Air Products

10.0 APPENDIX

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TASK 3 - SLURRY REACTOR DESIGN STUDIES

EXPERIMENTAL PLAN FOR 12 INCH COLUMN

The objective of Task 3 is to evaluate, through the use of cold-flow reactor simulators, the hydrodynamics of slurry reactors for the production of hydrocarbons from synthesis gas. The data obtained will enable:

a) The definition of heat, mass and momentum transfer parameters critical to the design of slurry reactors,
b) The establishment of operating limits for slurry reactors with respect to system physical parameters,
c) The correlation of gas hold-up, solid and liquid dispersion and heat and mass transfer for slurry reactors, and
d) The definition of the requirements for the design of large-scale reactors.

There are two complementary parts to the experimental program in this Task. Beginning January 1981, a 5" diameter column was used to simulate the operation of slurry reactors without internal heat transfer surfaces. Operation with internal heat transfer will be studied using a 12" diameter column from December 1981 through January 1983.

This experimental plan describes in detail the proposed testing program to be carried out in the 12" simulator. In addition to the range of variables studied with the 5" column, the proposed 12" simulator plan includes variations in distributor plate and heat transfer internals as independent variables, and the heat transfer coefficient as a dependent variable.

1. Apparatus

The 12" x 15' simulator and its associated equipment are illustrated diagramatically in Figure 1. The column will be constructed of borosilicate glass, with an outer plexiglass and aluminum lining, serving as ventilation and liquid containment in the event of a spill.

Two 200 gallon tanks equipped with stirrers designed to totally suspend the contained solids will serve as slurry reservoirs. The slurry will be pumped into the column at a constant measured rate by an air driven 1" Warren-Rupp sandpiper pump via a dual diaphragm tranquilizer.

Gas and slurry will exit at the top of the column via a gas/slurry separator. A level control for the separator will maintain a constant head at the slurry exit to minimize gas entrainment. The top section is so shaped that the column can be pressurized to approximately 5 PSIA in order to facilitate draining of slurry. The slurry flow rate will be measured by a venturi or other device. As the inlet slurry line requires some gas to maintain suspension at high slurry loadings, accurate slurry flow measurement will be only possible at the outlet. Inlet gas flow will be kept constant with a diaphragm differential flow controller.

The entire system will be fitted with all necessary safety devices.

The 12" column is supported so that it is possible to remove the bottom inlet section without moving the rest of the column. This simplifies the interchanging of distributor plates as well as the insertion of heat transfer internals.

2. Independent Variables

A) Solid Types and Particle Sizes

It is proposed to study two solids that are closely related to precipitated or supported Fischer-Tropsch catalysts: Fe_2O_3 and SiO_2. Their densities are listed in Table 1.

Three size ranges will be utilized: 1-5 μm, 45-53 μm, and 90-106 μm. Typically, Fischer-Tropsch slurry catalysts should be in the range of 30 μm (H. Kolbel and M. Ralek, Catal. Rev. Sci. Eng., 21 225 (1980)). For particle diameters <50 μm and solids concentrations of <16 wt%, three phase slurry reactors exhibit hydrodynamic behavior

similar to two phase gas/liquid bubble columns (W. D. Deckwer et al, Ind. Eng. Chem. Process Des. Dev., 19 699 (1980)). The chosen range of particle sizes should therefore both be typical of slurry catalysts and also indicate any transitions in the column hydrodynamics away from two phase flow.

B) Liquids

Two liquids will be used: isoparaffin and water. Table 2 compares relevant physical properties at 20°C with those of a typical paraffinic Fischer-Tropsch slurry oil at 260°C. While water presents no handling difficulties and facilitates mass transfer and liquid dispersion measurements, many of the physical properties of kerosene are closer to those of a heated paraffin oil. In particular, isoparaffin has a lower surface tension than water, and should exhibit surface interactions with the suspended solids that are similar to those occurring in a Fischer-Tropsch slurry and which are relevant to solids dispersion effects.

Because of the interest in behavior of the isoparaffin based slurries, the great bulk of the work will use isoparaffin.

C) Solids Concentration

Three solids concentrations will be studied: 0, 15 and 30 wt%. The zero solids measurement will be included only to allow the operation of the 12" column to be checked against existing correlations for two phase bubble columns and to facilitate the photographic determination of gas dispersion.

The 15 wt% concentration is typical of past Fischer-Tropsch slurry operations.

If the catalyst chosen for pilot plant study is of high selectivity and low activity, then it will be desirable to operate at as high weight loading as possible. The 30 wt% value is considered to be a pumpable limit.

D) Gas

Nitrogen will be used for all experiments except the determination of mass transfer, for which air, and possibly CO_2, will be utilized.

E) Gas Velocity

Four superficial gas velocities will be studied: 0.05, 0.16, 0.28 and 0.50 ft/sec.

For particles sizes <50 μm and zero liquid flow, gas velocities lower than 0.2 ft/sec are expected to produce a homogeneous (bubbly or quiescent) flow regime. With increasing gas velocity, a transition should occur to slug flow in the 5" column or heterogeneous (churn-turbulent) flow in the 12" column (Deckwer 1980).

The range of gas velocities is therefore chosen to span the expected change in flow regimes. The lowest gas velocity of 0.05 ft/sec, particularly at zero liquid flow rate, is expected to lie on the boundary of incomplete solids suspension. Since it is expected that the optimal operating point will be at the higher gas velocity, the bulk of the data will be obtained from the higher three gas velocities.

F) Liquid Velocity

Three superficial slurry velocities will be used: 0, 0.008 and 0.015 ft/sec. With internal heat transfer, slurry flow is no longer necessary for the control of the reaction exotherm. Instead, the slurry flow is determined by a) catalyst regeneration rate, and b) liquid make rate, both of which should be very small.

Work in the 5" simulator confirmed the literature assertion that liquid velocity has no significant effect on gas hold-up. If this is confirmed by initial work in the 12" column, then liquid velocity will be removed as a variable in order that more time can be devoted to other variables.

G) Distributor

Three perforated plate distributors will be examined, with hole diameters varying in the following range: a minimum hole size of 1/28", a maximum hole size corresponding to the largest single hole that will not weep during column operation, and an intermediate hole size corresponding to the logarithmic mean of the minimum and maximum hole diameter. The number of holes will be determined by equating pressure drop across the distributors for a given flow rate. The actual number of holes will depend on whether both gas and liquid flow through the distributor plate, or the slurry is input through a separate inlet above the distributor. This will be decided early in the program, once the magnitude of end effects have been observed.

By using three perforated plate distributors instead of three different types of distributor, the distributor hole size can be included as a continuous variable, increasing the range of applicability of the study.

H) Heat Transfer Internals

Figure 2 shows the layout of two heat transfer internals: a) 2 inch O.D. tubes, triangular spaced, 4 inches between centers, and b) the same tube arrangement with approximately 1 inch fins, 6 fins/tube. These two internals correspond to a hydraulic diameter of 4.46 and 1.92 inches respectively. By doing experimental runs without heat transfer internals as well, a hydraulic diameter of 12 inches can be included. Taken together with the 5 inch column study, it may be possible to correlate reactor performance with hydraulic diameter, again increasing the utility of the study.

3. Dependent Variables

The six dependent variables are:

a) gas hold-up,
b) solids concentration profile,
c) bubble diameter (measured photographically at zero weight percent only),
d) liquid dispersion (water based slurries),
e) gas/liquid mass transfer (water based slurries only), and
f) heat transfer coefficient.

Because of the large number of combinations of independent variables, a statistically designed experimental program will be developed in conjunction with the Applied Statistics Department at Air Products and Chemicals, Inc.

In order to maximize the amount of information from the experimental runs, it may be necessary to modify some of the discrete values of the independent variables during the course of the program as determined by the statistical design. However, the range of the independent variables will remain the same.

Because of the lead time in obtaining equipment and construction, it is not anticipated that experimental results will begin until about February 1982, or month 3 of this sub-task. The total number of experiments will largely depend upon the time for the 12" column to reach equilibrium under the conditions of the particular experiment. The experimental design, however, will enable a maximum amount of information to be obtained early on in the program, allowing further refinement of derived correlations to be made by additional experiments. The dependent variables that will be studied are:

a) Gas Hold-Up

Measurement of gas hold-up in the absence of solids is relatively rapid to carry out and will provide a check on the column operation by comparison with existing two phase correlations.

One of the major objectives of the initial task will be to confirm the suitability of the chosen gas distributor plates over the entire range of gas velocities. Gas hold-up measurement will be similar to the method used in the 5" column.

b) Solids Concentration Profile

Solids dispersion will be measured after equilibration of the column but prior to each gas hold-up determination, by sampling the column contents at four equally distant points up the length of the column. A peristaltic pump will be used to assure that each sample is withdrawn at the same rate and not at a rate dependent upon the column static head. Early on in the program, different sampling speeds will be tried to assure that a representative sample is being taken at each location.

c) Bubble Diameter

Gas dispersion and bubble diameters will be estimated from photographs of the equilibrated column as was done for the 5" column. It is envisioned that this will only be possible for the case of zero solids content.

d) Liquid Dispersion

Axial liquid dispersion coefficients will be determined as in the 5" column by numerically fitting computer generated curves to the output of a conductivity prove at several points along the column, following injection of a concentrated KCl solution spike into the inlet of the equilibrated column.

e) Gas/Liquid Mass Transfer

Overall gas/liquid mass transfer rates will be measured by determining the rate of transfer of oxygen from air into a continuous deoxygenated aqueous slurry supply. Oxygen concentrations will be measured at several points up the column using dissolved oxygen electrodes.

f) Heat Transfer Coefficient

In addition to the dependent variables that were measured in the 5" column, heat transfer coefficients will also be measured. A schematic diagram of the heat transfer measurement assembly is shown in Figure 3 and is described as follows: A cylindrical cartridge heater is inserted in the middle heat transfer tube at about the upper third of the 15' column. The heater is placed symmetrically within the tube so that no side of the tube is preferentially heated. On either side of this cartridge heater and tube is a teflon plug to minimize heat leak in that direction. A DC power supply, ammeter and voltmeter are included in the circuit to generate and accurately determine a given wattage (heat, Q) from the heater. A thermocouple is inserted in the tube wall to measure the wall temperature. Two thermocouples are placed at either end of the heater to account for any heat leak that occurs. A fourth thermocouple is placed in the bulk liquid to measure bulk temperature. All wires to the system run inside the center tube and will exit either out the top or bottom of the column.

From the rate equation; $Q = UA\Delta T$, where

Q = heat transfer rate, BTU/hr,
U = overall heat transfer coefficient, BTU/hr ft^2 °F,
A = surface area, ft^2,
ΔT = wall minus bulk temperature difference, °F,

it is possible to determine U, which in this system is equivalent to H_o, the film coefficient between the wall and the bulk fluid, BTU/hr ft^2 °F.

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TABLE 1

SOLID DENSITIES

Solid	Specific Gravity
SiO_2	2.65
Fe_2O_3	5.20

TABLE 2

PHYSICAL PROPERTIES OF LIQUIDS

Liquid	Temp. 0°C	Surface Tension dynes/cm	Viscosity cp	Density g/cm^3	Gas Diffusivity cm^2/sec	Specific Heat cal/g/°C	Thermal Conductivity cal/cm/sec/°C
Water	20	72.7	1.00	1.00	2.5×10^{-5} (O_2)	1.00	1.41×10^{-3}
Isoparaffin	20	22	1.20	0.73	1.2×10^{-5} (O_2)*	0.50	4.0×10^{-4}*
Rheinpreussen type paraffinic oil	260	11	0.33	0.67	8×10^{-5} (CO)*	0.70	3.1×10^{-4}

* Estimated

FIGURE 1
12 INCH COLUMN FLOW SIMULATOR SCHEMATIC

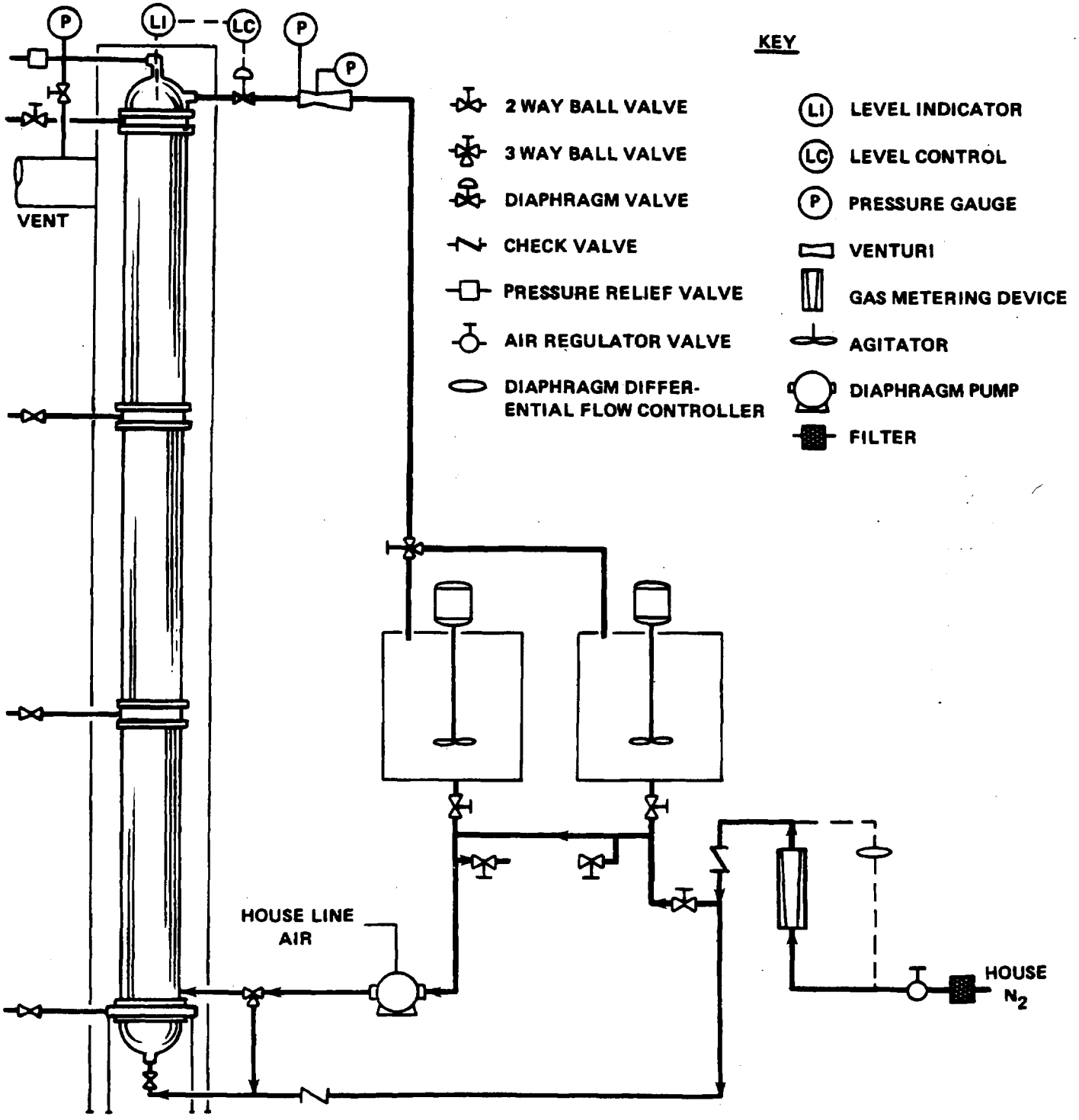

FIGURE 2
PROPOSED HEAT TRANSFER INTERNALS FOR 12"-COLUMN

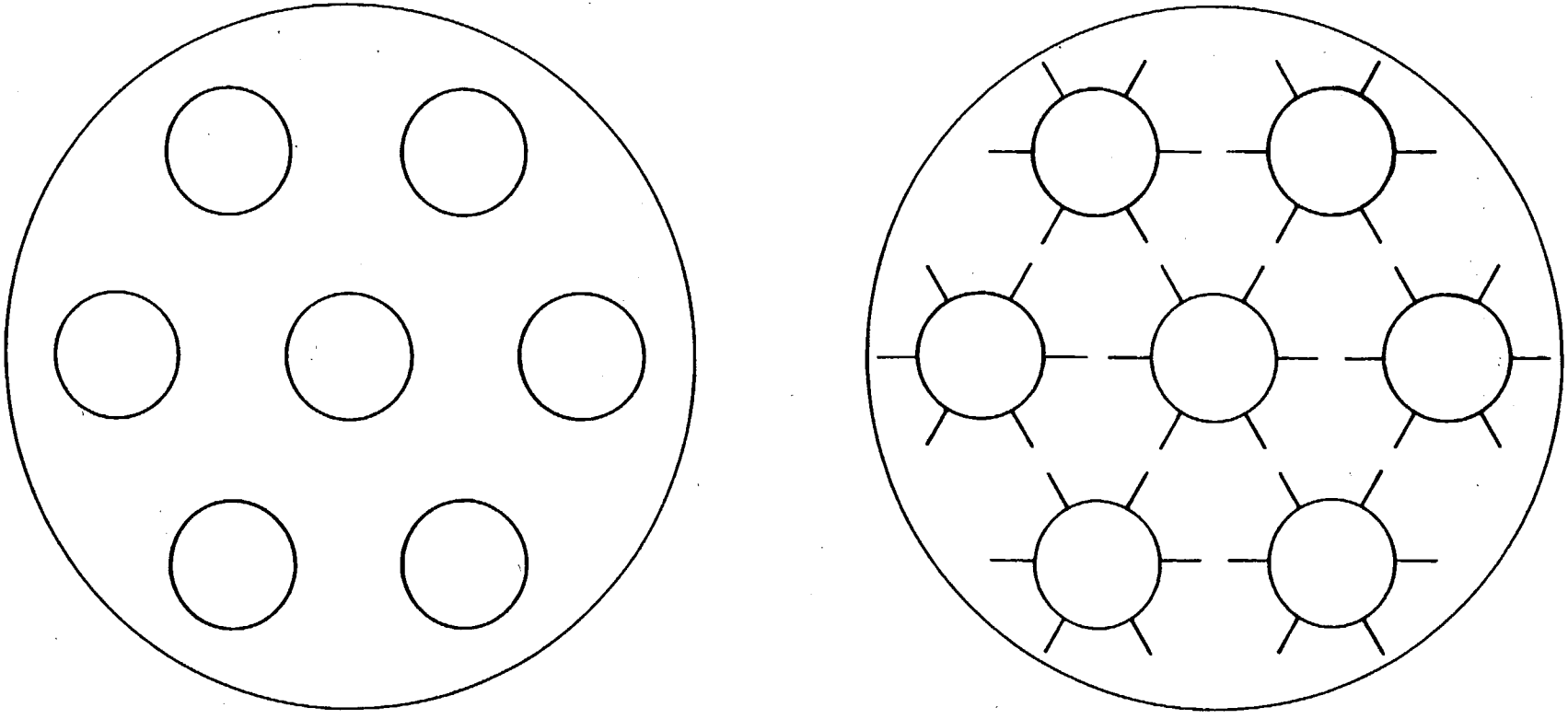

Figure 3. Exploded Schematic View of Heat Transfer Test Sample Assembly