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**ENGINEERING DEVELOPMENT OF SLURRY BUBBLE COLUMN REACTOR
(SBCR) TECHNOLOGY**

FINAL

Quarterly Technical Progress Report No. 2

For the Period 1 July - 30 September 1995

Contractor

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ENGINEERING DEVELOPMENT OF SLURRY BUBBLE COLUMN REACTOR (SBCR) TECHNOLOGY

Quarterly Technical Progress Report No. 2 for the Period 1 July - 30 September 1995

Contract Objectives

The major technical objectives of this program are threefold: 1) to develop the design tools and a fundamental understanding of the fluid dynamics of a slurry bubble column reactor to maximize reactor productivity, 2) to develop the mathematical reactor design models and gain an understanding of the hydrodynamic fundamentals under industrially relevant process conditions, and 3) to develop an understanding of the hydrodynamics and their interaction with the chemistries occurring in the bubble column reactor. Successful completion of these objectives will permit more efficient usage of the reactor column and tighter design criteria, increase overall reactor efficiency, and ensure a design that leads to stable reactor behavior when scaling up to large diameter reactors.

Summary of Progress

- Specific statements of work have been received from both Ohio State University and Washington University in St. Louis.
- A hydrodynamics plant trial was conducted. A review of results from previous tests allowed improvements in techniques. Qualitative results show:
  - predominant liquid downflow at the reactor wall and upflow in the center
  - some liquid upflow at the wall and downflow in the center
  - fully developed profiles, which will allow modeling using the one-dimensional dispersion equation, for liquid tracer injections far from injectors
  - standard gas phase profiles with evidence of tracer solubility.

Qualitative analysis of the results await data transmission from Tracerco.

(Air Products and Chemicals)

- A review of measurement techniques for two- and three-phase flow was completed. A draft copy of the topical report is under comment at Air Products. As expected, the review points out the need for new measurement techniques. Adequate techniques for measuring two-phase flow under laboratory conditions are available. Techniques for measuring three-phase flows are limited. The report contains recommendations for the best techniques for the LaPorte operation, as well as a general review.

(Washington University and Air Products and Chemicals)

- Experimental facilities have been modified at both universities:
  - The high-pressure, high-temperature column has been checked for safety.

Quartz windows on this column will be used for flow visualization.

- Pressure taps have been installed for dynamic gas disengagement measurements. A video camera for liquid level detection has also been installed.
- Wavelet filtering for improving the CARPT technique in identifying radioactive particle position and velocity was adapted for use in the present project. This technique was used to provide improved measurement of Reynolds shear stresses and turbulent energy in bubble columns.
- Methods for measuring particle motion as well as liquid motion by CARPT were considered.

(Washington University and Ohio State)

- A new phenomenological model, Recycle-Crossmixing with Dispersion Model (RCFDM), has been developed to overcome some of the shortcomings of the Axial Dispersion Model (ADM). This model accounts for convective recirculation within the liquid, as well as the dispersion accounted for by the ADM. CARPT-CT measurements can be used to provide estimates of the flow parameters for the model. Thus, in contrast to the ADM, the new model can also be used to model the flow structure revealed by the tracer experiments at LaPorte.

(Washington University)

- Techniques to measure liquid properties in a bubble column operating at high pressure and high temperature have been developed for surface tension, density and viscosity. Such *in situ* measurements are essential to the quantitative understanding of flow phenomena in operating bubble columns.

(Ohio State)

- Benchmarking the CFDLIB code for computational fluid dynamics continued. The major issue is the choice of a closure approximation for the interfacial momentum exchange terms in the averaged Navier-Stokes equations. Using drag, lift and virtual mass terms allows the simulation of circulation cells in a two-dimensional bubble column at least in a qualitative manner. Quantitative simulation and simulation of three-dimensional problems are the subjects of continuing work.

(Washington University)

Washington University Research

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

1. Introduction
2. Review of Measurement Methods (Task 1)
3. Tracer Studies (Task 4)
4. CARPT/ CT Modifications (Task 3.1)
5. Development of Phenomenological Models (Task 3.2, Task 6)
6. Computational Fluid Dynamics Simulation (Task 3.2)
7. Research Progress and Timetable (Task 7)
8. References

Slurry Bubble Column Hydrodynamics

Second Quarterly Report for Contract DOE-FC 22-95 PC 95051

July - September 1995

1 Introduction

The main goal of the subcontract to the Chemical Reaction Engineering Laboratory (CREL) at Washington University is to study the fluid dynamics of slurry bubble columns and address issues related to scale-up. Experimental investigations to examine the effect of operating conditions such as superficial gas velocity, solids loading, type of distributor etc. on the fluid dynamics are to be made. The specific objectives that have been set out for the first year of the project are as follows :

1. Assess the suitability of available experimental techniques for the measurement of global and some local hydrodynamic parameters in an industrial scale system and make recommendations for the use of these techniques at La Porte.
2. Interpret the existing tracer experiments and make recommendations for future tracer tests on La Porte reactor.
3. Modify the CARPT/CT experimental facility for study of slurry bubble columns.
4. Develop a phenomenological model for the key hydrodynamic features in bubble columns as a basis for an improved reactor model.
5. Introduce appropriate closure schemes and constitutive forms in the hydrodynamic codes to achieve agreements between data and models and test model reliability.

The activities that have been undertaken in the second quarter (after the initiation of the project in April 1995) towards fulfilling the above mentioned objectives are described in the subsequent sections.

2 Review of Measurement Methods

A survey of all the available methods for the measurement of fluid dynamic parameters in a high pressure high temperature multiphase chemical reactors has been completed and is

the subject of a separate and complete topical report which will be issued in the immediate future. The emphasis was placed on techniques that can be utilized under conditions of interest in practice such as high pressure and temperature, large solids' holdup etc. A draft of the topical report resulting from this review has already been submitted to Air-Products and in it an attempt was made to present a comprehensive review of the experimental methods available for multiphase systems. A summary of that report is presented here. The measurement methods for the determination of the following quantities were considered :

- Void fraction and solids' concentration;
- Bubble size distribution and rise velocities;
- Liquid and solid phase velocities.

Gas holdup and solids' concentration measurement methods can be broadly classified into two categories : (1) those providing an overall or global measurement and (2) those that provide a local or point measurement. The global measuring techniques yield information on the line, area or volume averaged gas or solids' holdup. In general, the measurement of the overall holdup is relatively simple. It provides information regarding what fraction of the system volume is occupied by the phase of interest. The global measuring techniques that were reviewed include the bed expansion method, pressure drop method and quick closing valve method in addition to a few others. In the bed expansion method the holdup is measured based on the initial static height of the bed and the dynamic height of the dispersion. In the pressure drop method the holdup in a section of the flow in between two pressure taps is related to the difference in pressure between the two taps. In the quick closing valves technique the dispersion between two sections of the test loop is isolated and the mass of phases in the isolated section are measured.

Another technique that is often used for the determination of the overall holdup is based on the measurement of impedance of the two phase dispersion. Gas (air) and liquid (water) have significantly different electrical conductivity and permittivity and it is this difference that is exploited by the technique. The variation in the flow structure is accompanied by a variation in the impedance of the two phase mixture which is measured by metallic electrodes introduced suitably in the flow. The void fraction is then estimated by adopting a relative impedance technique.

All the above methods for overall holdup measurement are adequate for use in two phase flow systems. For three phase systems no single method can provide both the solids' and gas holdup, and a combination of the above techniques along with some approximations has to be used for obtaining the relevant information. Upon review of various techniques the recommendation that emerges for estimation of the overall fractional gas holdup is to

measure the pressure profile along the reactor length and provide a rough comparison for it by the bed expansion method.

Techniques based on the use of radiation have also been reviewed in the report. This method can also be used for providing a chordal average measurement or a point measurement depending on the complexity of the measurement process. The basis for the measurement is the attenuation of radiation by matter. The absorption of a narrow beam of radiation of initial intensity I_0 by a homogeneous material with a mass attenuation coefficient μ is expressed as :

$$I = I_0 \exp(-\rho \mu l) \quad (1)$$

where I is the intensity of radiation detected after the beam has traveled a distance l through the absorbing medium. For a mixture of two substances, say a gas and a liquid with an attenuation coefficient μ_g and μ_l and densities ρ_g and ρ_l , respectively, the corresponding relation is

$$I = I_0 \exp[-(\rho_g \mu_g l_g + \rho_l \mu_l l_l)] \quad (2)$$

where l_g and l_l are the path lengths of the beam in the gas and the liquid, respectively. In terms of the measured intensities I_{tp} , I_f and I_{mt} corresponding to the test section with the two-phase mixture, full of liquid and completely empty, respectively, the chordal average void fraction is computed from:

$$\epsilon = \frac{\ln(I_{tp}/I_f)}{\ln(I_{mt}/I_f)} \quad (3)$$

If a few chordal measurements are obtained then it is only possible to obtain the chordal average holdup along the beam paths. This is the commonly used radiation technique and is called densitometry. On the other hand if several such measurements are obtained spanning the section of interest completely then the distribution of the holdup over an entire cross section can be obtained and the method is then referred to as Computed Tomography. In systems as large as the La Porte reactors a gamma ray densitometer for chordal averaged void fractions is recommended.

It is also possible to measure the local void fraction by means of probes. The commonly used probes are based on either electrical or optical principles. The electrical impedance probes can be further based on either conductive or resistive or capacitive effects. A conductivity probe makes use of the difference in conductivity of the gas and liquid phase and is quite suitable for aqueous gas-liquid systems. Resistivity probes sense the variation in resistance between two electrodes with the passage of bubbles through the gap between them.

They are more suitable for measurement of solids' concentration. Similarly, a capacitance probe uses the difference in the dielectric constant associated with each phase for phasic discrimination. They can be used in non-polar mediums and have been used more often for solids' concentration measurements in fluidized beds and three phase systems. Depending on the phase that exists at the tip of the probe the signal in principle is binary in nature and the integration of the periods of time corresponding to a particular phase along with the total length of time for the signal gives a measure of the holdup of that phase. Optical probes exploit the differences in the index of refraction of the two phases and rely on the application of Snell's law at the probe-fluid interface. Depending on which phase exists at the probe's tip the light from the tip is reflected or refracted. Once again the holdup of a given phase is obtained on the basis of the ratio of the sum of the time periods of the signal corresponding to the phase and the total time of the signal.

All the above probes can also be used for the measurement of bubble sizes and their velocity. Two such probes can be integrated together such that their tips are vertically aligned and a small distance apart so that from the measurement of the time of flight of a bubble between the two tips the bubble rise velocity can be estimated. Each of the sensors has a binary output signal depending on which of the phases is in contact with the tip. As a bubble passes over each of the tips there is a mutual time delay t between the signals from the two sensors due to the time needed for the bubble to proceed from one probe to the other. The distance d between the probe tips being known, the component of the bubble velocity along the direction defined by the line joining the probe tips can be estimated as :

$$v_x = d/t \quad (4)$$

This velocity along with the knowledge of the mean residence time of the bubble at one of the probe tips t_m can be used to estimate the pierced chord length of the bubble as :

$$l_g = v_x t_m \quad (5)$$

A rather simple method that has found wide acceptance for measurement of bubble velocities, and in turn their sizes, is the dynamic gas disengagement technique. The method requires an accurate recording of the rate at which the surface of the dispersion drops once the gas flow is interrupted. The measured disengagement profile is used to estimate the holdup structure that existed just before gas shut off. In its simplest form the technique assumes one or two dominant bubble sizes. The initial part of the disengagement profile is considered to be dictated solely by large bubbles. The small bubbles disengage only after all of the large bubbles have left the system. The disengagement profile (the height of the two

phase dispersion as a function of time) has two distinct regions, corresponding to the two bubble sizes, which are fitted with straight lines. The slope and intercepts of the straight lines are related to the holdup and the rise velocities of the corresponding bubble sizes. If some relation (correlation) can be assumed between bubble rise velocities and their sizes then, the latter can also be estimated.

The choice of probe to be used for local holdup as well as bubble size measurement depends to some extent on the physical properties of the liquid phase in the reactor. For liquids such as alcohols the conductivity probe is more suitable since they are polar in nature and therefore the use of capacitive probes is problematic. On the other hand if the liquid phase consists of paraffins and olefins the conductivity is much lower and also these liquids are not as polar as alcohols. Consequently, a capacitance probe would be a better choice. Also, the liquids should have as low a viscosity as possible so that the dewetting time of the probe is small. For the Fischer-Tropsch wax at 250°C this should not be a cause of problems. If only the local gas holdup is of interest then either the conductivity or the resistivity probe (depending on the liquid properties) is the best choice. If however, the solids' concentration is also desired, then either the multi-sensor resistivity probe or the capacitance probe can be used. However, despite all the claims that have been made about the capabilities of these latter probes one would still need to get a sample probe for testing in simulated conditions to determine their appropriateness for the specific application. In addition, it is highly recommended to perform dynamic disengagement studies on the La Porte reactor for the assesment of bubble classes and sizes.

Techniques that have been commonly used for the measurement of liquid velocities in multiphase systems are essentially the ones used in single phase flow with some modifications in the interpretation of the measured data. These commonly used methods include the simple pitot tube, devices based on the turbine flowmeter, hot wire or film anemometry, Laser Doppler Velocimetry (LDV), Particle Image Velocimetry (PIV), particle tracking and tracer techniques.

The principle of the pitot tube is very well known and is based on measuring the differences in the pressure at the point of interest and the static pressure at the wall. The tube is inserted close to the point of interest in the flow such that its opening faces the flow. The velocity at the point is calculated based on the dynamic pressure measurement. The relationship is

$$\Delta P = \frac{1}{2} \rho v^2 \quad (6)$$

and is applicable for single phase flow. For two phase flow situations the above relation needs to be modified to account for the holdup of the second phase and some additional assumptions need to be made.

In hot wire anemometry a small electrical resistance wire or film (supported on some base) is heated and exposed to the flow stream. Due to the removal of heat by the flowing fluid the resistance changes, and this change is a function of the flow velocity and the physical properties of the fluid. Thus, in single phase flow the heat flux is directly related to the velocity. For two phase flow systems complexities arise due to the presence of a second phase and calls for some rather careful signal processing.

In analogy to tracer techniques used for measurement of the residence time distribution of a phase in a reactor, Lubbert and Larson (1990) have developed a tracer technique for measurement of the local liquid phase velocity. The method relies on using heat instead of electrolytes or dyes as the tracer. Fluid elements are tagged by direct local ohmic heating using a high frequency alternating current between two small electrodes introduced inside the reactor. The dispersion of heat is measured at a small distance away from the source of heat using a hot-film anemometer switched as a temperature detector. The information concerning the time of flow distribution is obtained from the cross-correlation between the input and output signals. A probability density function (p.d.f.) is assumed for the number of tracer particles at a given distance from the source, at a given instant of time after injection. This distribution is assumed to be normal. A nonlinear fit of the measured time of flow data to the assumed p.d.f. provides the mean time of flow as well as certain other parameters related to the local dispersion. From the mean time of flow and the distance between the sensors the local liquid phase velocity can be estimated.

Laser Doppler Velocimetry is considered to be an accurate and reliable method of measuring flow velocities in single phase flow. In a dual beam system two laser beams of equal intensity are focused to cross at a point of interest in the flow field. The measurement volume is a small ellipsoidal region at the intersection of the beams. The fluid is seeded with minute tracer particles which follow the motion of the fluid. When one such particle passes through the control volume, light from each of the beams gets scattered and interferes in space. This is seen as a varying intensity fringe pattern by a detector and is referred to as a Doppler burst. The particle velocity U is then inferred from the Doppler shift frequency.

Particle Image Velocimetry (PIV) (Adrian, 1991) in its simplest form uses a sheet of laser light to illuminate a section of the flow and images of small scattering (tracer) particles are photographed at right angles to the sheet. The concentration of the particles used corresponds to volume fraction of the order of 10^{-8} to 10^{-5} and consequently does not affect the fluid rheology. The velocity field in the plane of the imaged sheet is measured by recording a series of exposures and extracting the mean displacement of the particle image between successive exposures. Similar to other optical techniques PIV is restricted to relatively transparent media. Thus the concentration of suspended solids (if one of the

phases is a solid) has to be low. Even if one resorts to refractive index matching of the solid and the liquid phase, high concentrations of the solids would mean a reduction in the transmission of the scattered light. The use of PIV techniques to bubble columns and gas-liquid-solid fluidized beds has been advocated by L. S. Fan and his group at the Ohio State University (Tzeng et. al. 1993).

Some of the techniques mentioned above for the measurement of liquid phase velocities can also be adopted for the measurement of solid particle velocities. The laser velocimetry and particle image velocimetry methods are applicable for solids' velocity measurements in system with relatively small solids loading, generally about 15 to 20 %. With higher solids' concentration the attenuation and scattering of the light beam or sheet leads to problems in the interpretation of the signal. The radioactive particle tracking technique in our laboratory is ideally suited for the measurement of solids' velocities.

The conclusion of the review is that the presently available instrumentation for measurement of the hydrodynamic parameters are by and large cumbersome to be used in a slurry bubble column on the scale of a pilot plant. However, some gross features of the flow in such a system are still measurable. The measurement of the overall gas holdup can be achieved by means of the bed expansion method and/or by the pressure drop measurement. The bed expansion can be conveniently measured by using the gamma densitometer already in use at La Porte. It is also recommended to install a series of pressure taps along the column height which would enable the measurement of the sectional holdup in the system. They can also be used in the estimation of bubble sizes by means of the dynamic gas disengagement technique. Installation of an Americium - 241 source in addition to the Cesium - 137 source is also recommended to provide some chordal average measurements of the solids holdup by means of dual energy densitometry principles (Bukur et. al., 1996). Measurement of center-line phase velocity can also be accomplished by means of a suitably calibrated pitot tube. Tests in using the heat pulse probe of Lubbert to provide some measure of the dispersion coefficient and in turn the velocity of the phases is also recommended.

3 Tracer Studies

During this quarter all the raw data collected by Tracerco for Air Products was assembled and analyzed for consistency. Correct operating conditions for all the experiments as well as the exact positions of all detectors were recorded. The mode of tracer injection was analyzed. Preparations were made to fit the data with the existing axial dispersion based models via a parameters estimation program developed at our Chemical Reaction Engineering Laboratory (CREL). Model development was also initiated for phenomenological interpretation of the

fluid dynamics that does not rely on axial dispersion concepts.

Since it is anticipated that all the tracer studies will be completed during the first year of the contract as planned, a detailed technical discussion of the approach used and results obtained will be presented in a subsequent quarterly report in full followed by a topical report.

4 CARPT / CT Modifications

Work was initiated in this area for improving the accuracy of the CARPT technique via wavelet filtering and in extending the auxiliary instrumentation for our slurry bubble column facility to include sectional differential pressure measurements and video camera flow visualization.

The above work should be completed during the subsequent quarter and all technical details will be presented then.

5 Development of Phenomenological Models

Work is in progress on using the CARPT/CT findings in developing a liquid recirculation model and gas backmixing model. Technical details will be shown in the next quarterly report.

6 Computational Fluid Dynamics Simulation

Work is in progress on the simulation of a two dimensional bubble column utilizing the CFDLIB codes of Los Alamos. Results and comparison to experiments will be presented in the next quarterly report.

7 Research Progress and Time Table

The time table for the work proposed for the first year of the contract is shown below together with the portions of the work actually accomplished. Clearly the work is progressing well on schedule.

DOE-AIR PRODUCTS SUBCONTRACT TO WASHINGTON UNIVERSITYSBCR HYDRODYNAMICS

Objectives set for the first year (4/1/95 - 3/31/96) and accomplishments to date (9/30/95)

1. State of the Art Review of Measurement Methods

2. Interpretation of Tracer Runs at La Porte

3. Modification of CARPT/CT for Slurry Systems

4. Phenomenological Model for Liquid Recirculation

5. CFDLIB Codes Testing and Simulation

8 References

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Lubbert, A., and Larson, B., (1990), Detailed Investigations of the Multiphase Flow in Airlift Tower Loop Reactors, Chem. Eng. Sci., 45, 3047-3053.

Tzeng, J. W., Chen, R. C. and Fan, L. S., 1993, Visualization of Flow Characteristics in a 2-D Bubble Column and 3 Phase Fluidized Bed, AIChE, J., 39, 733-744.

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

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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 pulsation 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-liquid-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.

$$\epsilon_s = \frac{W_s}{\rho_s A H} \quad (1)$$

$$\epsilon_s + \epsilon_g + \epsilon_l = 1 \quad (2)$$

and

$$-\frac{dP}{dZ} = (\rho_s \epsilon_s + \rho_g \epsilon_g + \rho_l \epsilon_l)g \quad (3)$$

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

magnification and a shutter speed of 1/20,000 second. This lens is placed outside of the column and the images are obtained through the windows.

3. *Developments of in-situ liquid property measurements*

Three of the most important physical properties of liquids in slurry bubble columns at high pressure and high temperature are surface tension, density and viscosity. In the process applications involving chemical reactions, the liquid properties in the reactor vary significantly with the chemical compositions of liquid phase, which inherently depend on those of the gas phase, the holdup of the solids phase, and may also vary spatially in the reactor. Thus, the *in-situ* measurements of these physical properties is essential to the quantitative understanding of the flow phenomena in the system.

A capillary probe has been developed to measure the interfacial surface tension. The schematic diagram of the system is shown in Fig. 1. The probe consists of a supporting rod and a capillary tube. The bed is pressurized by the gas as well as the liquid vapor. The interfacial surface tension is measured when the liquid is saturated with the pressurizing gas. The capillary tube is held in the column by the supporting rod and is illuminated through the visualization window. The level of the liquid in the capillary tube placed in the test liquid is identified via direct visualization, and thus, the interfacial surface tension is calculated.

The viscosity of the liquid under elevated pressure and temperature will be determined using the falling ball technique. The system involved consists of a ball releasing device, and a guiding tube (see Fig. 2). The magnetically operated ball releasing device is placed inside the bed to release the ball into the guiding tube. The falling distance (L) of the ball within a time interval (Δt) can be measured by visualization. The viscosity can then be calculated based on the Stokes law as

$$\mu_l = f_w \frac{d_p^2 (\rho_p - \rho_l) g \Delta t}{18Z} \quad (4)$$

where f_w is the correction factor for the wall effect. The liquid viscosity is measured when the liquid is in equilibrium with the pressurizing gas.

The liquid density changes with pressure and temperature due to its compressibility and

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 1. Schematic diagram of a capillary tube surface tension measurement technique for high pressure systems.

Figure 2. Schematic diagram of a falling-sphere viscosity measurement technique for high pressure and high temperature systems.

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.

Task 4.0 SBCR Experimental Program

Tracer Studies

Introduction

One of the few ways currently available to characterize the profiles in a high-pressure, reacting, slurry bubble-column is to use radioactive tracers. Two tracer trials have been performed at the LaPorte Alternative Fuels Development Unit (AFDU). The first trial was conducted during a methanol run and is discussed in an Air Products topical report (1). The second trial was conducted during the isobutanol dehydration trial. A paper by Toseland et al. (2) detailing this trial and analyzing some of the results is attached as Appendix 1. A third trial was held in June 1995 during a methanol run. This report discusses planning for the June 1995 trial, as well as the qualitative results of the trial. Only qualitative results are available, since the data from the trial are not available from Tracerco, the company that conducted the injection of the radioactive material in September 1995.

Previous Trial Results

A diagram of the reactor and the experimental setup are covered in an Air Products topical report (3). Typical gas phase profiles are shown in Figures 4.1 and 4.2. A good initial pulse of radioactive material was obtained. An initial high level of radiation shown on the inlet pulse is a spurious reading caused by the detection of the concentrated radioactive gas in the cylinder before injection. The actual pulse starts at about 30 seconds, peaks and quickly decreases, giving a reasonable approximation of a Dirac delta (impulse) function. The traces increase in width as the pulse moves up the column, as expected for a dispersion process. In general, the pulses appear typical for such a test. However, several issues must be discussed:

Figure 4.1
Typical 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 tracer profiles near the injection point shows a strong tendency for downward flow of the tracer (Figure 4.4). The profile shows a sharp spike as the flow passes; the spike then gradually relaxes. This behavior can be explained by the generally accepted reasoning that average 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 moves 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 be 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 Ar₄₁ 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.
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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 N₂ 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.

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