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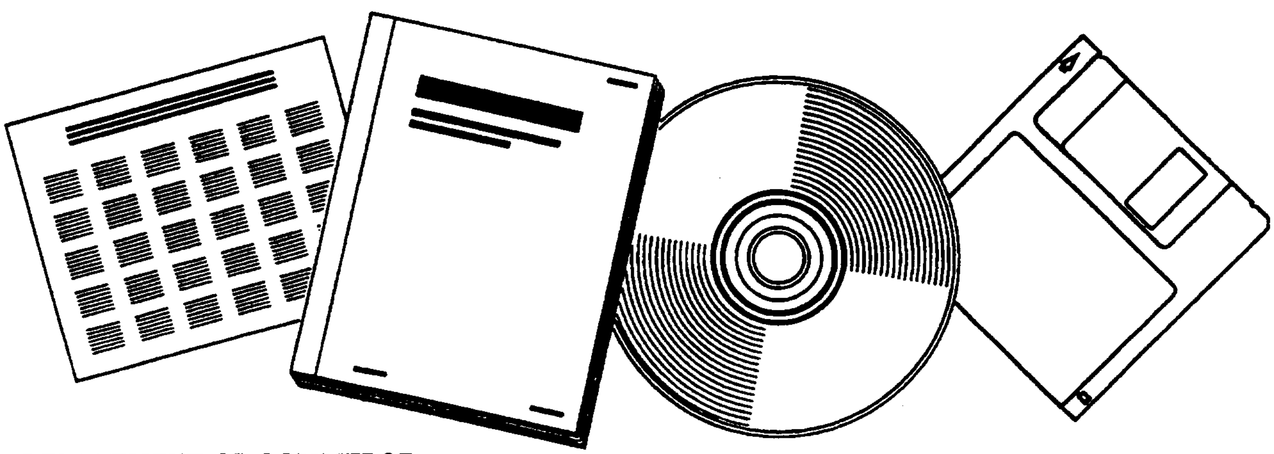
AIR PRODUCTS AND CHEMICALS, INC.
ALLENTOWN, PA

NOV 1982



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CATALYST AND REACTOR DEVELOPMENT FOR A LIQUID PHASE FISCHER-TROPSCH PROCESS

QUARTERLY TECHNICAL PROGRESS REPORT
FOR PERIOD 1 JULY 1982 - 30 SEPTEMBER 1982

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PATENT STATUS

This technical report is being transmitted in advance of DOE patent clearance and no further dissemination or publication shall be made of the report without prior approval of the DOE Patent Counsel.

TECHNICAL STATUS

This technical report is being transmitted in advance of DOE reviews and no further dissemination or publication shall be made of the report without prior approval of the DOE Project/Program Manager.

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ABSTRACT

Two major tasks were current in the eighth quarter of the Air Products and Chemicals Inc./U.S. Department of Energy contract "Catalyst and Reactor Development for a Liquid Phase Fischer-Tropsch Process": (1) Slurry Catalyst Development, and (2) Slurry Reactor Design Studies.

Parametric gas phase screening of supported conventional catalysts continued, enabling the optimum for diesel range product to be chosen for slurry testing.

Seven supported molecular clusters were tested in the slurry phase. One gave results similar to a previous screening test; a high 1-alkene content and small Schulz-Flory deviations in the $C_{10}+$ range, but with a cut off at $\sim C_{28}$.

The slurry test of another cluster catalyst showed a high bulk activity, with conversion levels four times higher than the baseline catalyst, and deviations from the Schulz-Flory limitation that increased with time. Up to 55.1 wt% C_{10}-C_{20} was produced with a low 5.7 wt% CH_4 yield. The results demonstrate potential for a good diesel fuel catalyst.

Shakedown runs and initial gas holdup determinations were completed for the 12" column, and a statistical experimental design was produced to maximize the information gained from this program.

The use of a hot-film anemometer probe to measure bubble diameter in the three phase systems was successfully demonstrated, and programing to interpret the data was begun. Viscosity measurements for hydrocarbon slurries showed non-Newtonian behavior, and are expected to result in a significant correlation parameter.

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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.

Therefore, Air Products (APCI), under contract to the DOE, has undertaken a program in catalyst and reactor development for a slurry phase Fischer-Tropsch process. This contract spans 36 months and is divided into four major tasks. This report describes the work accomplished during the eighth quarter.

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 effect the design of slurry reactors, (2) establish 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 pilot plant 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."

3.1.3 Sub-Task 2d - Metal Cluster Catalyst Preparation and Screening Tests

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

Shakedown and two phase runs without heat transfer internals were completed on the 12" column. Agreement on gas holdup between the experimental runs and literature correlations was reasonable. In order to maximize information, a seven-variable Box-Behnken experimental design was utilized producing 106 experimental runs to be conducted on the 12" column. This type of approach represents the most efficient method of studying the hydrodynamics of the 12" column.

A computer program to quantify the extent of liquid backmixing was improved to take into account the tracer injection location. The higher dispersion coefficient that was previously determined above the distributor plate was shown not to be due to the injection location.

The heater to be used in the heat transfer coefficient determinations was found to be too short to allow end heat leakage to be neglected. A longer heater is presently being tested to see if it will give accurate heat transfer coefficients.

The ability of a hot-film anemometer probe to determine bubble diameter in a three phase system was successfully demonstrated in the 5" column. The anemometer probe has been ordered and is expected to arrive in October.

Preliminary slurry viscosity data on isoparaffin systems shows dilatant behavior. The data is presently being analyzed to obtain a two parameter equation of viscosity as a function of shear rate.

4.0 ACKNOWLEDGEMENTS

The contributions to this program by C. B. A. Freed, P. A. Greene, J. M. LaBar, M. Louie, S. E. Madison, M. L. Morris, L. E. Schaffer and E. G. Valagene are gratefully acknowledged.

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5.0 RESULTS AND DISCUSSION

5.1 Task 2 - Slurry Catalyst Development

5.1.2 Sub-Task 2c - Catalyst Preparation and Slurry Reactor Tests

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5.1.3 Sub-Task 2d - Metal Cluster Catalyst Preparation and Screening Tests

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5.2 Task 3 - Slurry Reactor Design Studies

5.2.1 5" Cold Flow Simulator

(i) Liquid Dispersion

A Fortran program was written to numerically solve the Fick's Law equation,

$$\frac{\partial C}{\partial t} = E_L \frac{\partial^2 C}{\partial Z^2} \qquad 1)$$

for the boundary conditions where a tracer impulse is inserted at any longitudinal location:

$$\left.\frac{\partial C}{\partial Z}\right)_{0,\ T} = \left.\frac{\partial C}{\partial Z}\right)_{L,\ T} = 0 \qquad 2),\ 3)$$

where L = extended bed height, and

$$C(Z, 0) = \begin{cases} 0, & 0 \leq Z < Z_1 \\ C_o, & Z_1 \leq Z \leq Z_2 \\ 0, & Z_2 < Z \end{cases} \qquad 4)$$

The program then generated a family of residence time distribution (RTD) curves, plotted in Figures 1 to 4, for sample ports located at 3.5", 14.75", 29.75", and 44.58" above the distributor plate, with an expanded bed height of 48 inches.

The model represents the tracer injection as being evenly distributed across the column cross section within a 0.2" band width at time zero. In reality, tracer is injected through three 1/4" copper lines located 120° apart. Figures 1 to 4 place the injection midpoint at 2.1" while in Figure 5, the tracer midpoint is 0.1" above the distributor. Except for port 1, located 3.5" above the distributor, there are negligible differences between having the injection at 2.5" and having it at 0.1". Even for port 1, comparing Figures 1 and 5, it is only when dispersion coefficients are low that there is a detectable difference. Thus either injection location can be used to determine dispersion coefficients.

5.2.2 12" Cold Flow Simulator

(i) Experimental Design

In order to maximize information from the experimental data, a seven-variable Box-Behnken experimental design (SEVBBED) was utilized. Because it is unlikely that the silica and iron oxide particles can be treated as continuous variables, two separate SEVBBEDs, one for each solid type, were constructed.

Eliminating unnecessary repeats between the two designs produced Tables 1 and 2, showing the 106 experimental runs to be conducted on the 12" column.

This type of approach represents the most efficient method of operating the 12" column, and will enable the experimental program to be completed on schedule.

(ii) Gas Holdup

Shakedown runs and an operational readiness inspection were completed on the 12" cold flow simulator to assure that the system was operating correctly and safely. Gas holdup measurements were obtained for the water/air and isoparaffin/ nitrogen two phase systems and are shown in Tables 3 and 4, and Figures 6 and 7 respectively. The average gas holdup value, EG EXP, was obtained using the expanded and settled bed height. The intermediate values, EG12 to EG34, were obtained using the manometer tubes. Differences between these were probably due to experimental error in determining the expanded bed height. However, for either method, agreement with the literature for these runs was reasonable.

(iii) Bubble Diameter Measurement

A successful hot-film anemometer probe demonstration was performed in the 5" column. Quicker delivery time, anticipated lesser wear than an optical probe, and a sixty-day return guarantee are among the reasons why the anemometer prove was ordered instead of an optical probe for bubble diameter measurements.

A bubble diameter analysis program was obtained from Dennis Smith of Pittsburgh Energy Technology Center (PETC). While all program incompatibilities between the APCI and PETC computers have been resolved, there is still difficulty in getting satisfactory convergence when the program is run with sample data. Work is now focusing on testing alternative convergence methods.

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(iv) Slurry Viscosity Measurements

Preliminary information using a "Contraves" rheomat 115 viscometer showed dilatant behavior. In iron oxide slurries, the highest viscosity obtained was 14.2 cp at a shear rate of 1007 s^{-1} for a 30 wt%, 0-5 μm sample. The three viscosity vs shear rate curves obtained for the 0-5 μm, 90-106 μm iron oxide, and 90-115 μm silica systems, all at 30 wt%, will be correlated according to the relationship,

$$\mu = -m\ (dV_x/dy)^{n-1} \qquad 5)$$

where, μ = viscosity, g/(cm.sec) = [100 centipoise]

dV_x/dy = velocity gradient in y direction = shear rate, s^{-1}

m, n = coefficients to be determined.

6.0 EXPERIMENTAL

6.1 Task 2 - Slurry Catalyst Development

6.1.2 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

6.2.1 12" Cold Flow Simulator

(i) Heat Transfer

Figure 8 illustrates the 8" heater assembly that has been constructed to determine three phase heat transfer coefficients. If a cylindrical heater is long enough, the heater midpoint temperature difference, $T_{SM} - T_B$, should be unaffected by heat leak from the heater top and bottom. In this case,

$$T_{SM} - T_B = Q/SLh \qquad 6)$$

Where,
- h = local heat transfer coefficient, Btu/hr ft^2 °F
- L = length of the heating coil inside the heater, ft
- Q = power supplied to the heater, Btu/hr
- S = tube circumference, 0.594 ft
- T_B = bulk temperature, °F
- T_S = surface temperature, °F
- T_{SM} = temperature at the heater surface midpoint, °F

However, if the heater is too short or the heat transfer coefficient too low, a significant fraction of the total heat leaves at the heater ends and,

$$T_{SM} - T_B < Q/SLh \qquad 7)$$

leading to erroneous heat transfer measurements.

The cartridge heater in Figure 8 was therefore theoretically modeled to predict how well eqn. 6) was satisfied. In Figure 9, the normalized temperature difference, defined by:

$$NDT = (T_S - T_B)/(Q/SLh) \qquad 8)$$

is plotted against heater length at different h values. If NDT ~1, then no error is introduced in taking the midpoint temperature only. However, Figure 9 shows that for h $\leq$500 Btu/hr ft °F, erroneous measurements would occur from midpoint temperature measurement. Since the present correlations predict h at anywhere from 200 to 900 Btu/hr ft °F, the theoretical model showed that the cartridge heater was inadequate at the lower h range.

Experimentally measured temperature profiles were indeed non-linear over this range, indicating the need for a longer heater coil.

A 19" cartridge heater, identical otherwise to the 8" heater, was tested by measuring its temperature difference profile (see Figure 10). A successful test would have had: 1) a flat slope in the temperature profile, 0 to 1" from the midpoint, and 2) a temperature difference maximum at the midpoint. While the temperature difference from 0 to 1" was reasonably flat, varying only 6%, the midpoint temperature difference was not the maximum. This unexpected profile was due to one or both of the following reasons: 1) uneven heat transfer coefficients along the heater length, possibly due to differing amounts of water shear across the heater during the test, or 2) uneven heating.

To test these two possible reasons, the water test will be repeated changing the level of the inlet water stream. If this has no effect, then the profile in Figure 10 can be attributed to uneven heating only and a different heater will be used. If the profile does substantially change, then a separate forced convection air test will be run to determine if the heater is heating evenly.

7.0 REFERENCES

1. Akita, K., and Yoshida, Y., Ind. Eng. Chem. Proc. Des. Dev., 1973, 12, 76.

2. Hikita, H., and Kikukawa, Chem. Engng. J., 1973, 81, 74.

3. Pilhofer, T. H., Bach, H. F., and Mangartz, K. H., ACS Symp. Ser., 1978, 65, 372.

8.0 FIGURES

FIGURE 1

5 INCH COLD FLOW SIMULATOR

NORMALIZED CONCENTRATION VS TIME CURVES
AT 3.5 INCHES FOR 48 INCH BED
ANALYTICAL SOLUTION FOR 0.0–0.2 INCH INJECTION

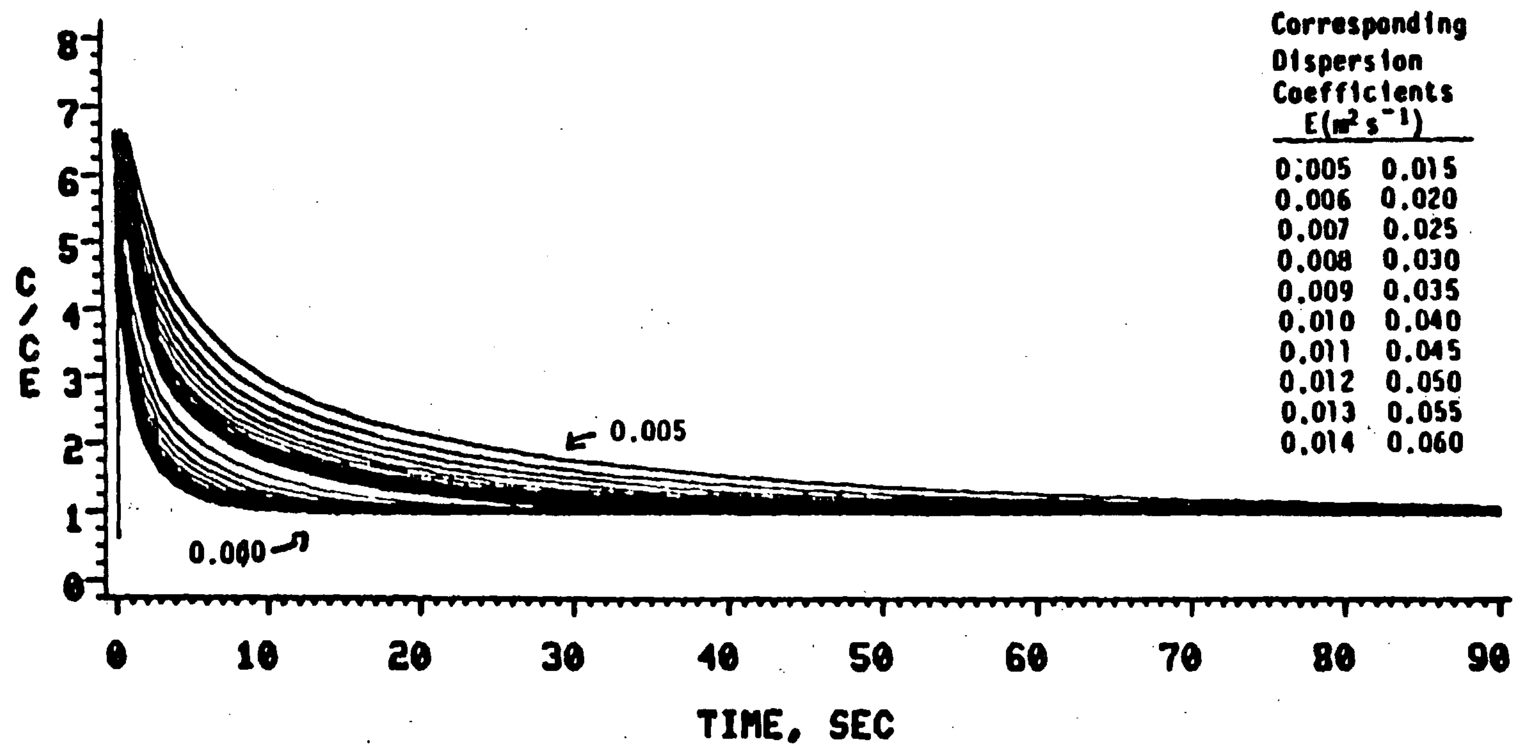

FIGURE 2

5 INCH COLD FLOW SIMULATOR

NORMALIZED CONCENTRATION VS TIME CURVES
AT 14.75 INCHES FOR 48 INCH BED
ANALYTICAL SOLUTION FOR 2.0–2.2 INCH INJECTION

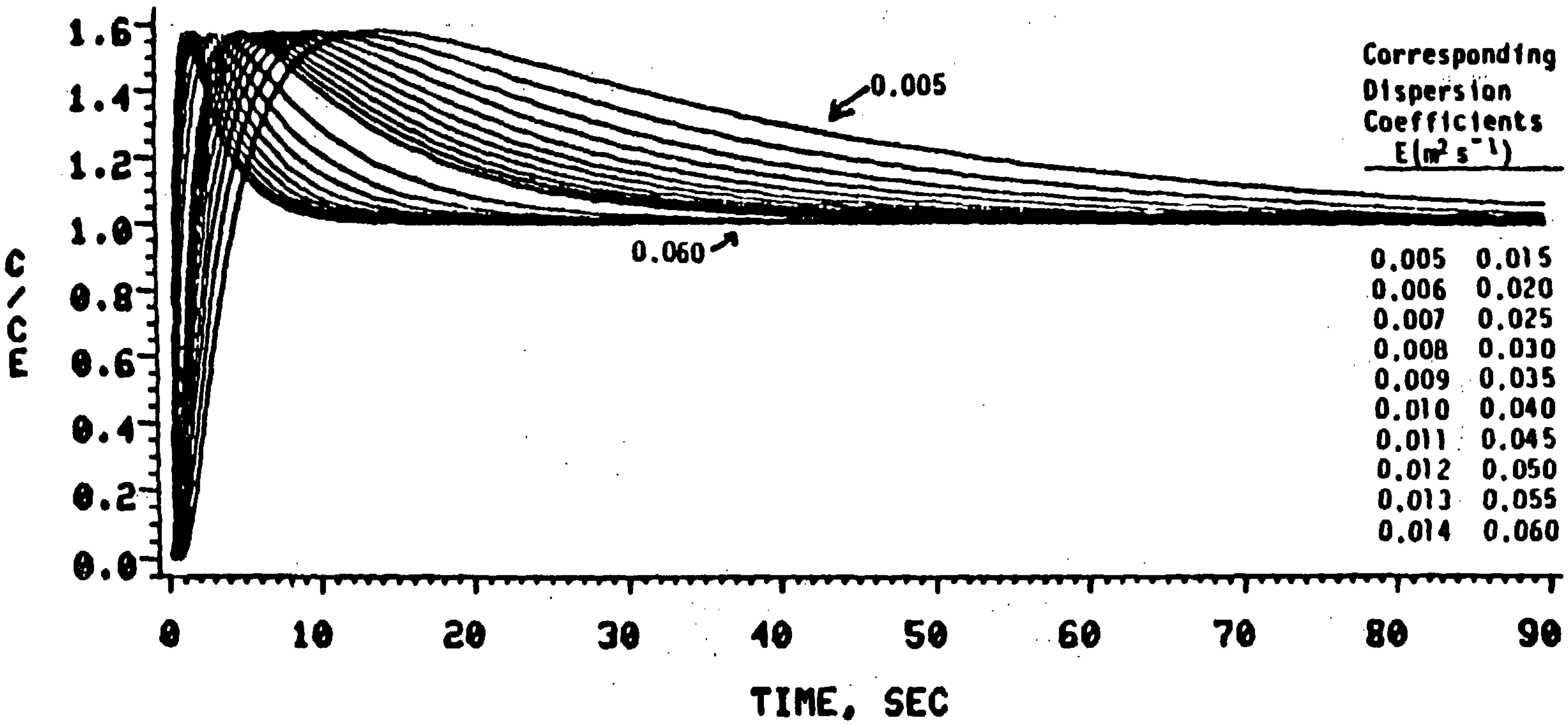

FIGURE 3

5 INCH COLD FLOW SIMULATOR

NORMALIZED CONCENTRATION VS TIME CURVES
AT 29.75 INCHES FOR 48 INCH BED
ANALYTICAL SOLUTION FOR 2.0–2.2 INCH INJECTION

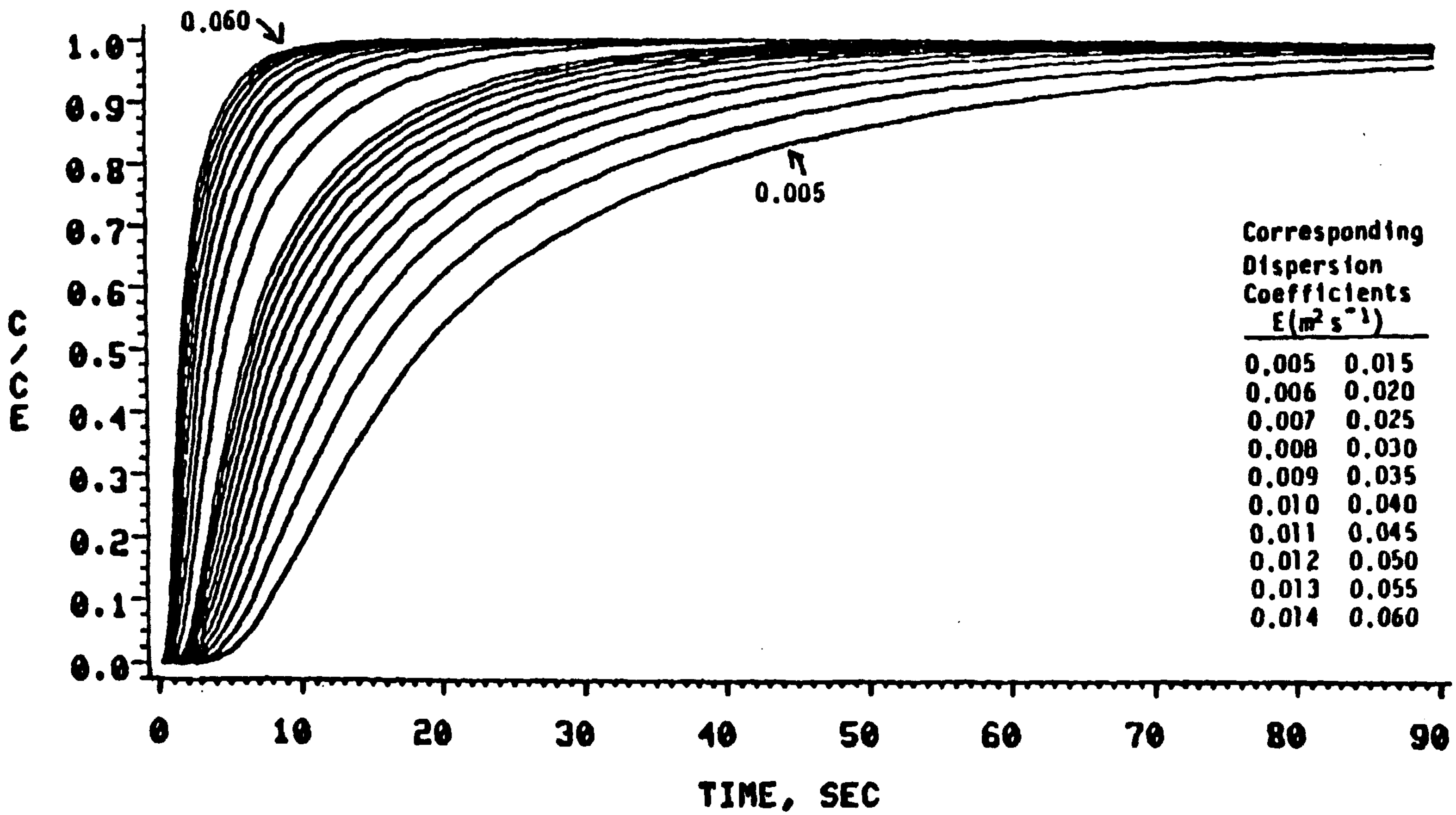

FIGURE 4

5 INCH COLD FLOW SIMULATOR

NORMALIZED CONCENTRATION VS TIME CURVES
AT 44.58 INCHES FOR 48 INCH BED
ANALYTICAL SOLUTION FOR 2.0-2.2 INCH INJECTION

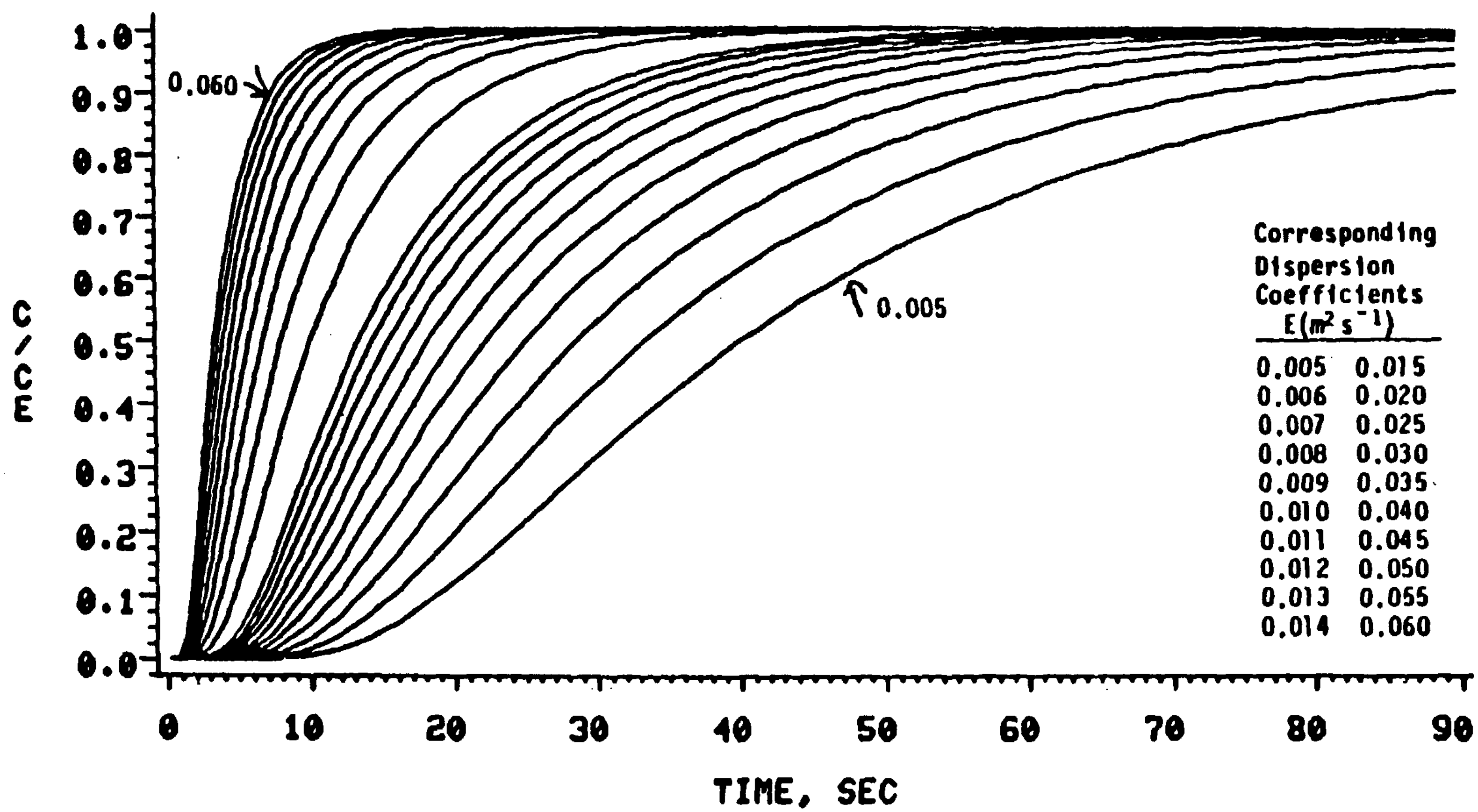

FIGURE 5

5 INCH COLD FLOW SIMULATOR

NORMALIZED CONCENTRATION VS TIME CURVES
AT 3.5 INCHES FOR 48 INCH BED
ANALYTICAL SOLUTION FOR 2.0–2.2 INCH INJECTION

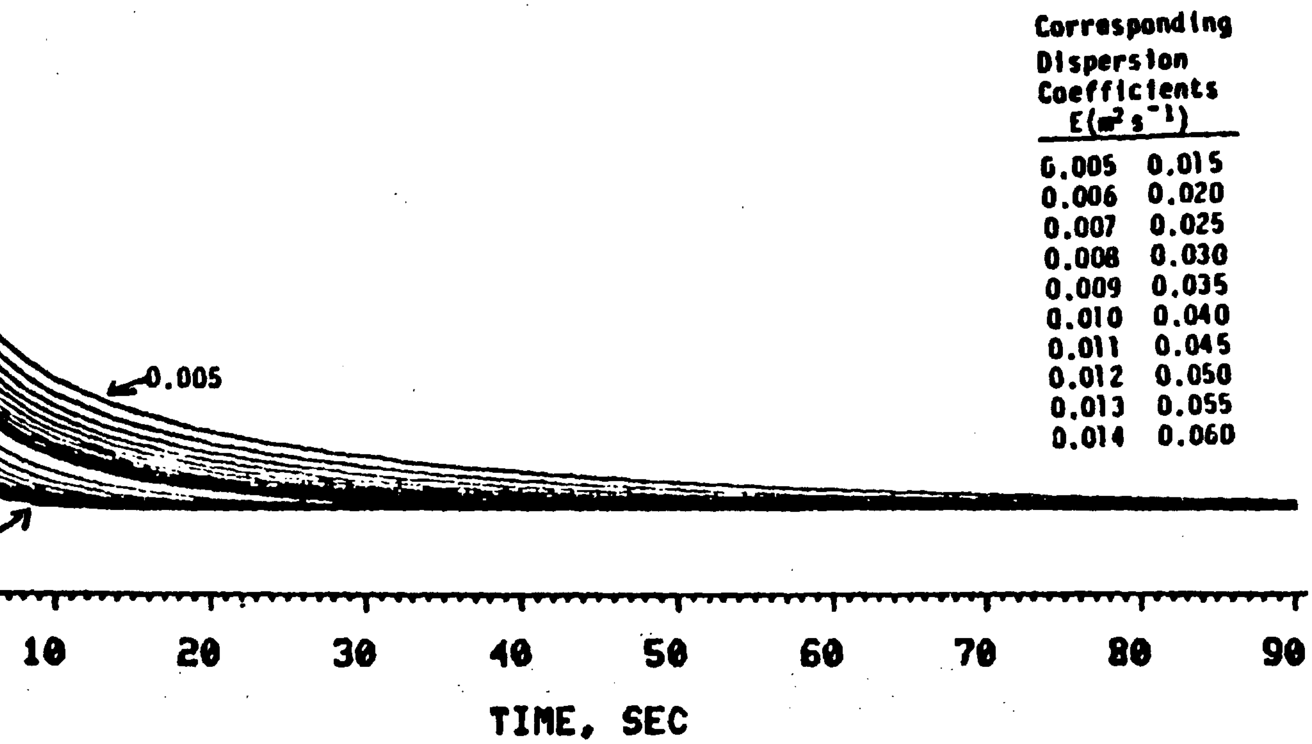

FIGURE 6

12 INCH COLD FLOW SIMULATOR

WATER, AIR

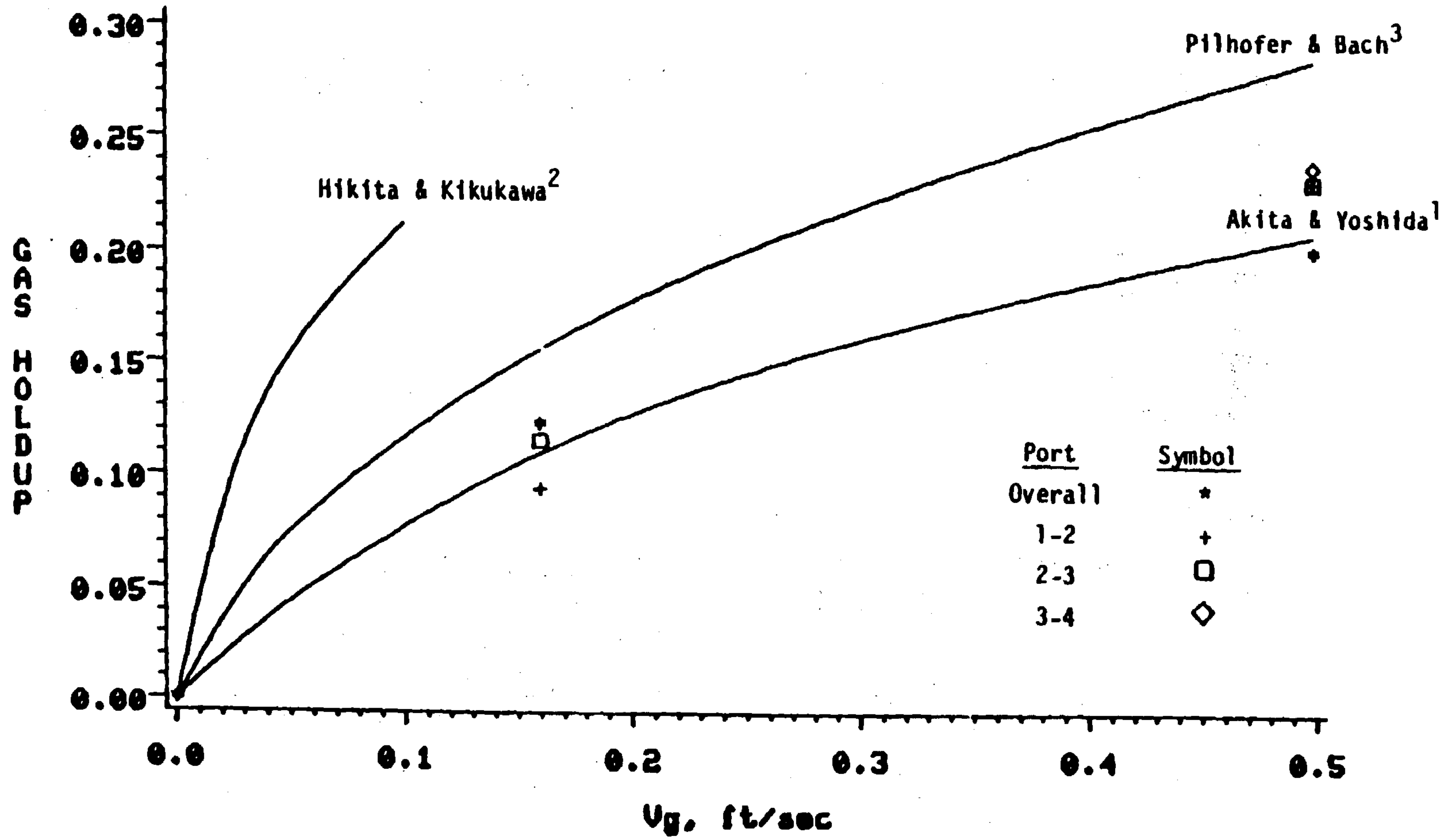

FIGURE 7

12 INCH COLD FLOW SIMULATOR

ISOPARAFFIN, N2

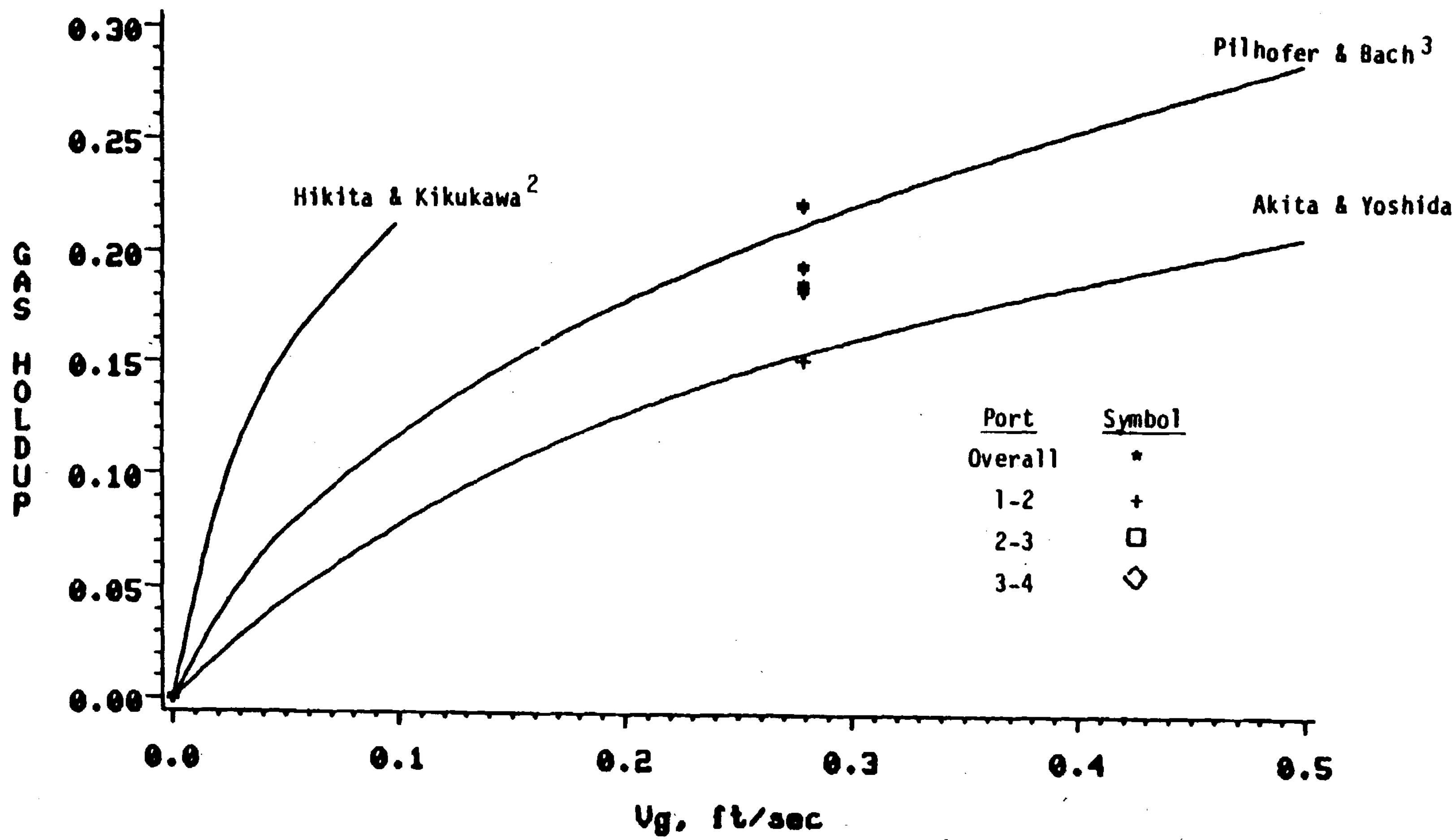

FIGURE 8

CARTRIDGE HEATER ARRANGEMENT

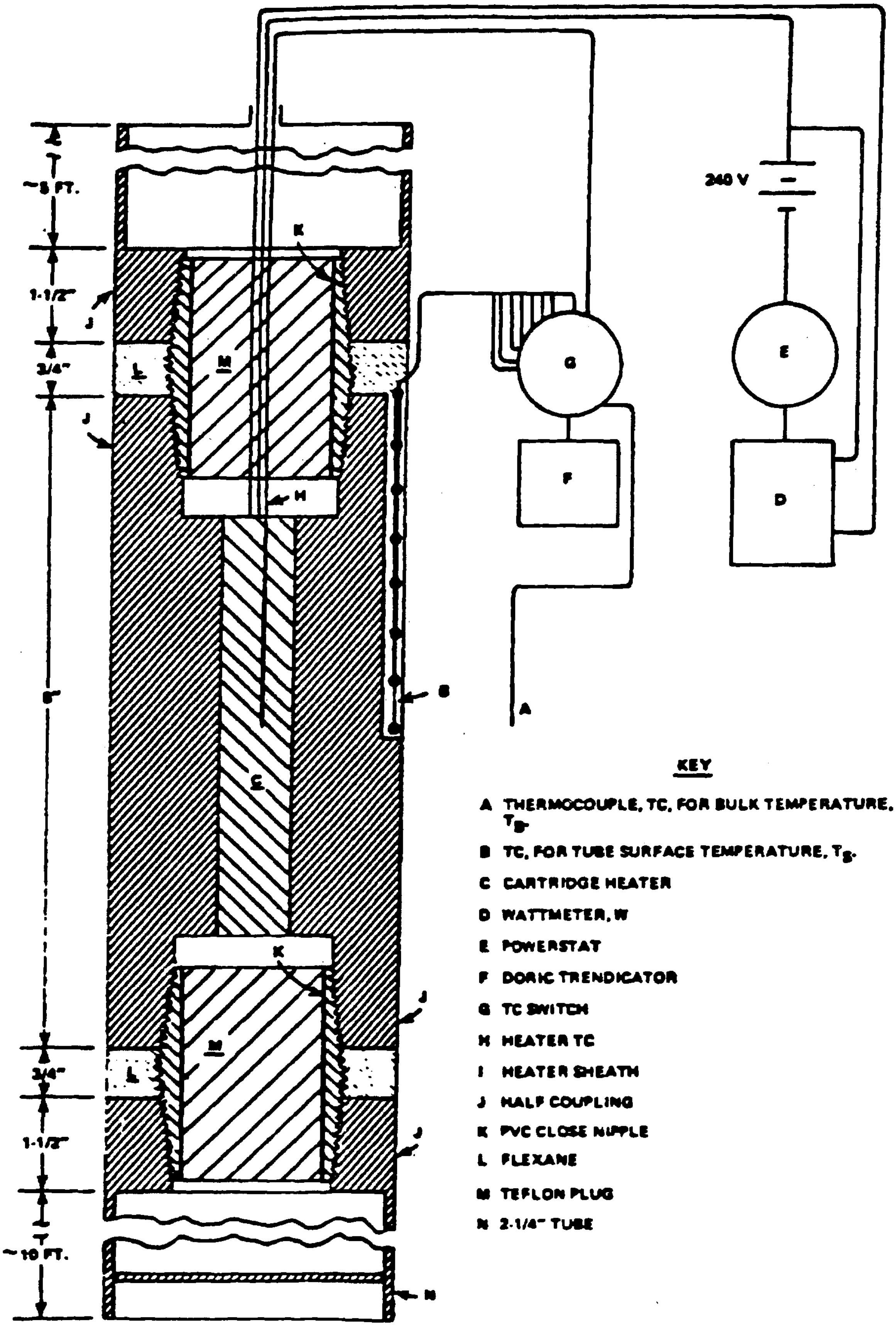

FIGURE 9

12 INCH COLD FLOW SIMULATOR

8" CARTRIDGE HEATER SHAKEDOWN
NORMALIZED TEMPERATURE PROFILES VS HEATER LENGTH
PREDICTED ANALYTICAL SOLUTION

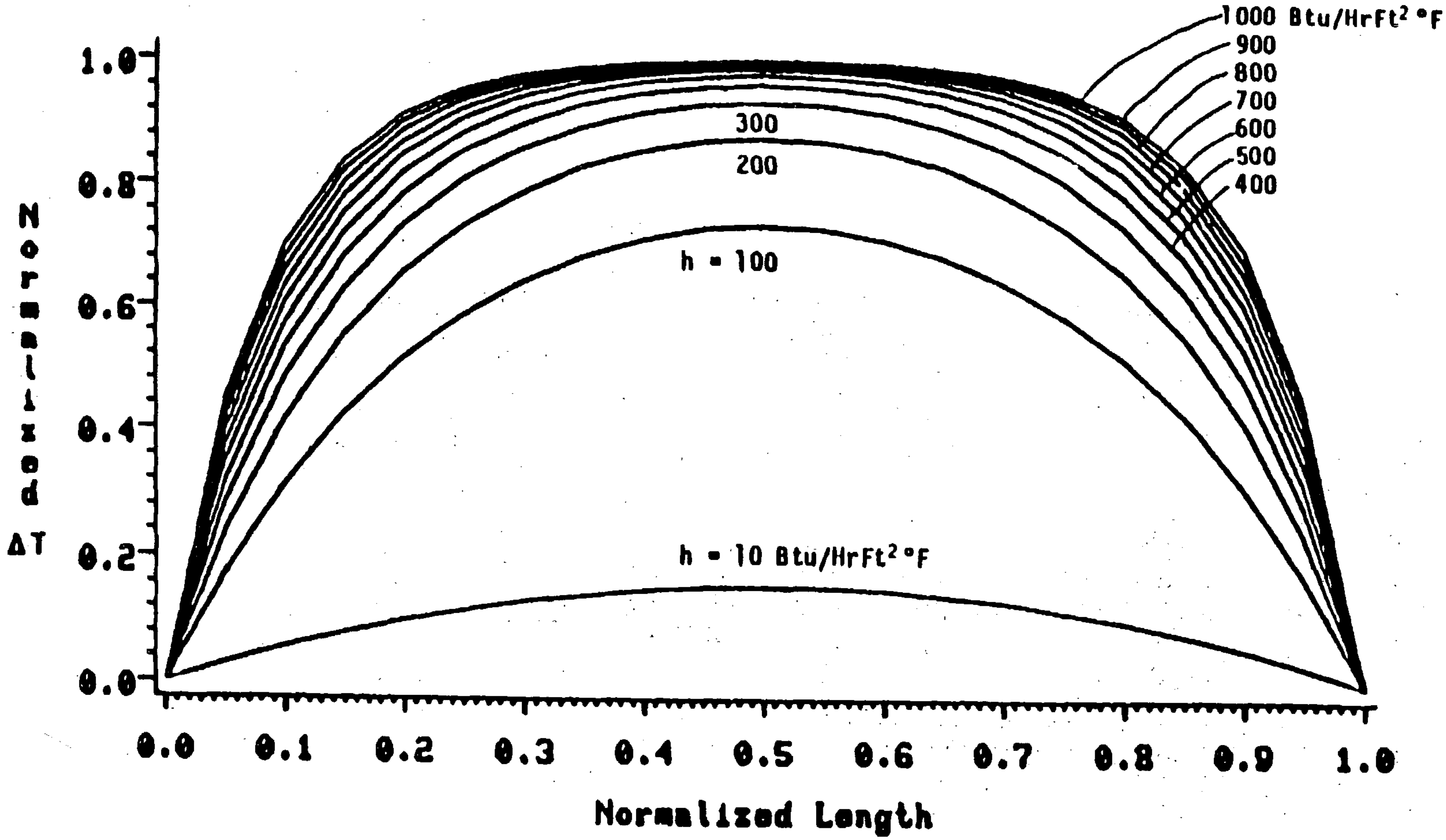

FIGURE 10

19" Heater Water Test

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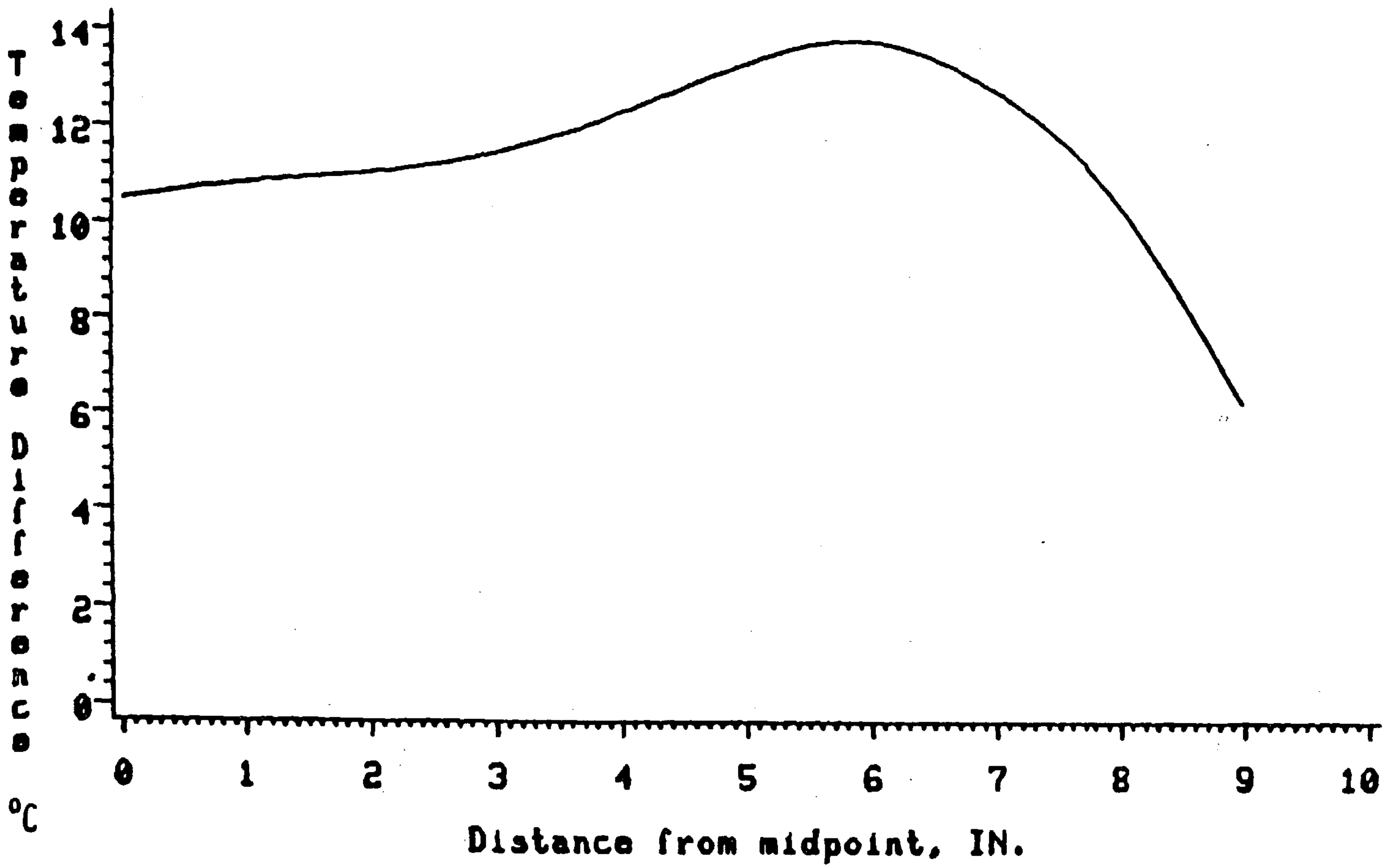

9.0 TABLES

TABLE 1

LEVELS OF EACH INDEPENDENT VARIABLE

	=	-	0	+
heat transfer tubes		None	Plain	Finned
liquid type		Aqueous	Organic	N/A
solid type		None	SiO_2	Fe_3O_4
solid particle size, μm		0-5	45-53	90-106
slurry loading wt%		0	15	30
distributor hole size, in.		1/28	1/8	1/2
V_G ft/sec	0.05	0.16	0.28	0.50
V_L ft/sec		0	0.008	0.015

TABLE 2

LIST OF 12 INCH COLUMN EXPERIMENTAL RUNS*

(a combined experimental design of 106 runs)

V_G	Wt%	Liquid	V_L	Tube	Solid Size	Distributor	Solid Type
-	0	0	+	+	-	0	+
0	0	0	+	-	+	0	+
0	0	-	-	+	-	0	-
0	0	0	-	-	-	0	-
+	0	0	0	0	+	-	0
+	0	0	0	0	-	+	0
-	0	0	0	0	+	+	0
-	0	0	0	0	-	-	0
0	+	0	0	+	0	-	0
0	+	0	0	-	0	+	0
-	-	0	-	+	-	+	-
0	-	0	-	-	0	-	-
+	-	0	-	0	0	0	-
-	+	0	+	0	0	0	+
-	-	0	-	0	0	0	-
-	0	-	+	0	0	-	+
0	0	-	-	0	0	+	-
0	0	-	+	0	0	+	+
0	0	-	-	0	0	-	-
+	0	-	0	-	0	0	0
+	0	-	0	+	0	0	0
-	0	-	0	+	0	0	0
-	0	-	0	-	0	0	0
0	+	-	0	0	-	0	0
0	+	-	0	0	+	0	0
0	-	-	-	0	+	0	-
0	-	-	-	0	-	0	-
0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0
0	0	0	+	+	+	0	+
-	0	0	+	-	-	0	+
+	0	0	0	0	+	+	0
+	0	0	0	0	-	-	0
-	0	0	0	0	+	-	0
-	0	0	0	0	-	+	0
0	+	0	0	+	0	+	0
0	+	0	0	-	0	-	0
-	-	0	-	+	0	-	-
0	-	0	-	-	0	+	-
-	+	0	+	0	0	0	+
0	0	0	0	0	0	0	0

*See Table 1 for key.

TABLE 2 (cont'd)

LIST OF 12 INCH COLUMN EXPERIMENTAL RUNS*

(a combined experimental design of 106 runs to be run)

V_G	Wt%	Liquid	V_L	Tube	Solid Size	Distributor	Solid Type
0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0
+	-	-	-	-	-	0	-
-	-	-	-	-	-	0	-
0	-	0	-	0	-	-	-
+	0	0	+	-	+	-	+
0	-	0	0	-	0	+	0
-	+	0	0	-	-	0	0
0	0	0	-	+	+	0	+
0	0	0	-	-	-	0	+
+	0	0	0	0	+	-	+
+	0	0	0	0	-	+	+
-	0	0	0	0	+	+	+
-	0	0	0	0	-	-	+
0	+	0	0	+	0	-	+
0	+	0	0	-	0	+	+
0	-	0	0	+	-	+	-
0	-	0	0	-	-	-	-
+	+	0	-	0	0	0	+
+	-	0	+	0	-	0	-
0	0	-	-	0	0	+	+
0	0	-	-	0	0	-	+
+	0	-	0	-	0	0	+
+	0	-	0	+	0	0	+
-	0	-	0	+	0	0	+
-	0	-	0	-	0	0	+
0	+	-	0	0	-	0	+
0	+	-	0	0	+	0	+
0	-	-	0	0	-	0	-
0	0	0	0	0	0	0	+
0	0	0	0	0	0	0	+
0	0	0	0	0	0	0	+
0	0	0	-	+	-	0	+
-	0	0	-	-	+	0	+
+	0	0	0	0	+	+	+
+	0	0	0	0	-	-	+
-	0	0	0	0	+	-	+
-	0	0	0	0	-	+	+
0	+	0	0	+	0	+	+
0	+	0	0	-	0	-	+
0	-	0	0	+	-	-	-
0	-	0	0	-	-	+	-

*See Table 1 for key.

TABLE 2 (cont'd)

LIST OF 12 INCH COLUMN EXPERIMENTAL RUNS*

(a combined experimental design of 106 runs to be run)

V_G	Wt%	Liquid	V_L	Tube	Solid Size	Distributor	Solid Type
-	+	0	-	0	0	0	+
-	-	0	+	0	-	0	-
0	0	0	0	0	0	0	+
0	0	0	0	0	0	0	+
0	0	0	0	0	0	0	+
0	0	0	+	+	-	0	0
-	0	0	+	-	+	0	0
0	0	0	-	+	+	0	0
-	0	0	-	-	-	0	0
-	+	0	-	0	0	0	0
-	+	0	+	0	0	0	0
0	0	-	+	0	0	-	0
0	0	-	-	0	0	+	0
0	0	-	+	0	0	+	0
0	0	-	-	0	0	-	0
0	0	0	+	+	+	0	0
0	0	0	+	-	-	0	0
0	0	0	-	+	-	0	0
0	0	0	-	-	+	0	0
-	0	0	0	0	+	-	0
+	+	0	+	0	0	0	0
-	+	0	-	0	0	0	0

*See Table 1 for key.

TABLE 3

GAS HOLDUP: 12" COLD FLOW SIMULATOR

SYSTEM:TWO PHASE

GAS- AIR

LIQUID- WATER

RUN	VG FT/SEC	VL FT/SEC	EG EXP.	EG12 EXP	EG23 EXP	EG34 EXP
7310-02-1	0.500	0.015	0.201	0.231	0.231	0.238
7310-01-1	0.160	0.0	0.123	0.094	0.115	NA

TABLE 4

GAS HOLDUP: 12" COLD FLOW SIMULATOR

SYSTEM:TWO PHASE

GAS- NITROGEN

LIQUID- ISOPARAFFIN

RUN	VG FT/SEC	VL FT/SEC	EG EXP.	EG12 EXP	EG23 EXP	EG34 EXP
7310-03-1	0.280	0.0	0.186	0.169	0.185	NA
7310-04-1	0.280	0.0	0.183	0.151	0.182	NA
7310-05-1	0.280	0.015	0.183	0.153	0.178	0.189
7310-06-1	0.280	0.0	0.221	0.214	0.222	NA
7310-07-1	0.280	0.008	0.194	0.189	0.197	0.199

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