spent extrudate catalyst.

1. Kerosene-nitrogen - catalyst
2. Kerosene-nitrogen - catalyst - 4 W % fines
3. Kerosene-nitrogen - catalyst - 16 W % fines
4. Kerosene-nitrogen - catalyst - 35 W % fines
5. Circosol 304-nitrogen - catalyst
6. Circosol 306-nitrogen - catalyst

Pertinent physical properties of these systems are given in Table 2.

Bed Expansion

Bed-expansion data were obtained for liquid velocities up to 0.21 ft/sec and gas velocities up to 0.20 ft/sec. The results are summarized in Tables 3 through 6.

Effect Of Liquid/Gas Velocities on Bed Expansion

Bed expansion in the six systems studied varied strongly with the superficial liquid velocity, as shown in Figures 2 and 3.

In each case, relatively little expansion was observed until the catalyst became fluidized at a superficial liquid velocity of 0.05 ft/sec. Expansion increased thereafter faster than linearly with increasing liquid flow. Only with Circosol 306, which has a viscosity of 9 cps, was the percent expansion above 10% at a liquid velocity of 0.025 ft/sec.

Changes in gas velocity had less effect on bed expansion than liquid velocity changes. In general, increases in gas velocity increased expansion once the bed was ebullated.

Similar effects of gas and liquid velocity on bed expansion were observed in PDU Run 10 (see PDU 10 bed expansion data in Section IV).

Effect of Solids on Bed Expansion

Silicon carbide fines with a median diameter of 17 microns and a density of 3.2 g/cc were used to simulate the solids in the feed slurry to the H-Coal reactor. Changes in the fines concentration in the slurry had a significant effect on bed expansion. The addition of 4 W % silicon carbide fines increased bed expansion by a factor of approximately 1.6 (Figure 2). An increase by a factor of 1.4-1.8 was measured when a 16 W % fines/kerosene slurry was tested. Thirty-five weight percent fines increased the expansion by a factor of 2.3-3.0 at a slurry velocity of 0.10 ft/sec.

The effect fines concentration has on the bed expansion can be explained on the basis of its effect on the slurry's apparent viscosity. Increasing the apparent viscosity would increase the bed expansion as it increases the drag force on the catalyst particles. A higher fines concentration results in a higher apparent viscosity and therefore a higher bed expansion.

Effect of Liquid Viscosity on Bed Expansion

Figure 3 shows the percent expansion for kerosene ($\mu \approx 1.4$ cp), Circosol 304 ($\mu \approx 5$ cp), and Circosol 306 ($\mu \approx 8.6$ cp) as a function of superficial liquid velocity at various gas rates. With the gas and liquid velocities both at 0.10 ft/sec, the bed expansion for Circosol 304 was higher than that for kerosene by a factor of about 3 while the bed expansion for Circosol 306 was higher by a factor of about 3.5. While most of this increase was due to the differences in viscosity, some of it was probably due to differences in other properties such as liquid density and surface tension.

Gas Holdup

A parameter of interest in the ebullated-bed is gas holdup, which affects liquid residence time and bed expansion. Gas holdups based on pressure-drop and bed-expansion data were calculated using the method outlined in Appendix A. As shown in Figure 4, the gas holdup in the catalyst bed with a kerosene/nitrogen system increased with increasing gas velocity. However, increasing liquid velocity reduced gas holdup. In the slurry system, kerosene with 15 W % fines, the

gas holdup showed a similar dependency on gas and slurry velocity (Figure 5). The estimated gas holdups for the slurry system showed more scatter, probably caused by uncertainties in pressure-drop measurements.

Fines Segregation

No significant segregation of fines was found during the three different studies with silicon carbide. The particle size distribution and weight concentrations were nearly identical for the feed, internal recycle and overhead streams at the conditions tested. Four conditions were studied during the nominal 4 W % fines concentration experiment and the nominal 16 W % fines concentration experiment. Six different overhead samples were examined during the 35 W % fines study. As shown in Table 7, each of these had basically the same particle-size distribution, indicating that significant fines segregation in the column and particle saltation in the lines did not occur during the slurry fluidization tests.

CATALYST CARRYOVER

The rates at which catalyst carried over into the ebullating-liquid recycle line and product withdrawal line were obtained as functions of the liquid and gas superficial velocities. In all cases, the carryover into the product line was only a fraction (20-50%) of that into the recycle line. In the kerosene/N_2 system, catalyst carryover into the recycle line was small (<0.1 lbm/hr ft^2) at gas and liquid velocities below 0.2 ft/sec. Directionally, carryover rate was slightly higher for the more viscous liquid systems (Circosol 304, 306) and the slurry systems (kerosene with 15 W %, 35 W % fines). In the system studied, significant catalyst carryover did not occur when bed expansion was maintained above 25-30%, and proper disengaging distance (40" minimum) was provided between the top of the bed and the bottom of the separator.

Catalyst carryover rates were also obtained at spouting-bed conditions (i.e. high gas velocity and low/zero liquid velocity). Specifically, this study was made to determine probable causes of catalyst carryover in the Pilot Plant reac-

tor during a previous unit upset.[4] The estimated maximum gas velocity in the Pilot Plant reactor was about 0.18 ft/sec, and the liquid velocity was low. The separation distance between the top of the bed and bottom of the separator in the Pilot Plant reactor was more than 60 inches.

The amounts of catalyst carryover measured in the cold-flow model using 1/16" spent 1442A catalyst fluidization with N_2 and kerosene are summarized in Table 8. At separation distances of 45" and higher, no catalyst carryover was observed even at gas velocities as high as 0.24 ft/sec. The net liquid velocity was zero, but the liquid level reached the top of the cup. At the same gas velocity but with a liquid velocity of 0.04 ft/sec and a lower separation distance of 30", catalyst carryover rate increased to about 3.6 lbs/hr-ft^2. However, this carryover rate was still lower than that observed in the Pilot Plant reactor (5 lb/hr-ft^2). Since the Pilot Plant reactor upset occurred during unit startup, the viscosity of the liquid in the reactor could have been higher than that of the kerosene used in the simulation study. The higher carryover rate in the Pilot Plant reactor was probably caused by the higher viscosity of the reactor fluid and flow channelling in the reactor.

[4] Personal Communication, H. Delooper to Allen Li, Oct. 1980.

SYSTEM CHARACTERISTICS

SYSTEM	FLUIDIZING MEDIA	FINES CONCENTRATION W %	LIQUID OR SLURRY DENSITY (G/CC)	LIQUID OR SLURRY VISCOSITY (CP)	LIQUID SURFACE TENSION (DYNES/CM)	CATALYST
1	Kerosene/Nitrogen	0	0.82	1.4	24	Spent
2	Kerosene/Fines/Nitrogen*	3-4	0.84	3.1	24	
3	Kerosene/Fines/Nitrogen	16	0.91	3.6	24	
4	Kerosene/Fines/Nitrogen	33-36	1.01	5.2 - 6.0	24	HDS-1442A+
5	Circosol 304/Nitrogen	0	0.89	4.6 - 5.5	35	
6	Circosol 306/Nitrogen	0	0.90	8.6	35	
7	PDU-10 Reactor Fluid	17-23	0.89	1.5 - 2.3	6	Amocat-1A
8	Kerosene/Nitrogen**	0	0.82	1.4	24	HDS-2A
9	Kerosene/Fines/Nitrogen**	32	0.91	5.6	24	

PROPERTIES OF CATALYST

CATALYST	HEYWOOD PROJECTED DIAMETER (CM)	LIQUID-SATURATED PARTICLE DENSITY (G/CC)
Spent HDS-1442A+	0.30	1.93 (Circosols) 1.90 (Kerosene)
Amocat 1A	0.24	1.65
HDS-2A	0.31	1.64

* Silicon carbide with median diameter of 17 microns and density of 3.2 G/CC.
** Amoco Study
+ Obtained from HRI PDU Run for a client

TABLE 2

TABLE 3

BED EXPANSION DATA

FOR KEROSENE/NITROGEN SYSTEM

V_L (ft/sec)	V_G (ft/sec)	Bed Expansion (%)
0.10	0.05	23
0.10	0.10	26
0.10	0.20	36
0.10	0.30	42
0.15	0.05	42
0.15	0.10	26
0.15	0.20	58
0.15	0.30	68
0.18	0.05	58
0.21	0.10	105
0.21	0.20	129

TABLE 4

BED EXPANSION DATA

FOR KEROSENE/FINES/NITROGEN SYSTEM

Nominal W % Fines	V_L (ft/sec)	V_G (ft/sec)	Bed Expansion (%)
4	0.10	0.05	39
	0.15	0.05	66
	0.20	0.05	92
16	0.08	0.05	26
	0.08	0.10	30
	0.08	0.20	35
	0.10	0.05	46
	0.10	0.10	50
	0.10	0.20	55
	0.15	0.05	76
	0.15	0.10	84
	0.15	0.20	89
35	0.05	0.05	29
	0.05	0.10	35
	0.05	0.20	49
	0.08	0.05	44
	0.08	0.10	51
	0.08	0.20	65
	0.10	0.05	68
	0.10	0.10	75
	0.10	0.20	81

TABLE 5

BED EXPANSION DATA

FOR CIRCOSOL 304/NITROGEN SYSTEM

V_L (ft/sec)	V_G (ft/sec)	Bed Expansion (%)
0.05	0.05	31
0.05	0.10	33
0.05	0.20	33
0.08	0.05	50
0.08	0.10	54
0.08	0.20	54
0.10	0.05	75
0.10	0.10	75
0.10	0.20	80
0.15	0.05	135
0.15	0.10	144
0.15	0.20	174

TABLE 6

BED EXPANSION DATA

FOR CIRCOSOL 306/NITROGEN SYSTEM

V_L (ft/sec)	V_G (ft/sec)	Bed Expansion (%)
0.05	0.03	38
0.05	0.05	41
0.05	0.10	48
0.05	0.15	55
0.05	0.20	61
0.10	0.03	90
0.10	0.05	88
0.10	0.11	88
0.10	0.15	85
0.10	0.19	101
0.14	0.20	157
0.15	0.06	155
0.15	0.11	169
0.15	0.17	144
0.16	0.02	136

TABLE 7

PARTICLE SIZE DISTRIBUTION

GAS VELOCITY FT/SEC	SLURRY VELOCITY FT/SEC	SAMPLE STREAM	FINES W %	SMALLER THAN (MICRONS) 10%	50%	90%
.025	.023	Feed	3.5	7.77	16.6	33.3
		Overhead	3.5	7.48	16.6	31.7
		Recycle	3.5	7.99	17.1	30.2
.102	.025	Feed	3.5	7.09	16.5	30.1
		Overhead	3.5	5.62	15.3	29.7
		Recycle	3.5	7.24	16.8	32.4
.027	.194	Feed	4.4	4.93	15.6	29.9
		Overhead	4.4	6.19	16.2	31.9
		Recycle	4.4	5.07	15.1	29.4
.198	.199	Feed	4.4	5.50	15.7	30.9
		Overhead	4.4	4.26	15.4	32.8
		Recycle	4.4	4.59	15.0	29.3
.022	.050	Feed	14.9	6.71	16.6	30.9
		Overhead	14.9	6.26	16.4	30.4
		Recycle	14.9	6.46	16.4	30.4
.137	.050	Feed	14.4	5.86	16.3	30.4
		Overhead	14.4	5.94	15.8	30.9
		Recycle	14.4	6.33	16.2	30.7
.023	.150	Feed	16.8	6.43	16.5	31.4
		Overhead	16.8	6.03	15.8	30.6
		Recycle	16.8	5.86	16.3	31.9
.144	.150	Feed	16.2	6.90	16.9	31.4
		Overhead	16.2	6.50	16.5	30.0
		Recycle	16.2	6.94	16.6	30.6
.022	.025	Overhead	35.8	6.36	16.0	30.2
.180	.025	Overhead	35.8	6.57	16.2	29.3
.023	.100	Overhead	36.0	6.50	15.9	29.6
.092	.100	Overhead	36.0	5.96	15.4	28.9
.020	.200	Overhead	35.3	6.79	16.2	29.9
.088	.206	Overhead	36.2	5.99	15.5	28.9

TABLE 8

CATALYST CARRYOVER INTO RECYCLE CUP

AT SPOUTING CONDITIONS

SYSTEM: N_2 - KEROSENE

CATALYST: 1/16" SPENT CATALYST, HDS-1442A

COLUMN DIAMETER: 6 INCHES

SEPARATION DISTANCE (inch)	GAS VELOCITY (ft/sec)	LIQUID VELOCITY (ft/sec)	CATALYST CARRYOVER (lb/hr)	(lb/hr-ft^2)
60	0.24	---	none	-
45	0.24	---	none	-
37	0.24	---	0.1	0.5
30	0.24	---	0.1	0.5
30	0.24	0.04	0.7	3.6

FIGURE 2

EFFECT OF FINES CONCENTRATION ON BED EXPANSION

V_G GAS VELOCITY IN FT/SEC

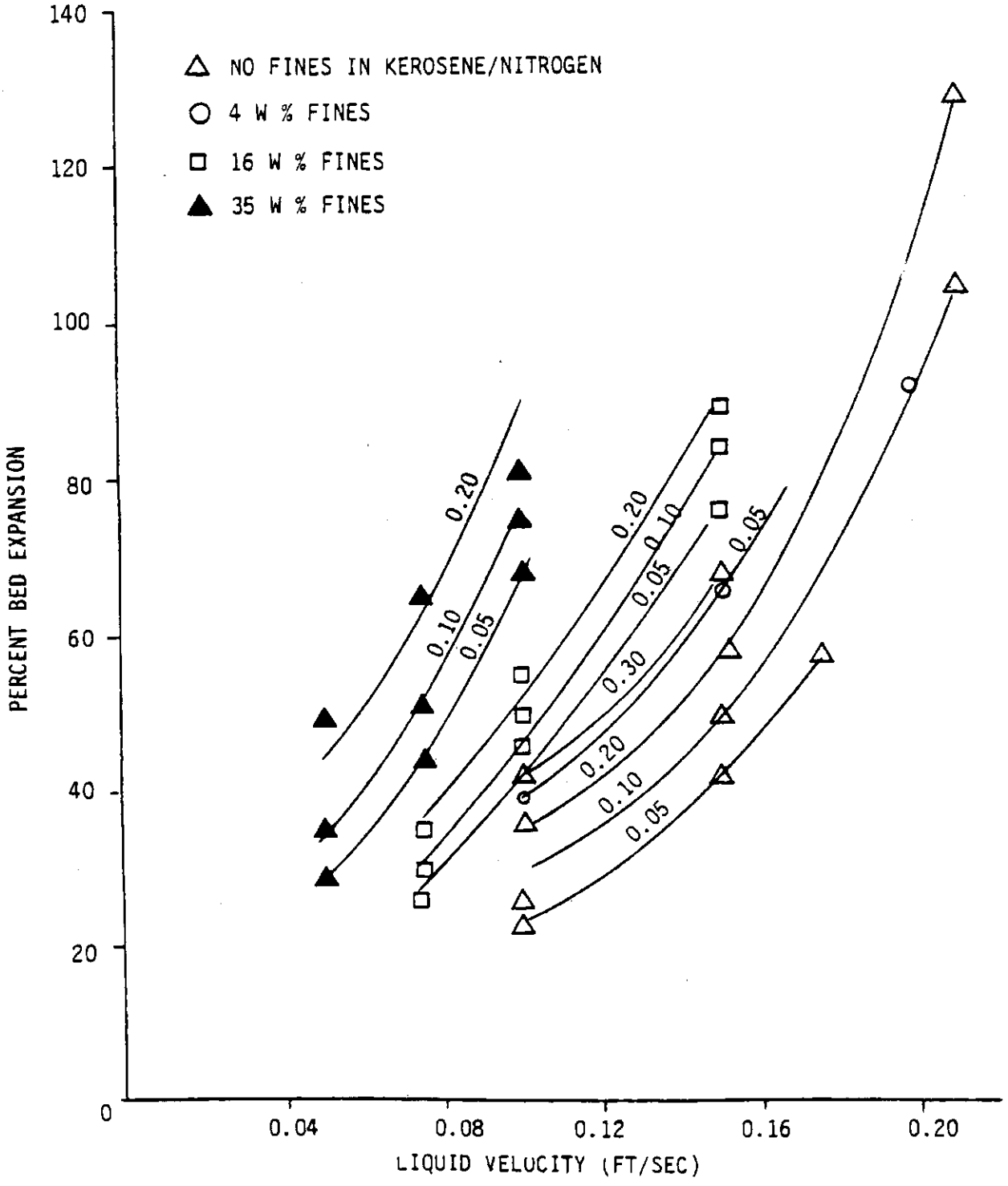


FIGURE 3

EFFECT OF LIQUID VISCOSITY ON BED EXPANSION

V_G GAS VELOCITY IN FT/SEC

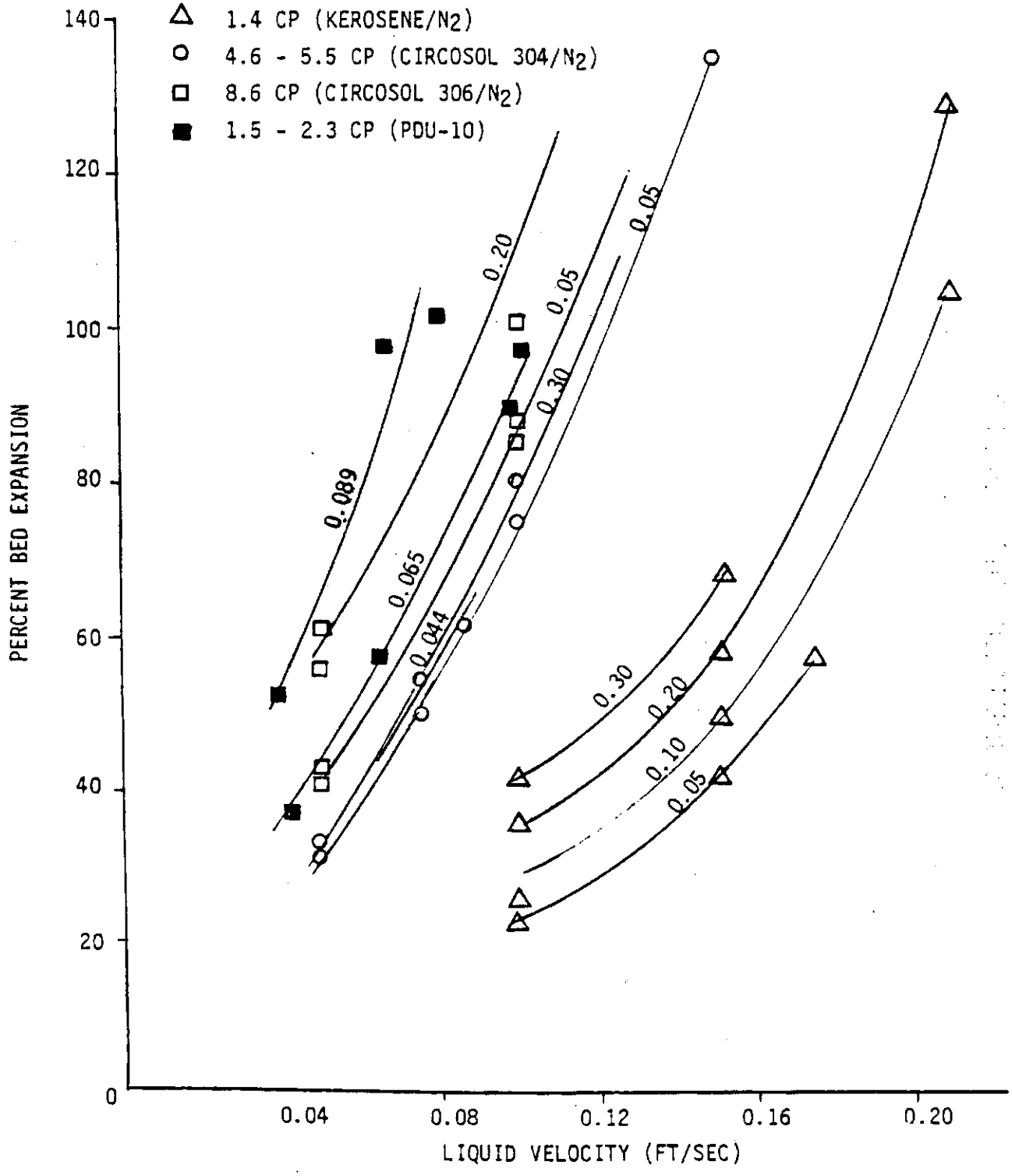


FIGURE 4

GAS HOLDUP IN KEROSENE-NITROGEN-CATALYST SYSTEM

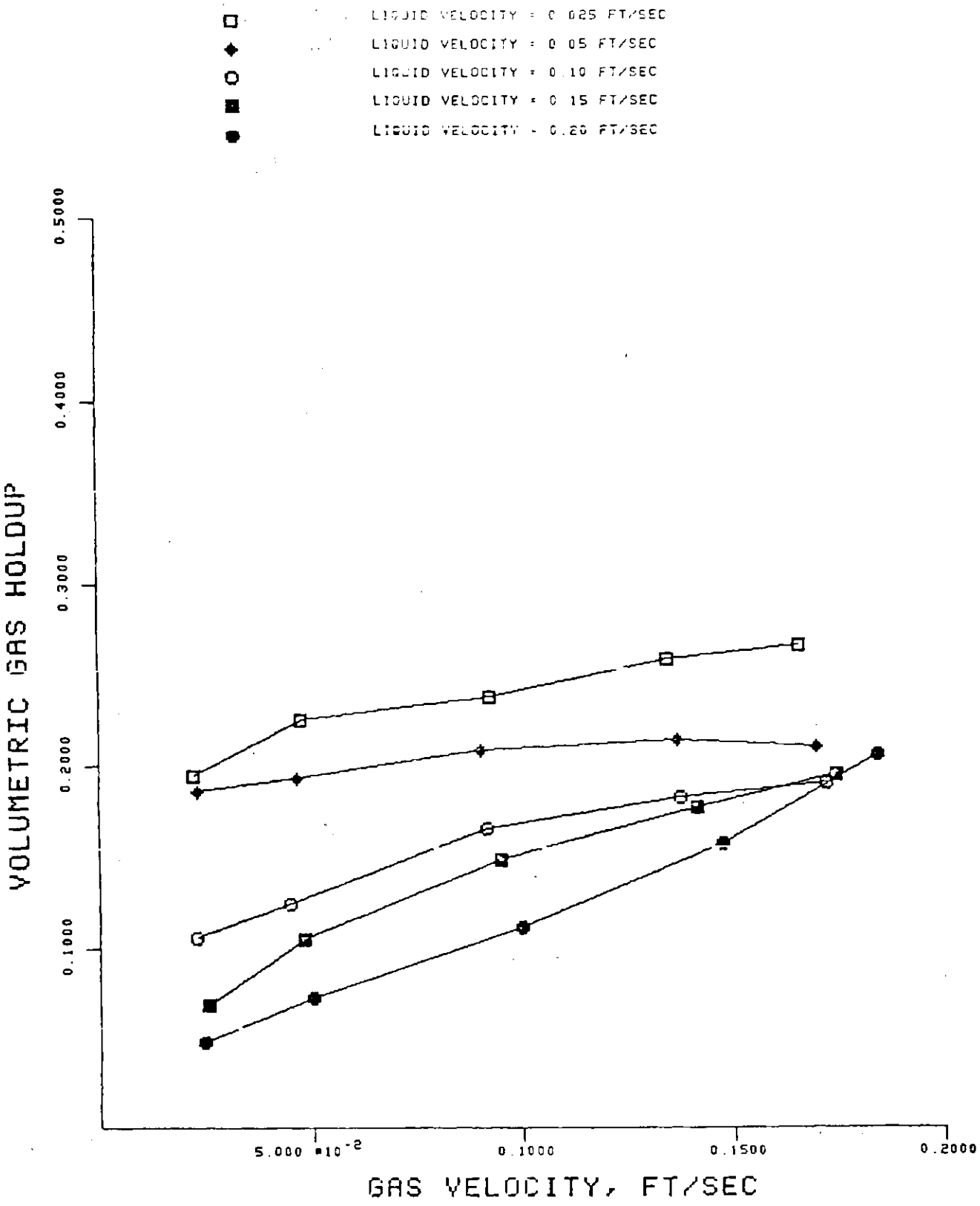
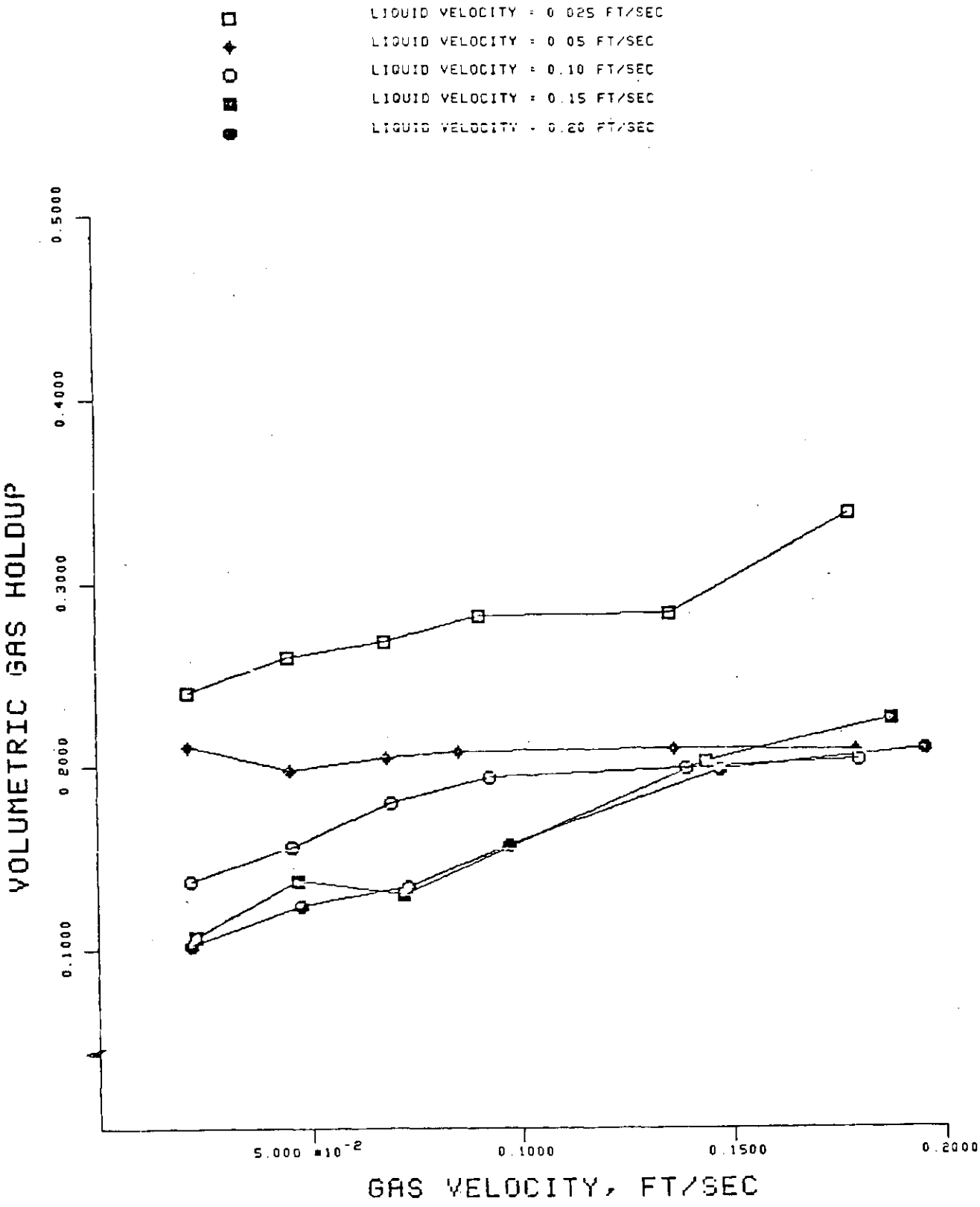


FIGURE 5

GAS HOLDUP IN KEROSENE-NITROGEN-CATALYST
15% FINES SYSTEM



SPHERICAL CATALYST STUDY

Two samples of spherical alumina beads from American Cyanamid were fluidized with kerosene/nitrogen in the 6-inch-diameter column. The two spherical catalysts differ only with respect to particle size distribution. Their physical properties are listed in Table 9. Although the median diameters of both samples were 2.0 mm, one catalyst had a diameter ratio of $D_{97}/D_3 = 2^*$ while the other sample had a wider size distribution of $D_{97}/D_3 = 3.0$. 2.0 mm diameter is equivalent to an average HDS-1442A extrudate. The Heywood equivalent diameter of an average HDS-1442A extrudate is 3.0 mm.

Bed Expansion

Bed expansion for both catalyst varied strongly with superficial liquid velocity. As shown in Figures 6 and 7, there was relatively little expansion until the catalyst fluidized at a superficial liquid velocity of about 0.05 ft/sec. Expansions then increased almost linearly with increasing liquid flow. At the same gas velocity, the bed expansions at high liquid velocities were significantly higher for the narrow-size-range catalysts.

Changes in gas velocity at liquid velocities below approximately 0.1 ft/sec did not apparently affect the bed expansion. At liquid velocities above 0.1 ft/sec, increasing gas velocity increased bed expansion slightly until reaching a gas velocity at which no further expansion occurred. Increasing gas velocity above this velocity caused slight contraction of the bed. Increasing gas velocity further caused violent bubbling through the top of the bed and further contraction increased with increasing liquid rates.

*D_{97}/D_3 = Ratio of diameter at which 97% (by weight) is smaller to diameter at which 3% is smaller.

Catalyst Carryover

The rising of individual catalyst particles above the bed was monitored by screening the recycle and product streams. There was virtually no carryover of the narrow-size-range catalyst at all liquid and gas rates. However, the wide-size-distribution catalyst was carried into the recycle line at all liquid velocities when gas velocity was above 0.1 ft/sec. No catalyst was found in the product stream. Analysis on the wide-distribution catalyst particles carried over from the recycle stream revealed that the majority were in the 10-20 mesh (0.841-1.68 mm) size range. Although accurate carryover rates were not measured, estimates showed this rate to be 2.6 to 5.3 lbs of wet catalyst per hour per square foot of reactor cross-sectional area.

Bed Stratification

Layering of the catalyst bed by particle diameter was observed during the wide-size-distribution runs. To quantify this, the bed was ebullated at 0.075 ft/sec and 0.05 ft/sec liquid and gas velocities, respectively, and then suddenly slumped. During withdrawal of the catalyst from the column, samples were taken from different levels and analyzed for size. Table 10 summarizes these results which show that stratification by size occurred at moderate liquid and gas rates using the wide-distribution catalyst. Stratification was not apparent with the narrow distribution catalyst.

Catalyst Suitability for H-Coal Application

From a fluid dynamics point of view, a spherical catalyst with a diameter ratio (D_{97}/D_3) of 2.0 or less is acceptable for use in the ebullated-bed reactor. A diameter ratio of 3.0 or larger is not recommended as the bed of wide-size-distribution catalyst contracts, stratifies, and carries over much more readily.

TABLE 9

ALUMINA BEAD

PHYSICAL PROPERTIES

HRI No.	4486	4487
American Cyanamid No.	5439	5440
Compacted Bulk Density, g/ml	0.58	0.60
Total Pore Volume, ml/g (mercury porosimetry)	0.66	0.66
Liquid-Filled Bead Density, g/ml (pore-saturated with 0.8 spec. grav. fluid)	1.44	1.44
Median Bead Diameter, mm	2.0+	2.0+
Diameter Ratios*		
D_{90}/D_{10}	1.7	2.1
D_{95}/D_5	1.9	2.7
D_{97}/D_3	2	3
Screen Analysis (U. S. Mesh), % by Weight		
-8 + 12	59	50
-7 + 14	95	81
-6 + 16	>99	92
-6 + 20	>99	>99

*D_{90}/D_{10} = Ratio of diameter at which 90% (by weight) is smaller to diameter at which 10% is smaller.

+2.0mm is an equivalent sphere diameter (based on particle volume/surface area) of an extrudate where D=1.6 mm and L=4.3 mm.

TABLE 10

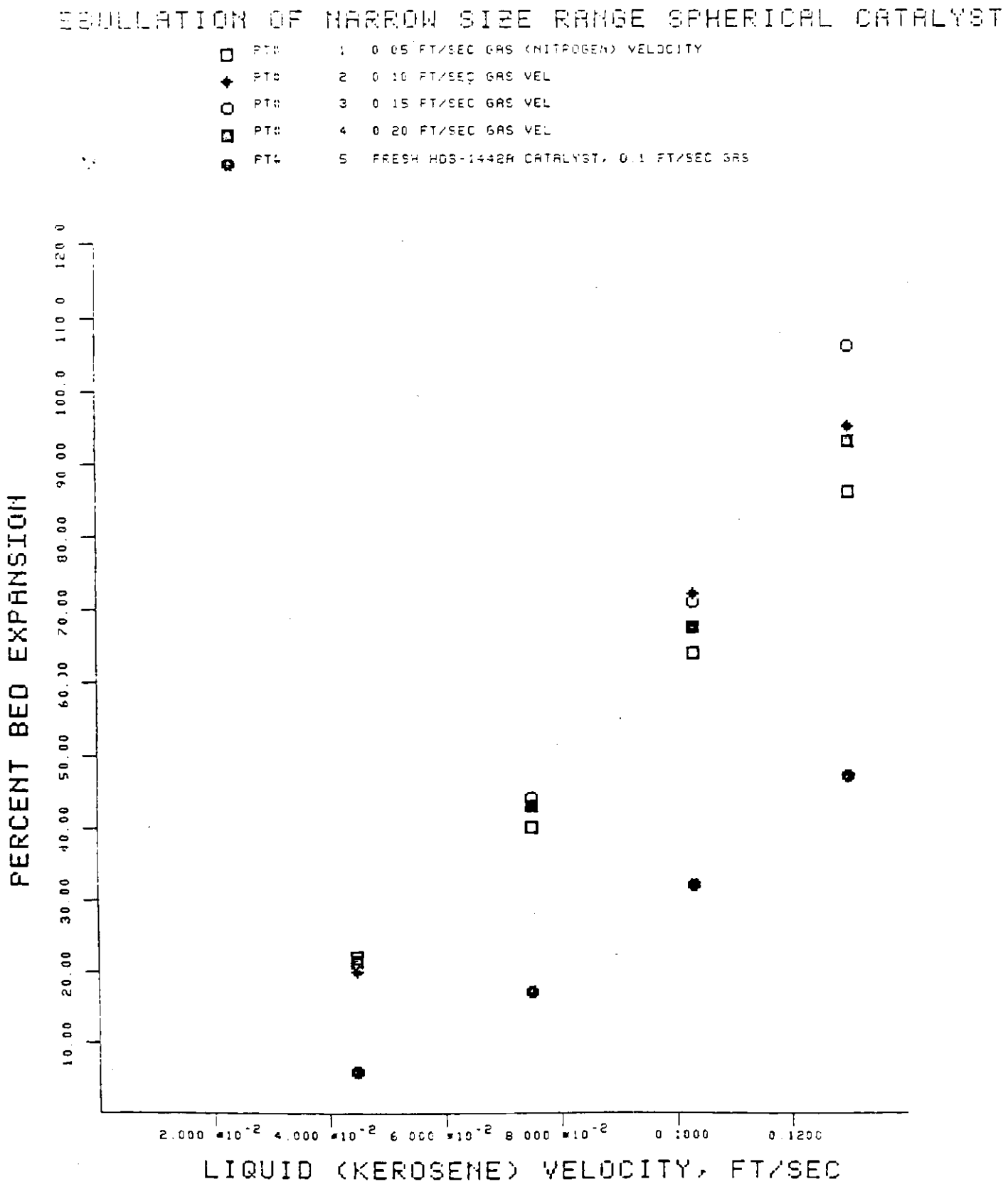
STRATIFICATION OF WIDE-DISTRIBUTION CATALYST
DURING EBULLATION

SCREEN SIZE (mesh)	SAMPLE LOCATION+ 0 ft W %	0.5 ft W %	1.0 ft W %	1.5 ft W %	*2.0 ft W %
+6	4.43	3.16	0.40	0.19	1.99
6-8	51.26	45.57	20.80	12.18	41.50
8-10	31.06	34.58	33.35	30.67	34.03
10-12	11.29	13.85	28.23	33.30	16.90
12-16	1.89	2.58	15.33	20.71	5.10
16-20	0.02	0.11	1.83	2.88	0.44
-20	0.04	0.15	0.06	0.07	0.04

+Distances indicated are measured from top of grid plate.

*Funneling of catalyst resulted in poor sample.

FIGURE 6


EBULLATION OF NARROW SIZE RANGE SPHERICAL CATALYST
PT# 1 0 05 FT/SEC GAS (NITROGEN) VELOCITY
PT# 2 0 10 FT/SEC GAS VEL
PT# 3 0 15 FT/SEC GAS VEL
PT# 4 0 20 FT/SEC GAS VEL
PT# 5 FRESH HDS-1442A CATALYST, 0.1 FT/SEC GAS
PERCENT BED EXPANSION
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
90.00
100.0
110.0
120.0
2.000 *10^-2
4.000 *10^-2
6.000 *10^-2
8.000 *10^-2
0.1000
0.1200
LIQUID (KEROSENE) VELOCITY, FT/SEC