Ohio State University Research

The following quarterly report from Ohio State University for the period July - September 1995 contains the following brief chapters:

1. Preparation of Apparatus (Task 2)
2. Windows and Visualization Technique (Tasks 2 & 3)
3. Developments of In-Situ Liquid Property Measurements (Task 5)

INTRINSIC FLOW BEHAVIOR IN A SLURRY BUBBLE COLUMN AT HIGH PRESSURE AND HIGH TEMPERATURE CONDITIONS

(Quarterly Report)

(Reporting Period: August 1 to September 30, 1995)

L. -S. Fan

DEPARTMENT OF CHEMICAL ENGINEERING
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO 43210

September 21, 1995

Prepared for Air Products and Chemical, Inc.

This report documents our activities in August and September, 1995. This is a short quarter, so this report will serve as both a monthly report as well as a quarterly report for the first quarter.

WORK PERFORMED

1. *Preparation of the apparatus*

A high pressure and temperature three-phase flow visualization apparatus developed earlier in our laboratory will be used for this study. A safety and leakage test has been conducted in this quarter, and all major equipments are proven to be leakage free. Installation and calibration of instruments (e.g., pressure gauges, liquid flow meters, gas flow meters, thermal couples) are completed. A system shakedown has been conducted to verify conditions for planned experiments. The details of this system shakedown are given below.

In the operation, liquid in the supply tank and vertical column is gradually heated first. By simultaneous heating, the buildup of undesirable thermal stresses around the windows on the column is prevented. The electric heating wire is arranged uniformly along the supply tank wall to minimize temperature gradient in case some component in the liquid phase decomposes under high local temperature. The temperatures in the supply tank, gas heater and vertical column are controlled independently with an accuracy of ± 2 °C. All ventilation valves are kept open during heatup. When the desired temperature is reached, the liquid is circulated at a flow rate less than 0.1 GPM around the system to warm all related components. The liquid circulation system is used to raise the system pressure to the desired level with a maximum value of 21 MPa. The system pressure is controlled by a back pressure regulator installed at the outlet of the column. The pressure can be accurately controlled throughout a wide range. The inlet gas pressure is regulated by a two-stage regulator; gas flow rate is controlled by a flow control valve. A large volume vessel is employed to stabilize the gas flow. The liquid flow rate is controlled by the pump, and its velocity in the column can be varied from 0 to 10 cm/s. A pullsation dampener is used to minimize the liquid flow rate fluctuation to less than 5%. The gas flow control valve and back pressure regulator are adjusted at the same time when the operating conditions are changed. The liquid flow rate is measured by a pneumatic flow meter with accuracy of 1%. A

gas flow rate indicator is installed in the gas line before the gas heater; the gas flow rate is measured after the gas is cooled down to room temperature at the exit.

Another unique feature is that the system can be either operated in no-lliquid-circulation or liquid-circulation mode of operation. For a highly viscous liquid, the gas bubbles with diameter less than 1 mm inherently exists in the liquid phase. Tiny bubble removal is difficult in slurry bubble columns for such a viscous liquid. The presence of gas bubbles could be harmful to the liquid pump and makes accurate measurements of flow rate difficult. For viscous liquid, this system can be operated in the no-liquid-circulation mode to circumvent this difficulty. With the 30-Gallon liquid supply tank, the no-liquid-circulation mode of operation can sustain for 15 minutes at the maximum liquid velocity throughput.

The overall volume fractions for each phase can be determined by the pressure drop method.

$$\varepsilon_s = \frac{W_s}{\rho_s A H} \tag{1}$$

$$\varepsilon_s + \varepsilon_g + \varepsilon_l = 1 \tag{2}$$

and

$$-\frac{dP}{dZ} = (\rho_s \varepsilon_s + \rho_g \varepsilon_g + \rho_l \varepsilon_l) g \tag{3}$$

The effective bed height, H, can be obtained either by visualization or by the pressure drop measurement.

2. *Windows and Visualization Technique*

Three pairs of plane windows made of quartz are installed on both sides of the column; each window is 1/2" wide and 7" long. These three pairs of windows cover the entire test section in the vertical direction. A plane observation window prevents optical distortion of the photographic process. The bubble behavior (e.g., size, shape and rising velocity) occurring in the column can be obtained using a high resolution Infinity lens with maximum 150X

gas absorption. The hydrostatic weighing method is adopted to measure the effective liquid density, i.e., the density of a mixture of liquid and absorbed gas. The schematic diagram of the density measurement system is shown in Fig. 3. The submerged volume of a floating body in the liquid changes with the density of the liquid based on the Archimedes principle. Thus, the liquid density can be determined from the submerged float volume change.

WORK TO BE PERFORMED NEXT QUARTER

1. In-situ measurements of interfacial surface tension. In these experiments, nitrogen will be used as the pressurizing medium.
2. Bubble effects on the transient flow pattern in bubble columns at ambient conditions. Experiments will be conducted at various gas and liquid velocities.

NOTATIONS

A	cross-sectional area
D	column diameter
d_p	particle diameter
f_w	correction factor for wall effect
g	gravitational acceleration
H	expanded bed height
Z	vertical distance
P	pressure
Re	Reynolds number
T	temperature
t	time
W_s	mass of solid particles

Greek Symbols

ε_g gas holdup

ε_l liquid holdup

ε_s solid holdup

μ liquid viscosity

ρ_g gas density

ρ_l liquid density

ρ_s solid density

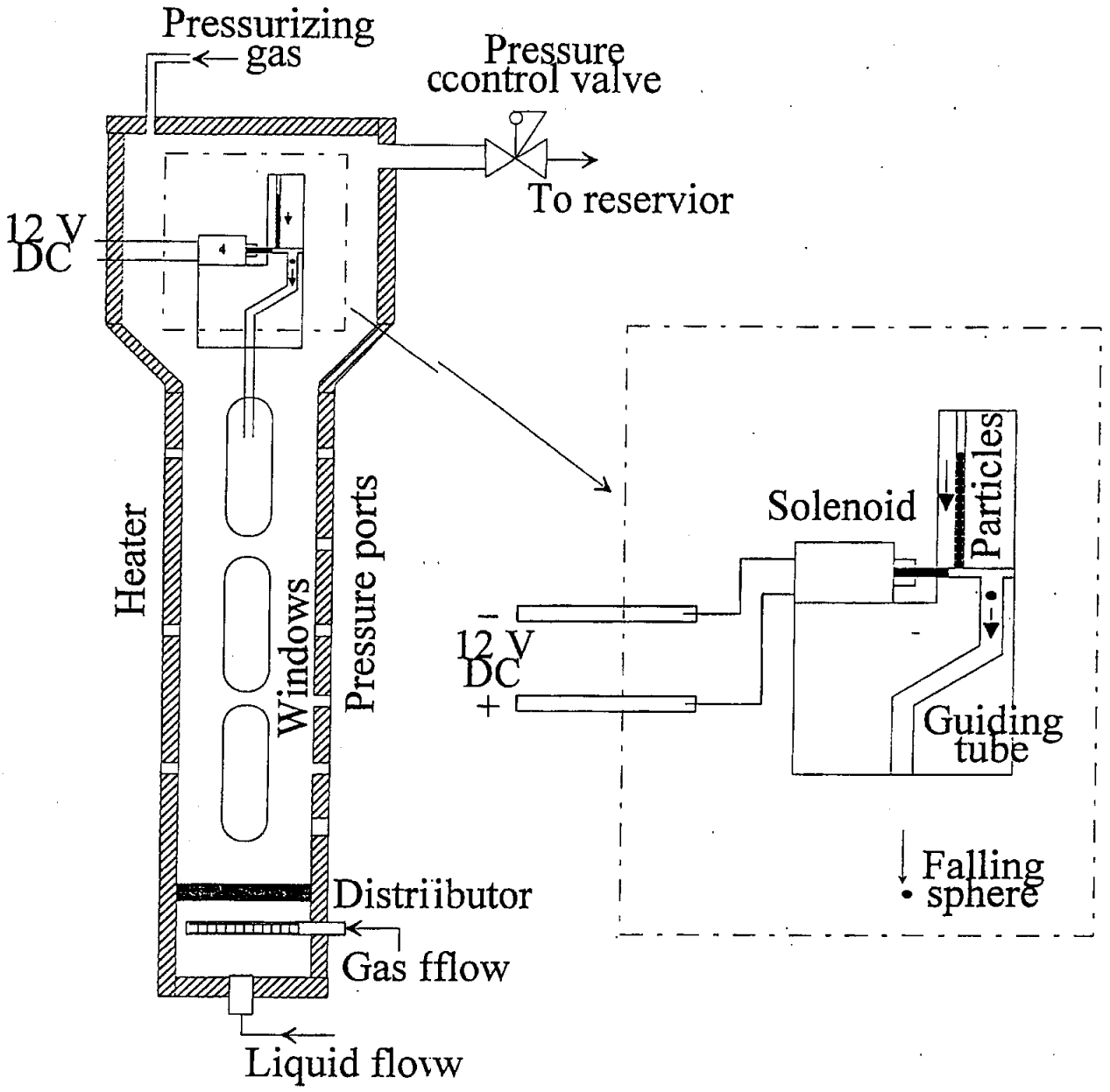
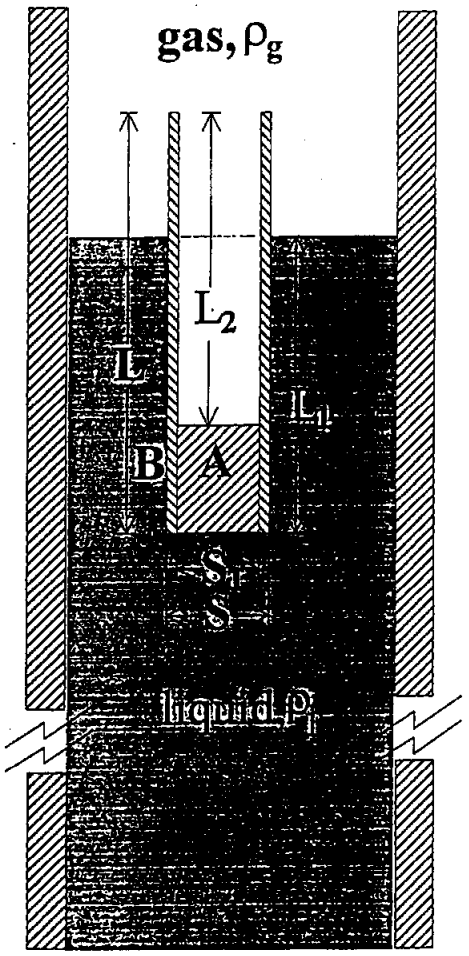


Figure 2. Schemaatic diagram of a falling-sphere viscosity measurement tecbhnique for high pressure and high temperature systeems.



Force Balance Equation

$$S[\rho_l L_1 + \rho_l (L - L_1)]\, g = (W_1 + W_2) + \rho_g L_2 S_1 g$$

W_1 : weight of metal A
W_2 : weight of tube B

Figure 3. Experimental setup for the measurements of liquid density in the high pressure and high temperature system.

Figure 4.1
Typicall Gas Tracer Profiles at One Height

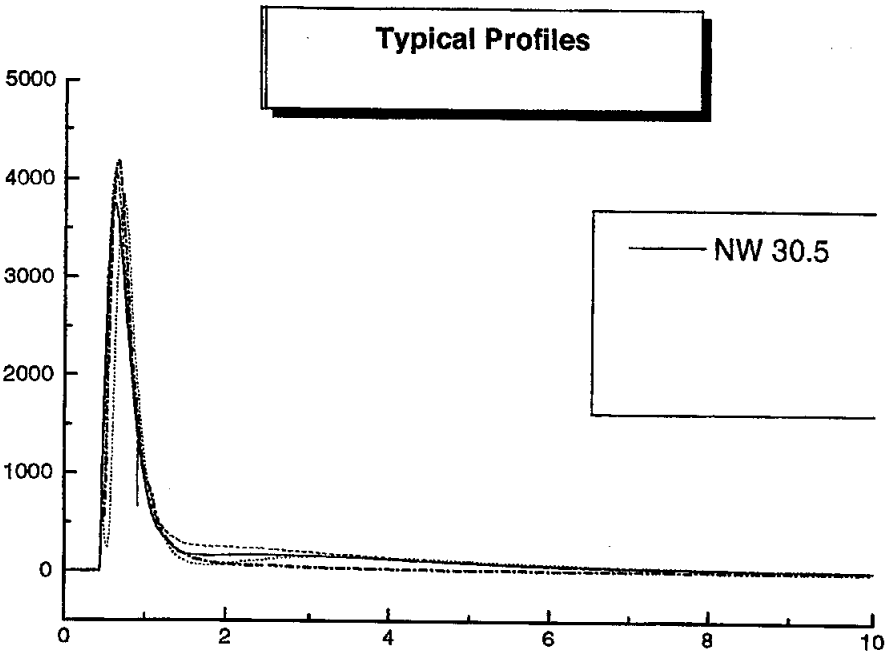
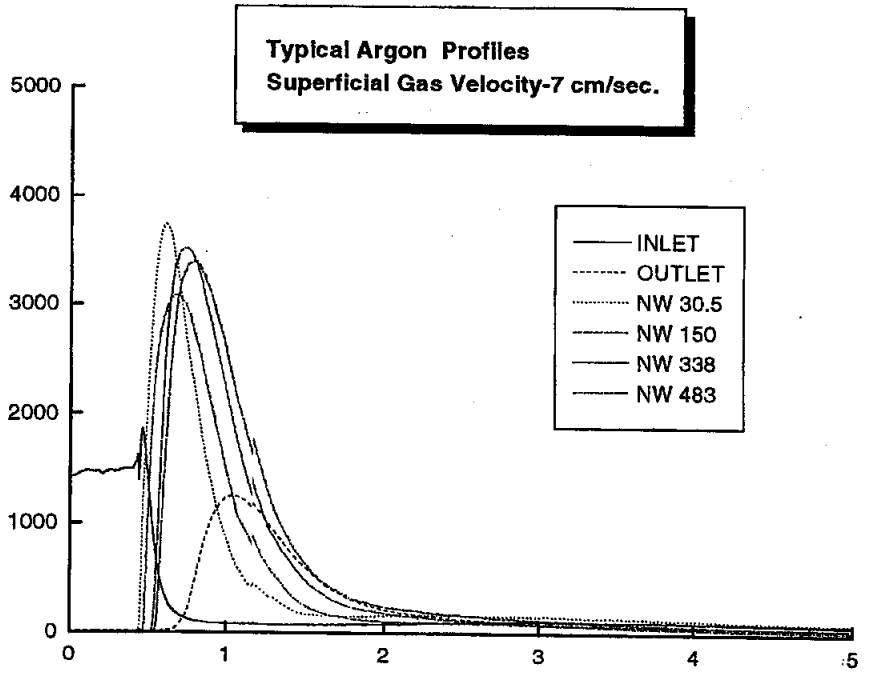


Figure 4.2
Spreading of Gas Tracer Moving Up the Column



a. Calibration

The detectors at one level were calibrated to each other. However, the detectors were not calibrated from one level to another. Thus, the height of the curves as the pulse moves up the column is not significant. The calibration is usually done so that a material balance can be made. The material balance on the tracer material is generally important to assure that there is no "dead" spot where tracer is accumulating. We can be sure that this did not occur during the trial since the entire reactor volume was scanned after the injection, and no radiation buildup was apparent. (Since the holdup and, therefore, the attenuation coefficient of the column changes as the height increases, calibration from height to height does not insure that a material balance can be made.)

b. Gas Solubility

As discussed in Appendix 1, argon gas has some solubility in the reaction medium. This makes interpretation of the gas residence time distribution (RTD) possible only by analysis using an equation. In addition, as discussed in Appendix 1, this solubility affects the apparent residence time of the gas in the column.

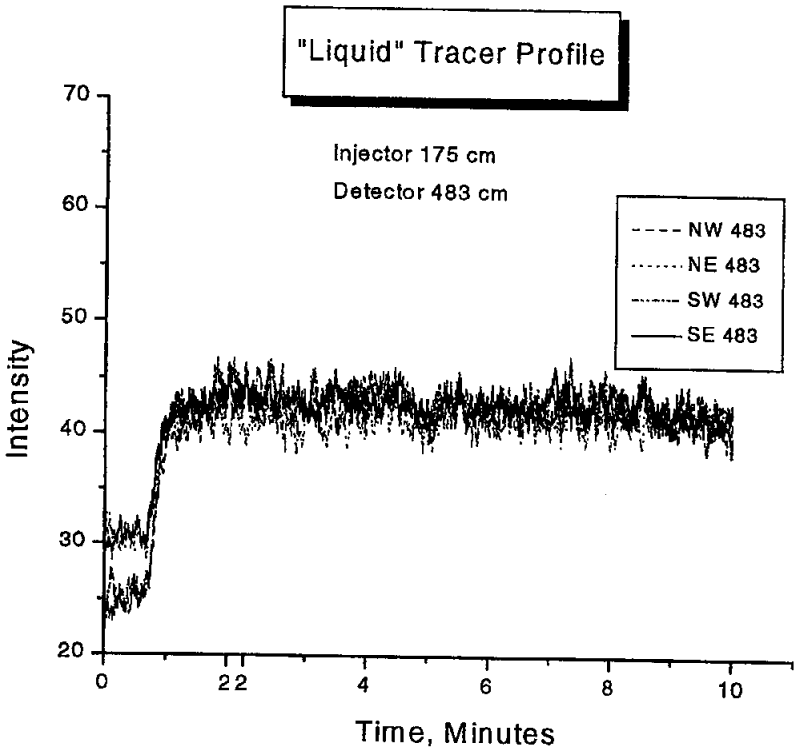
c. Initial Tracer Distribution

While the initial input is a good impulse function, rapid spreading is seen by the first 30 cm of the column. A series of tracer measurements moving up the column is shown in Figure 2. In fact, as discussed in Appendix 1, with standard models it is impossible to reconcile the initial rapid increase in width with the slower increase in width as the tracer moves up the column. Thus, we posit that the initial tracer distribution is affected by the sparger independent of the column. We therefore define a "forcing function" for the equations which allows a reasonable interpretation of the data and an estimate of the dispersion parameters for the one-dimensional dispersion model.

d. "Liquid" Tracer

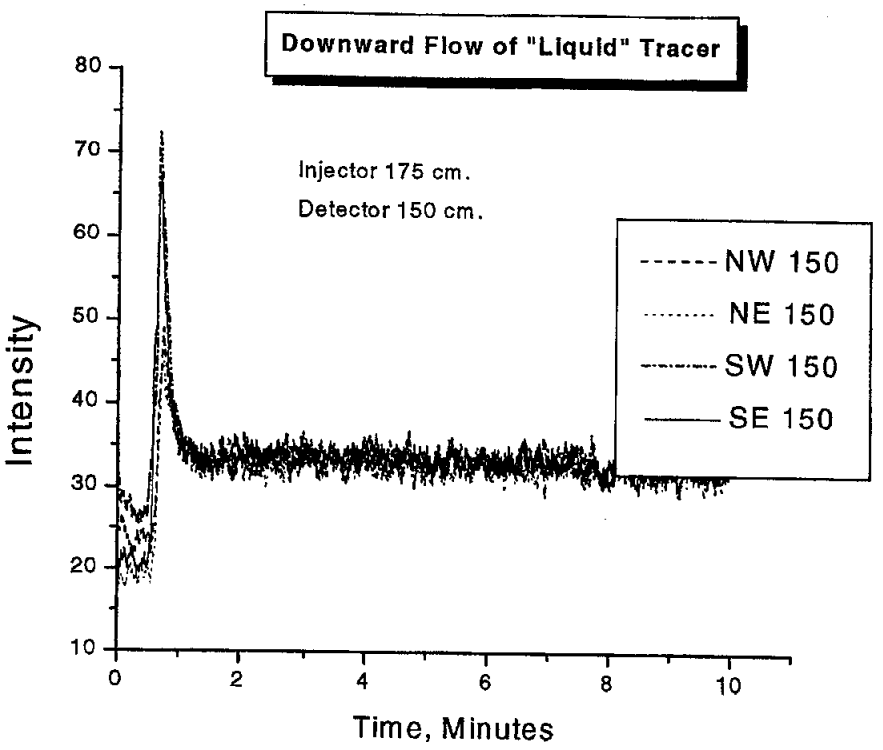
As discussed in (1), the "liquid" tracer is a solid radioactive material whose particles are small enough to follow the liquid flow. The tracer was injected at the wall in two locations. A typical profile far from the injection point is shown in Figure 4.3. The profiles are typical of what one would expect for a dispersive process as discussed in the report in Appendix 1.

Figure 4.3
Typical Liquid Tracer Profiles
Far From Injector.



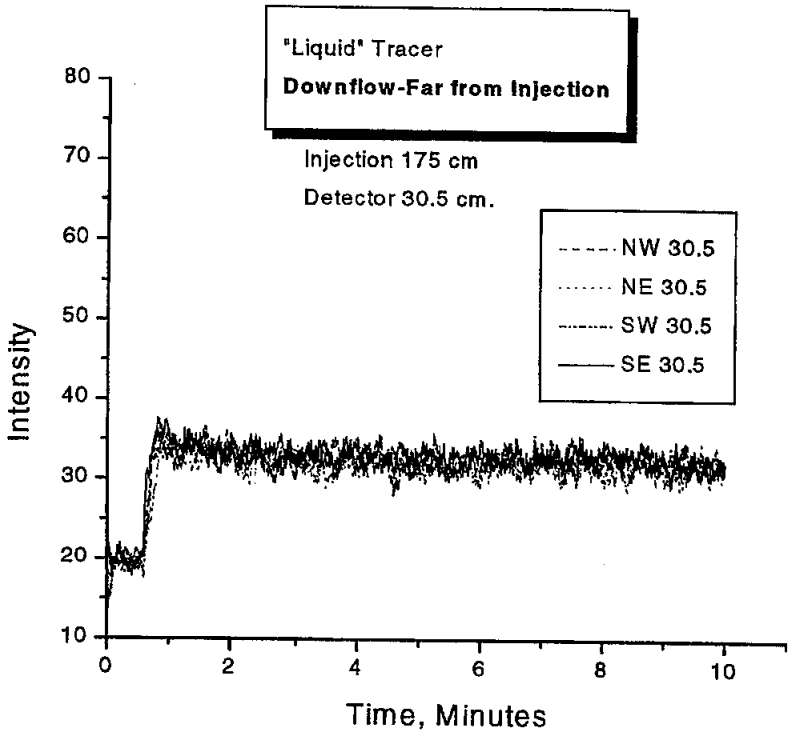
However, inspection of the traacer profiles near the injection point shows a strong tendency for downward flow of the traccer (Figure 4.4). The profile shows a sharp spike as the flow passes; the spike then graduallyly relaxes. This behavior can be explained by the generally accepted reasoning that averagge flow is up in the center of the column and down at the sides.

Figure 4.4
Downward Flow of Liquid Tracer at Wall



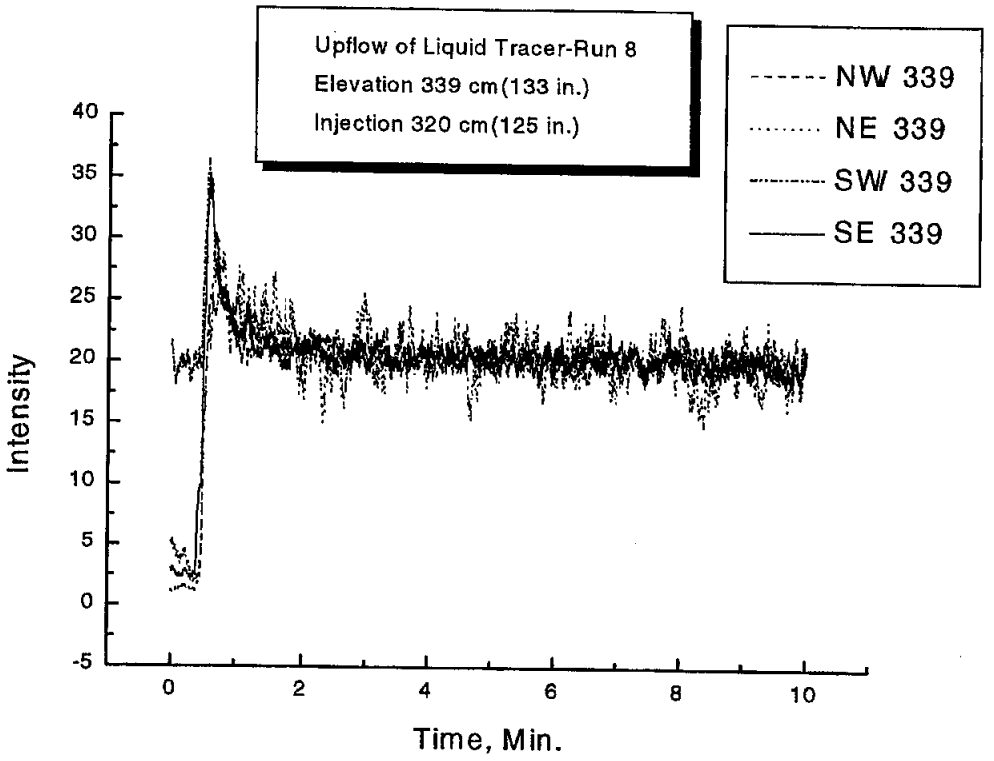
The pulse from the downflow tends to disappear due to dispersion as one mowes farther from the injection point (see Figure 4.5).

Figure 5
Liquid Trace Downstream Far From Detector



In some cases, upward flow near the liquid tracer injection (Figure 6) can been seen as well as the downflow. In this case a spike of radiation is seen immediately above the injection point.

Figure 6
Upflow of Liquid Tracer



The tracer was injected with considerable force radially into the flow. It is possible that the upflow demonstrated by Figure 6 occurred because the radially directed flow had sufficient momentum to allow some of the tracer flow to enter the central core, which is generally believed to move on average up the column. Of course, it is also possible that the upflow is evident because the flow is turbulent, and fluctuations occur in this type of flow field.

Plan for Tracer Testing for Hydrodynamics Trial

Planning for the hydrodynamics trial took into account the issues raised above, as well as several other issues that had been raised previously. The approach to address these issues is described below:

Unreacted Gas Recycle

Methanol synthesis operates at equilibrium, but this is only 20% conversion. Unreacted gas is recycled back to the process. This recycle gas will contain some radioactive material, which could interfere with measurements of the tail of the initial pulse if the cycle time were rapid. Calculations indicate that the mean residence time in the recycle loop is 5-10 minutes. As can be seen from Figure 1, recycle of radioactive gas does not interfere with the initial measurement, since the detectors have returned to baseline before this.

Detector Calibration
All detectors will be calibrated, which should allow a better material balance. However, since the absorption coefficient varies with holdup and holdup varies with axial distance, a tight material balance cannot be expected.

Gas Solubility
Review of the literature and consultation with Tracerco did not reveal any other candidate gases. Thus Ar_{41} will be used again. The pressure of methanol synthesis is 750 psi, much higher than isobutylene synthesis, which will reduce the partial pressure of argon and should lead to less solubility. However, it is expected that argon solubility will have to be considered in analysis of the results.

One way around this problem is to use a gas chromatograph or a GC/MS to measure concentrations of gas in the outlet. Thus, a gas of low solubility such as helium could be used, and the effect of gas solubility could be quantified. While this would allow measurement of an overall residence time distribution, no measurements could be made axially along the column. Thus, this measurement would be of limited use, and the cost to install such equipment would be high. In addition, the problem of obtaining a real-time sample with little lag is formidable for a large-scale unit such as the AFDU. However, this technique remains a possibility for the future.

Liquid Injection
Liquid tracer was injected at two radial locations, the wall and as far into the reactor as the presence of the heat transfer tubes allowed. Furthermore, the injector ports at the wall were shaped so that the pulse of material was injected circumferentially to eliminate the possibility of the pulse traveling a significant distance radially. The axial locations for the injectors were selected so that the distances between the top injector and the bottom detectors and the distance between the bottom injector and the top detectors were large. This allowed for the development of a standard profile so that one-dimensional modeling could be used. Finally, additional detectors were added so that the upward and downward flow at the injection locations, as well as the entire axial length of the column could be monitored.

Initial Profile of Gas Trace
In the tracer interpretation presented in Appendix 1, we also assumed that the sparger effect is independent of the column so that the deconvolution can be done rigorously. This assumption allows separation of the effects of the column dispersion from the dispersion in the bottom of the column and the sparger. We determined that the sparger volume is large compared to the flow so that sparger flow is independent of volume.

Injection of the gas tracer into the bottom of the reactor without use of the sparger was considered and rejected. The injection port is not at the centerline, and the highly turbulent nature of the bottom region of the reactor will tend to distort the initial impulse shape. Since this turbulence is not necessarily independent of the reactor dynamics and since the dispersion equation is parabolic, the independence of the initial impulse from

the reactor cannot be assured. Thus, the deconvolution will not be valid, and this approach can be too problematic.

Therefore, while injection through the sparger causes some problems in obtaining a physical picture of the dispersion in the column itself, it is the best method known. This technique makes interpretation of the tracer results in the column alone a little more difficult, but gives a true picture of the system as a whole.

Qualitative Results from Hydrodynamic Trial

Complete analysis of the tracer results requires extensive data interpretation. However, results from the injection can be viewed in real time while the tracer runs are made. In addition, the traces can be briefly reviewed between runs. Thus, one is able to make some qualitative judgments by viewing the trial. The following observations were made during the trial:

General Observations

The trial went smoothly, and data acquisition appeared as expected. One partial set of data was lost because of a computer storage problem, but a duplicate run was made so that this should cause no problem. Both liquid injectors functioned well, and gas phase profiles appeared as expected.

Recycle of Unreacted Gas

Recycle of radiation from the unreacted gas was observed. The peak appeared at about 4 minutes (expected time 5-10 min.) The discrepancy was attributed to the good mixing behavior of some of the tanks in the recycle line. The initial signal had returned to baseline before the recycle signal appeared. Thus, as hypothesized, recycle of the unreacted gases did not interfere in the trial.

Gas Solubility

The time of passage of the gas was longer than would be expected from superficial gas velocity considerations alone. This was taken as an indication of the solubility of the gas. The difference between calculated and measured results was smaller than for the previous trial, which is in accord with the hypothesis of lower solubility from the dilution effect of higher pressure. Further analysis will have to be done with the dispersion model, and these observations indicate that the effect of solubility should definitely be included in this model.

Liquid Injection

As expected, evidence of downward flow was again seen at the wall, while evidence of a smaller amount of upward flow at the wall was also observed. This occurred even though the injection was not made radially. Thus we must conclude that the upward flow is due to turbulent fluctuations. Both upward and downward flow was observed in the injections at the centerline, again confirming the highly turbulent nature of this flow.

Developed profiles were achieved at the bottom detectors when the liquid was injected at the top of the columns. Similarly, developed profiles were seen at the top when the liquid tracer was injected at the lower detectors. Thus, reasonable fits should be obtained for dispersion coefficients for the one-dimensional model, even though as indicated by the flow patterns noted above, this model is not physically justified.

Task 7.0 Management and Reporting

Statements of Work

Statements of work for the entire project were provided in the proposal. Detailed statements for the first year of the program were obtained from both Washington University in St. Louis and from Ohio State University. These are presented in Appendix 2.

References

1. Air Products and Chemicals, Inc. 1990. "Task 2.3 - Tracer Studies in the LaPorte LPMEOH™ PDU." Topical Report Rev. 1. Prepared for the U.S. Department of Energy under Contract No. DE-AC22-87PC90005.

2. Toseland, B. A., Brown, D. M., Zou, B.-S., and Dudukovic, M. P. 1995 (April). "Flow Patterns in a Slurry Bubble Column Reactor under Reaction Conditions." Trans. I. Chem. E. 73(A)297-301.

3. Air Products and Chemicals, Inc. 1995. "Catalytic Dehydration of Isobutanol in a Slurry-Phase Reactor. Final Topical Report. Prepared for the U.S. Department of Energy under Contract No. DE-AC22-91PC90018.

Appendix 1

Flow Patterns in a Slurry Bubble Column Reactor under Reaction Conditions

Reprint - Removed for Separate Processing

Appendix 2

Statements of Work
Washington University in St. Louis
Ohio State University

AIR PRODUCTS' SUBCONTRACT WITH WASHINGTON UNIVERSITY CHEMICAL REACTION ENGINEERING LABORATORY

DOE Contract DE FC22-95PC95051

Goals for Year 1 (April 1995 - March 1996)

For the first year of the project, we plan to accomplish the following tasks:

1. A comprehensive review of the state of the art on the suitability of available measurement methods for various hydrodynamic parameters in high-temperature, high-pressure systems. This review will include recommendations for testing those existing techniques that show potential for use at high-temperature, high-pressure conditions.

2. Interpretation of the results of existing tracer experiments and recommendations for improved methodology for new tracer experiments that are to be made at LaPorte.

3. Design and completion of modifications for CARPT/CAT experimental facilities for studying slurry bubble column systems. This will include purchasing, designing and fabricating the necessary setup for obtaining pressure fluctuation measurements and dynamic gas disengagement studies for bubble class and size determination.

Upon completion of the needed equipment modification, Washington University will be in the position to provide data for the following directly measured quantities:

- instantaneous solids and liquid velocity everywhere in the column
- sectional pressure drop and pressure drop fluctuations along the column
- holdup (or density) distributions in column cross sections at various axial positions above the distributor
- bubble size distribution

The quantities derived from the directly measured quantities will include:

- time-averaged (ensemble-averaged) velocities in 2D and 3D
- backmixing parameters
- turbulent kinetic energy distribution throughout the column
- Reynolds stress profiles in the columns
- turbulent viscosity/mixing length profiles.

The above data will be collected during years 2 - 5 of the project.

4. Assessment of one-dimensional models for prediction of liquid recirculation based on the available phase velocity and holdup measurements. The effect of scale on liquid recirculation will be assessed.

5. Continuation of ongoing efforts for programming and testing the appropriate closure schemes and constitutive relations for improving the predictive capabilities of the CFDLIB codes of Los Alamos.

OHIO STATE UNIVERSITY

Goals for Year 1 (1 October 1995 - 30 September 1996)

This statement sets forth the major activities to be accomplished during the first year. The overall objectives of this work are to investigate the intrinsic flow behavior of a bubble column and slurry bubble column operated under high-pressure and -temperature conditions. These include the effects of various system variables such as gas and liquid velocity on the hydrodynamic properties (e.g., flow regime transition and gas holdup) of the system. Direct visualization of bubble and slurry bubble columns operated under high pressure and temperature conditions provides instantaneous flow phenomena and allows for the quantification of bubble dynamics, including the bubble formation, coalescence, and breakup processes. Information obtained at high pressure and temperature can then be compared with data obtained at low pressure to extend our understanding of the slurry bubble column. The tasks proposed for the first year are summarized below:

1. *Preparation of the apparatus.* A high-pressure and -temperature, three-phase flow visualization apparatus developed earlier in our laboratory will be used for this study. A safety and leakage test will be conducted first. After procurement of instrumentation and other needed equipment, a system shakedown will be used to verify conditions for planned experiments. All instruments (e.g., pressure gauges, liquid flow meters, gas flow meters, temperature measurements) will be calibrated during this period.
2. *Measurement of liquid and gas physical properties.* Physical properties of the gas and liquid, including liquid density and viscosity and gas density and viscosity, under high-pressure and -temperature conditions must be known *a priori,* in order to better understand the experimental results of the hydrodynamic properties. *In situ* measurements of these physical properties will be performed. A capillary-rise tube probe will be used to measure interfacial surface tension, which is measured when the liquid is saturated with pressurizing gas. Viscosity of the liquid under elevated pressure and temperature is determined by using the falling-ball technique. This system consists of a ball-releasing device, a guiding tube, and visualization windows. The magnetically operated ball releasing device is placed inside the bed to release the ball in to the guiding tube. Liquid density changes with pressure and temperature due to its compressibility and the absorption of gas. The hydrostatic weighing method is adopted to measure the effective liquid density (density of a mixture of liquid and adsorbed gas). This technique is based on the Archimedes buoyancy law. Physical properties obtained by in situ measurements will be used in conjunction with analysis of the experimental results on the transport phenomena in slurry bubble columns. It may be possible to present the hydrodynamics in terms of gas and liquid properties instead of operating pressure and temperatures.
3. *Measurement techniques for the hydrodynamic properties of bubble and slurry columns.* Differential pressure transducers will also be installed for gas holdup measurement and determination of flow regimes. An optical probe and associated

data acquisition system will be developed for the measurement of bubble properties. This will be used in conjunction with direct visualization of bubble behavior.

4. *Transient flow structure in a two-dimensional bubble column at ambient conditions.* The Particle Image Velocimetry technique will be used to quantify flow behavior in a two-dimensional bubble column. Experiments will be conducted at various gas and liquid velocities, and their effect on the macroscopic and microscopic flow structure will be studied. The purpose of this study is to provide key information required for verification of computational results generated by Professor Dudakovic at Washington University in St. Louis.
5. *Bubble behavior in a pressurized bubble column.* Experiments on bubble behavior in a pressurized bubble column will be conducted at the end of the first year. Pressure effects on hydrodynamic properties of bubble columns will be investigated in a bubble column with N_2 and Paratherm heat transfer fluid. This study will include flow regimes, gas holdup, and bubble size distributions with emphasis on bubble characteristics (e.g., size, shape, size distribution, bubble rising) under high-pressure conditions.