ABSTRACT

The order of magnitude scaleup of the SRC-II Demonstration Plant Dissolver from the pilot plant units introduced uncertainty in hydrodynamic behavior and its impact on process performance. This led to an extensive program to study hydrodynamic parameters such as gas holdup, backmixing, and mass transfer. Cold flow bubble column experiments provided data for testing generic models at conditions representative of those expected in a dissolver. On-line radiotracer studies of the Ft. Lewis SRC Pilot Plant were conducted to verify projected hydrodynamic behavior in an operating environment. Finally, mathematical models were developed for simulating the performance of large scale reactors. All of these programs reinforced a general perception that the hydrodynamic behavior of the large SRC-II reactors will be complex, and not readily characterized by simple flow models. A conservative design philosophy and identification of viable contingencies to deal with hydrodynamics uncertainty will be necessary for first generation plants.

Summary

Anticipation of the hydrodynamic behavior in the SRC-II Demonstration Plant dissolvers would have been crucial in achieving the plant's operating goals. During the plant design, technical uncertainties with respect to scaleup of phase holdup, backmixing, and mass transfer in large bubble column reactors were recognized. Experimental programs and modeling studies were undertaken to mitigate risks associated with hydrodynamic behavior in the dissolver vessel.

The primary conclusion from these studies was that caution must be exercised in applying conventional bubble column hydrodynamic models to coal liquefaction reactors. These models have generally been based on cold flow, aqueous systems having phase properties much different than would be realized in a liquefaction reactor. These models also have generally been developed from small scale experimental units, which would be expected to exhibit flow behavior somewhat different than behavior in large commercial vessels. For the Demonstration Plant dissolver, this suggests that provision of operating flexibility and identification of operating contingencies was necessary to overcome the hydrodynamic uncertainties. Subsequent characterization of the hydrodynamic behavior in an operating Demonstration Plant dissolver would have extensively expanded knowledge in this area, and would have provided a sound basis for optimization of second generation commercial facilities.

The inadequacy of conventional hydrodynamic models was most evident in phase holdup. Radiotracer tests on the dissolver at the Ft. Lewis pilot plant suggested that gas phase holdup was approximately twice as high as expected based on conventional holdup correlations. At the operating conditions normally practiced in the pilot plant, the high level of gas holdup is believed to have resulted in a 10% reduction in actual slury phase residence time in the reactor. Extrapolation of these results to the Demonstration Plant dissolver, with its higher superficial gas velocity, suggests that actual slurry residence time would have been reduced by 20% from the design basis established in the P-99 pilot plant studies. A reduction in residence time of this magnitude would have significantly impacted yield distributions and integration with downstream units. Unit derating to either a lower coal concentration or reduced feedrate might have been necessary. In future plant design,

this issue should be addressed in a revised evaluation of risks associated with dissolver size and number.

Characterization of backmixing and hydrogen mass transfer in large bubble columns by conventional models is unproven. Use of the axial dispersion model to characterize backmixing in an SRC-II dissolver is obviously a major simplification of the stochastic flow behavior likely to occur in such a system. Conventional models of mass transfer involve estimation of interfacial surface area, which is dependent on bubble size and gas holdup, both of which are uncertain in a coal liquefaction system. Fortunately, the zero-order slurry phase reaction kinetics, and the slow rate of reaction relative to the estimated rate of hydrogen mass transfer suggest that conservative design can successfully address these uncertainties. In addition, reactor internals such as downcomers, feed distributors, flow redistributors and strategic location of quench nozzles were identified as viable approaches for influencing flow behavior.

1.0 Introduction

Scaleup of the SRC-II dissolver from pilot plant to commercial size represented a significant challenge to designers due to the multifunctional requirements of the vessel. The three phase, high temperature, high pressure environment in the dissolver complicated this task by creating uncertainty in hydrodynamic behavior. As conceptually designed for the SRC-II Demonstration Plant, the dissolver was to serve the following functions:

- Provide appropriate reaction conditions (residence time, temperature, reactant concentrations, etc.) to produce the desired product yield distribution.

- Act as a direct contact heat exchanger to transfer the exothermic heat of reaction from reaction products to the feed slurry, reducing both feed preheat and reactor quench requirements. The direct contact heat exchange was to be achieved by intense backmixing in the dissolver, primarily due to a high gas velocity relative to the slurry velocity.

- Provide effective gas and slurry phase flow distribution, both axially and radially, to assure hydrogen availability for mass transfer and reaction, and to minimize velocity gradients and stagnant liquid zones which might lead to coking or "hot spots".

- Provide sufficient gas and liquid velocity to create an "entrained bed" of coal-derived solids, thereby preventing solids settling. A continuous solids purge system was provided to extract any large solids which inadvertently were present in the feed slurry.

- Provide a safe and effective system of temperature control using gas quench.

Each of these functions would be affected by the hydrodynamic behavior within the dissolver. The sparcity of experience with commercial scale, high temperature, high pressure bubble column reaction vessels created a significant degree of uncertainty in the effects of fluid dynamic behavior in such vessels. Successful design of the commercial scale SRC-II reactors depended on adequate anticipation of this phenomenon.

Phase holdup, phase backmixing, and interphase mass transfer were aspects of hydrodynamic behavior that were addressed in the Demonstration Plant design. These factors have typically been considered in the design of large scale bubble columns by applying empirical models developed from laboratory scale aqueous cold flow experiments to predict behavior. However, there is evidence that the models are inadequate for extrapolation to large scale non-aqueous systems. Phase holdup models must address the bubble formation and coalescence properties of the system. In an SRC-II reactor, the gas phase density and liquid phase surface tension differ by orders of magnitude from the properties of the aqueous systems upon which the general holdup models are based. Bubble column backmixing has generally been characterized by the axial dispersion model. While this model may adequately represent minor backmixing phenomena in small diameter vessels which approach plug flow behavior, the concept of characterizing backmixing in large diameter, fairly well-backmixed reactors by mass dispersion is unproven.

A substantial effort was devoted to development of fluid dynamic data and models in support of the Demonstration Plant design to improve confidence in the basic design concepts. The modelling effort was of use in investigating operating strategy and process stability. Major programs included:

- Experimental studies of reaction kinetics on the A-1 CSTR to determine the reaction pathways, kinetic parameters and critical reactants. This work was crucial in establishing reaction order, which plays a major role in conversion differences between plug flow and backmixed reactors.

- Experimental studies of gas holdup in cold flow bubble columns with a variety of liquid phase components.

- Qualitative and quantitative cold flow studies of backmixing in bubble columns with a variety of liquid phase components.
- Development of integrated mass and energy balances to evaluate the performance of an SRC-II dissolver under various fluid dynamic assumptions.
- Radiotracer studies at Ft. Lewis to evaluate the adequacy of the cold flow models for holdup and backmixing.

The results of these studies, the impact on coal liquefaction reactor design, and additional studies which would reduce design uncertainty are discussed in the sections that follow.

2.0 Phase Holdup

Although three phases (gas, liquid, solid) are present in an SRC-II dissolver, the system can be simplified to a two phase system (gas and slurry) because of the extremely small size of the solid particles. The Demonstration Plant design was based on 100% of the solids in the dissolver being smaller than 100 microns in diameter, with 85-95% smaller than 10 microns in diameter.[1] For such small particles, the drag force on the particles due to fluid flow is several orders of magnitude greater than the gravitational settling forces. This causes the solid phase to become suspended in the liquid phase creating a slurry that can be treated as a single phase. This simplified analysis of the fluid behavior in the dissolver, as it obviated the need for consideration of solids concentration profiles or solids phase holdup. Slurry samples taken from the Ft. Lewis dissolver showed comparable solids concentrations at the top, middle, and bottom of the dissolver, and in the downstream separators, supporting this assumption.[2]

Gas phase holdup is a crucial variable in evaluating the performance of an SRC-II reactor. The gas holdup influences mean slurry residence time and interfacial area for mass transfer between the gas and slurry phases. A vast amount of information on general phase holdup relationships in bubble column reactors has been published. A discussion of basic results in the open literature is presented below. Due to the extreme differences in system properties that existed between these experimental studies and an SRC-II reactor, a series of cold flow bubble column tests was carried out in support of the SRC-II Demonstration Plant design to study specfic parameters. This work was complemented by radiotracer tests that were done at Ft. Lewis to define phase holdup in an actual reaction environment. These results specific to the SRC-II process are discussed below, along with thoughts about the impacts of phase holdup on the design of a commercial reactor.

2.1 Summary of Open Literature

In developing design criteria for the SRC-II dissolver, Gulf Science and Technology Company (GS&TC) conducted an extensive review of phase holdup correlations reported in the open literature through the late 1970's. They concluded that these studies had shown that phase holdup was influenced by the following major variables:

- superficial gas velocity
- superficial liquid velocity
- solids size and concentration
- liquid-gas surface tension
- bubble column diameter

Of these variables, the second and third were considered to be of minimal importance for an SRC-II reactor due to the relatively low liquid velocity and very small particle size. In addition, bubble column diameter was believed to have no effect on holdup beyond 61 cm (2 ft). GS&TC proposed the following gas holdup correlations for use in the design of SRC-II dissolvers.[3]

For a superfical gas velocity range of 0.5-3.0 cm/sec:

$$h_g = 0.042\ \sigma_\ell^{-0.1} U_{og}^{1.1}$$

For a superficial gas velocity range of 3.0-22 cm/sec:

$$h_g = \sigma_\ell^{-0.1} D_t^{-0.08} (0.181n(U_{og}) - 0.05)$$

Where h_g = gas holdup, volume fraction
σ_ℓ = liquid surface tension, dynes/cm
D_t = column diameter, cm; for D_t more than 61cm, use D=61cm
U_{og} = superficial gas velocity, cm/sec.

The high gas velocity equation is of a different form than the typical literature - reported gas holdup correlation of:

$$h_g \propto U_{og}^{b}, \quad (\text{with } b \simeq 0.6)$$

Within the limited range of gas velocities considered for the SRC-II Demonstration Plant dissolver (5-12cm/sec), the GS&TC equation and the standard literature equation produce similar trends, with GS&TC's equation providing a better fit of reported holdup data.

The problem in extending the gas holdup relationships to an SRC-II reactor is that the correlations, including GS&TC's, are highly empirical, based on air-water or similar systems operated at near-ambient conditions. The physical properties of the liquid and vapor phases in a high temperature, high pressure SRC-II reactor would be quite different. A comparison of major differences is shown in Table I. The two greatest differences are vapor stream density (SRC-II density more than 25 times greater than typical cold flow system vapor density), and liquid surface tension (SRC-II surface tension approximately an order of magnitude lower than that of the air/water system). These physical properties would be expected to have profound consequences on gas holdup, buoyancy of the vapor bubbles, bubble rise velocity, bubble stability, bubble size, and coalescence.

The order of magnitude extrapolation of the effects of these properties is well beyond the region for which the holdup correlations were developed. Therefore, it was recognized that it would be desireable to validate the holdup relationships with components having properties similar to the phases in a coal liquefaction reactor, and on actual coal liquid systems at design operating conditions.

2.2 SRC-II Design Data

To better define the effects of specific variables on gas phase holdup, studies were conducted in support of the SRC-II Demonstration Plant design. Cold flow studies were made on laboratory scale equipment at the University of Pittsburgh, and on a 1 ft diameter diameter by 25 ft tall bubble column at GS&TC. An effort was also made to measure holdup in an actual SRC-II reaction environment during radiotracer tests at Ft. Lewis.

2.2.1 University of Pittsburgh Cold Flow Studies[4]

Gas holdup relationships were observed as part of a comprehensive study of bubble column fluid dynamics. A continuous liquid flow bubble column (6" ID x 11 ft high) and a batch liquid bubble column (12" ID x 8 ft high) were used in this program. Gas holdup was studied as a function of gas and/or liquid velocity for a number of vapor/liquid systems. Liquid phase parameters studied included viscosity, surface tension, solids size and concentration, and electrolyte concentration.

Typical batch column gas holdup results for various liquid systems are shown in Figure 1. The observation of very large gas holdup with the dilute propanol solution was consistent with levels of gas holdup observed for other dilute alcohol systems in the University of Pittsburgh work. Figure 1 also shows estimated gas holdup for the air/water system from the Hikita, et. al. correlation[5], and observed levels of gas holdup for 10% glycerin/air, and 12% and 30% concentrations of 33 micron coal in the air/water system. All of the curves are consistent in showing increasing gas holdup at increasing superficial gas velocity.

As observed from Figure 1, the presence of small diameter (33 micron) coal solids contributed to a decrease in gas holdup relative to the air/water system at all gas velocities studied. The holdup was also observed to decrease as coal concentration increased. Analysis of solids concentraton profiles along the length of the column during these runs indicated that solids concentration in the liquid phase was independent of height, suggesting that the coal particles were completely suspended in the liquid phase, even at gas velocities as low as 2.2 cm/sec.

Other tests conducted on the same column with sand/water solutions showed that the higher density and larger diameter sand did not reduce gas holdup as much as for the coal slurries. In the air/water/sand runs, gas holdup was noted to be relatively constant along the length of the column, but solids concentration was observed to decrease with increasing height, indicating that some settling was occurring.

The different gas holdup relationships observed with the coal and sand systems suggest that the interaction of density, particle size and concentration of the solids phase must be considered in determining potential effects on gas holdup. Based on these cold flow results, the high concentration (more than 25 wt%) and small particle size (less than 10 microns) of coal-derived solids in an SRC-II dissolver qualitatively would be expected to inhibit gas holdup to some extent. Unfortunately, guidelines for quantifying this effect are non-existent.

Because the surface tension of the liquid phase in an SRC-II dissolver was expected to be very low (5-10 dynes/cm), this parameter was extensively investigated in the University of Pittsburgh bubble column program. Aqueous solutions of straight chain alcohols were selected to study the impact of chain length and surface tension on gas phase holdup. As the results in Figure 2 indicate, a general trend of increased holdup with increased chain length was observed. Holdup for the dilute propanol and butanol solutions was noted to be very high--much higher than would have been predicted by literature correlations for surface tension effects. As Figure 3 shows, a study of different levels of surface tension of propanol and butanol aqueous mixtures did not indicate a direct correlation between surface tension and gas holdup. The inability to theoretically explain the high level of gas holdup observed with propanol and butanol solutions is an indication that a substantial degree of uncertainty exists in the empirical relationships for gas holdup.

The study of the effect of liquid velocity indicated that increased liquid velocity tended to reduce gas holdup, but the extent of this effect was not consistent in all cases. Some of the most pronounced effects are illustrated in Figure 4.

The fundamental conclusion drawn from the bubble column tests at the University of Pittsburgh was that existing correlations for gas holdup were inadequate for accurately predicting holdup relationships for untested systems. There was a complex interaction among the many variables which impacted holdup in a given system. Bubble formation and coalescence characteristics are likely to be the cause of this, but unfortunately, fundamental knowledge about bubble formation and coalescence characteristics is lacking. These results suggested that confident prediction of gas holdup in the SRC-II Demonstration Plant dissolver depended upon verification of model suitability on actual coal liquid systems at operating conditions.

2.2.2 Gulf Science & Technology Cold Flow Studies[6]

Gas holdup measurements on a 25 ft high x 12" ID plexiglass bubble column operated with air/water and air/water/sand systems were in reasonable agreement with values predicted from literature correlations. These correlations had been developed from data obtained on small diameter columns, with similar or identical liquid and vapor systems. The agreement between observed and predicted levels of gas holdup was interpreted to indicate that column diameter effects were adequately addressed in the existing holdup models, increasing confidence in predicting holdup in large units from laboratory data.

2.2.3 Ft. Lewis Dissolver Radiotracer Tests[2]

Residence time distribution and phase holdup data in an SRC-II reactor environment were obtained through radiotracer studies on the Ft. Lewis dissolver during normal SRC-II operations. Gas (argon-41), liquid (bromine-82 as bromophenanthrene), and solid (flaked or colloidal gold-198) radioactive tracers were injected either into the dissolver or upstream of the dissolver. The concentration of radioactive material was measured as a function of time with scintillation detectors at various locations along the dissolver. The unique problems associated with the injection and detection of radiotracers in a high pressure system, and with the interpretation of the data, resulted in the need to develop specific injection and analytical techniques for these studies. Four series of radiotracer tests were completed at Ft. Lewis from June, 1979 through February, 1981. Due to the evolutionary nature of this program, the best results were believed to be those from the February, 1981 test series, which are discussed below. The major emphasis in the radiotracer tests was to study backmixing in the reactor. However, by analyzing the tracer concentration data, it was also possible to obtain estimates of mean residence time and phase holdup.

Results from the gas and liquid phase radiotracer injections at the inlet of the dissolver are presented in Table II. Three gas phase radiotracer injections were made. The first and third injections resulted in similar estimates of mean residence time to the top detector (58.7 and 65.3 seconds) and bottom detector (23.5 and 26.8 seconds). Results from the second gas tracer injection produced much different estimates of residence time. A review of the tracer concentration curves produced in the second injection revealed substantial noise in the detector signals. In light of this, and the apparent anomaly in mean residence time, the results from the second injection are not included in the discussion that follows.

The operating conditions and analytical results from the first and third gas tracer injections are summarized in Table III. The injections resulted in different estimates of gas phase residence time at the top and bottom detectors. This indicated that vapor flow through the dissolver approached plug flow, with the bulk of the radiotracer passing the bottom detector well in advance of passing the top detector. The distinct peak in the detector curves supported this conclusion. The mean residence time to the top detector was a reasonable indication of total residence time in the dissolver, as it included approximately 95% of the dissolver volume.

To analyze the tracer curve results, it was necessary to consider the flow conditions and detection techniques at the measurement points. The Ft. Lewis dissolver system was representative of an open vessel (undisturbed flow at measurement points) with radiotracer measurement via a "through the wall" detection technique.[9] The first moment (Mean Residence Time) of the concentration curves produced in this system was related to actual mean residence time by the following equation:

$$\text{Actual Residence Time } (\bar{t}) = \frac{\text{Concentration Curve MRT } (\bar{t}_c)}{1 + 2 \times \text{Dispersion Number } (\frac{D}{uL})}$$

Fractional gas holdup was calculated by the following relationship:

$$\text{Gas Holdup } (h_g) = \frac{\text{Actual Mean Residence Time } (\bar{t}) \text{ X Volumetric Flowrate}}{\text{Vessel Volume to Detector}}$$

Actual mean residence time and fractional gas holdup for the gas phase injections are shown in Table III. Both injections produced estimates of overall gas holdup in the dissolver of approximately 20% of the dissolver volume. Both injections also produced estimates of extremely large gas holdup at the bottom of the dissolver (45%). Whether this large gas holdup was real, possibly due to the simple nozzle-type feed distributer at the dissolver inlet, or incorrect due to problems in radiotracer injection or measurement techniques is uncertain. Further studies would have been warranted to resolve this, had the SRC-II project continued. The overall vapor phase holdup of 20% shown in Table III is believed to be representative of conditions in the Ft. Lewis dissolver during normal SRC-II processing.

This estimate of gas holdup (20%) differed significantly from the 10.5% holdup estimated for Ft. Lewis using the SRC-II Demonstration Plant gas holdup correlation. At the 20% overall gas holdup estimated from the radiotracer study, the actual slurry residence time in the Ft. Lewis dissolver would have been only about 90% of what it was believed to have been based on the Demonstration Plant correlation.

The evidence of higher than expected gas holdup in the Ft. Lewis dissolver is consistent with results reported for the EDS pilot plant (ECLP), which also experienced high levels of gas holdup.[7] In fact, the 20% holdup suggested by the Ft. Lewis radiotracer results corresponds closely to extrapolation of the ECLP holdup data to the lower superficial gas velocity employed at Ft. Lewis. High gas holdup was not identified as a process problem at Ft. Lewis because at the normal pilot plant gas velocities, the impact on slurry residence time in the dissolver and process yields was small relative to the normal process yield scatter. High holdup was an identifiable problem at ECLP, and led to reduced conversion to distillate products at ECLP because of the higher gas velocities employed there.

It is clear that if the SRC-II project had continued, additional efforts at defining gas holdup under actual operating conditions would have been desireable. It is also likely that, based on the Ft. Lewis and ECLP holdup results, reconsideration of the Demonstration Plant dissolver design to provide additional slurry residence time would have been warranted.

2.3 Impacts of Gas Holdup on Reactor Design

The acknowledgement of the inadequacy of existing correlations for accurately predicting gas holdup for simple systems such as those studied at the University of Pittsburgh, and the observation of high levels of holdup at Ft. Lewis would have required some reevaluation of design philosophy. The most critical concern obviously would have regarded conversion in the dissolver. Higher than expected gas holdup in the Demonstration Plant would have resulted in less actual slurry residence time in the dissolver than required in the Design Basis. This shorter residence time would have led to less conversion of heavy coal liquids to hydrocarbon distillate and gaseous products.

Extrapolation of the Ft. Lewis gas holdup results to the Demonstation Plant scale suggests that gas holdup of more than 40% would have occurred in the single dissolver vessel per train design at normal gas velocities (10.8 cm/sec.) This would appear to be an unreasonably large gas holdup, based on most cold flow bubble column studies. However, the University of Pittsburgh studies discussed above indicated that such large gas holdups can occcur in some systems. At a gas holdup of 40%, the actual slurry residence time in the Demonstration Plant dissolver would have been approximately 80% of the design level. The lower slurry residence time would likely have produced a significant increase in SRC yield, perhaps of 5% m.f. coal or more. A shift from the design yields of this magnitude would have resulted in decreased liquid product yield and increased vacuum bottoms production. Such a shift could have presented a serious long term problem in the operability of the highly integrated demonstration facility. To balance the overall plant, it might have become necessary to decrease coal thoughout or otherwise change operating conditions to lower the vacuum bottoms yields. This would have amounted to derating the unit.

Table I

Comparison of System Physical Properties
Typical Cold Flow Fluid Dynamics
Test Unit Vs. Expected Conditions in an SRC-II Dissolver

	Air/Water Cold Flow System	SRC-II Dissolver*
Operating Conditions		
Pressure	20 PSIA	2000 PSIA
Temperature	80°F	860°F
Major Differences in Vapor Stream Properties		
Molecular Weight	29	19.5
Components	79 v% Nitrogen 21 v% Oxygen	68 v% Hydrogen 14 v% C_1-C_4 7 v% C_5 + 11 v% Non-hydrocarbons
Density at 60°F, 1 atm	0.0764 Lb/Ft^3	0.0514 Lb/Ft^3
Density at Temp/Pressure	0.1001 Lb/Ft^3	2.64 Lb/Ft^3
Major Differences in Liquid Stream Properties		
Surface Tension	72 dynes/cm	5-10 dynes/cm

*SRC-II data based on Demonstration Plant Dissolver PFD (DWG. E7341-11-106-2) and SRC-II Physical Properties Data Book

TABLE II

SUMMARY OF DATA FROM RADIOTRACER INJECTIONS AT REACTOR INLET
February 1981
SRC-II MODE

Date	Time	Phase	Detector Location	Mean Residence Time*	Dispersion Number
2/20/81	14:20	Gas	Top	58.7 sec.	0.092
			Bottom	23.5 sec.	0.081
2/23/81	14:51	Gas	Top	104.0 sec	0.104
			Bottom	11.3 sec.	0.077
2/23/81	17:09	Liquid	Top	63.6 min.	0.145
			Bottom	65.6 min.	0.149
2/24/81	16.06	Gas	Top	65.3 sec.	0.076
			Bottom	26.8 sec.	0.165
2/24/81	20.48	Liquid	Top	65.4 min.	0.143
			Bottom	63.4 min.	0.154

*Mean Residence Time Based on the First Moment of the detector concentration curve.

TABLE III
Inlet Gas Tracer Injection Results

	2/20/81 Injection	2/24/81 Injection
Plant Conditions		
Feed Slurry Rate, LB/HR	6903	6583
Feed Gas Rate, LB/HR	739	760
Gas Molecular Wt.	4.35	4.50
Gas Volumetric Flow, SCFH	64471	64093
Gas Volumetric Flow, ACFH (860°F,2000 psig)	1278	1264
Tracer Data		
Top Detector		
Concentration Curve MRT $(\bar{t}_c)$	58.7 sec	65.3 sec
Concentration Curve Dispersion Number $(\frac{D}{uL})$	0.092	0.076 sec
Estimated Gas Phase Mean Residence Time	49.6 sec	56.7 sec
Vessel Volume to Detector	88.4 Ft^3	88.4 Ft^3
Fractional Gas Holdup	0.199	0.225
Bottom Detector		
Concentration Curve MRT $(\bar{t}_c)$	23.5 sec	26.8 sec
Concentration Curve Dispersion Number $(\frac{D}{uL})$	0.081	0.165
Estimated Gas Phase Mean Residence Time	20.2 sec	20.2 sec
Vessel Volume to Detector	16.1 Ft^3	16.1 Ft^3
Fractional Gas Holdup	0.445	0.441

3.0 Backmixing

The flow regime and extent of backmixing in an SRC-II dissolver are of interest because of their impact on reaction rates, conversion, and reactor temperature profile. The main hydrogenation and hydrocracking reactions in the dissolver are temperature sensitive and exothermic. Temperature control within the dissolver is a major concern due to slow reaction rates at low temperatures and the retrogressive coking reactions that occur at high temperatures. Ideal reaction temperatures for the SRC-II process are believed to be in the relatively narrow range of 850-860°F.

A major premise in the conceptual design of the Demonstration Plant dissolver was to have it act as a direct contact heat exchanger, transferring process exothermic heat of reaction to the feed slurry.[8] This concept provided a beneficial reduction in both the slurry preheater heat duty and reactor quench requirements. A major assumption in the design was that effective direct heat transfer could be achieved by slurry phase backmixing created by intense agitation resulting from the relatively large vapor flowrate through the dissolver.

Large commercial bubble columns have been built and operated, but information on fluid dynamic behavior in these units is scarce. Modeling of backmixing in the large units has been based on results obtained from small scale aqueous cold flow systems. As discussed above for gas holdup modeling, the result has been development of mathematical relationships specific to those systems. Whether those relationships apply to the large diameter, high height, high temperature, high pressure SRC-II dissolvers is uncertain.

3.1 Bubble Column Flow Models

Most of the reported bubble column modeling studies have been based on application of the axial dispersion model (or dispersed plug flow model) to bubble column systems. Conceptually, this model considers the flow within the vessel to be essentially "plug flow, on top of which is super-imposed some degree of backmixing".[9] An assumption in this model is that there can be no stagnant conditions or radial variations in fluid velocity (such as flow channeling). The mathematical description of the dispersion model is equivalent to Fick's law of molecular diffusion. The axial dispersion coefficient, D_ℓ , is introduced in place of the molecular diffusion coefficient in Fick's law. The axial dispersion model is frequently presented in dimensionless form with the dispersion parameter rearranged to the form D_ℓ /uL, known as the dispersion number, where u is the fluid velocity and L is the reactor length. (The inverse form of this parameter (uL/D_ℓ), the Peclet Number, is occasionally used). Historically, this model has been used to describe nonideal flow in systems which approach plug flow, such as packed beds and small diameter bubble columns. Efforts to apply the model to commercial bubble column systems have been common, but the success of the model in predicting actual flow behavior in large systems has been limited.

The dispersion number parameter is an indication of the degree of backmixing in a reactor system. The implication of the value of the dispersion number is:

as $\frac{D_\ell}{uL} \to 0$, the system approaches ideal plug flow, and

as $\frac{D_\ell}{uL} \to \infty$, the system approches fully backmixed behavior.

Flow behavior between the extremes of ideal plug flow and perfect backmixing is characterized by intermediate values of the dispersion number. The dispersion number for an existing reactor system can be estimated from effluent concentration data obtained after injecting a pulse of tracer material into the reactor. Concentration curves for various dispersion numbers in open systems are shown in Figure 5.

Small scale bubble columns have been used to study the relationships between system operating conditions and the resulting dispersion number. These relationships have been used to develop fundamental relationships for the dispersion coefficient, which can be used for scaleup. Two of the most commonly used dispersion coefficient correlations are:[11]

$$D_\ell = 2.7 \quad D_t^{1.4} \quad U_{og}^{0.3} \text{ and} \tag{1}$$

$$D_\ell = 2.41 \quad D_t^{1.5} \left(1 + 0.43 \frac{U_{og}^{0.85}}{D_t^{0.43}} \right) \tag{2}$$

Where

D_ℓ = dispersion coefficient, cm^2/sec

D_t = Column diameter, cm

U_{og} = superficial gas velocity, cm/sec.

A major concern in applying the dispersion model for scaleup has been that the flow patterns in large vessels may be very different from flow patterns in small diameter experimental columns.[11] There has also been some indication that churn turbulent flow, which is believed to predominate in commercial vessels like the SRC-II dissolver, may lead to the development of stable internal circulation "cells", as shown in Figure 6. Such flow patterns violate the uniform radial velocity assumption of the axial dispersion model and can lead to misleading interpretations of fluid dynamic behavior.

Another model used to represent non-ideal flow in reactors is the tanks-in-series model, which visualizes a number of perfectly backmixed continuous stirred tank reactors (CSTR) in series. As the number of tanks in the series is increased, the model can be made to simulate plug flow. This model is better suited than the dispersion model for characterizing highly backmixed systems. Unfortunately, this model has not been extensively developed for bubble column systems. Empirical relationships for model parameters are therefore weak or unproven.

Large bubble columns like the SRC-II dissolver are likely to experience complex fluid dynamic behavior that cannot be fully modeled by the simple axial dispersion or tanks-in-series models. Multi-parameter models can prove useful in modeling these complex systems. These models consider the reactor to consist of an intercorrected arrangement of idealized flow regimes (dispersed plug flow, backmixed flow, recycle, stagnant zones, etc.). The major shortcoming of this model is that it is an after-the-fact type of model. It can be used to establish an empirical arrangement of interconnected flow units that will explain flow in an existing reactor, but whether a similar arrangement would result upon scaleup is uncertain.

Conceptual depictions of how the axial dispersion, tanks-in-series, and multiparameter models might be applied to an SRC-II reactor are shown in Figure 7. It is desireable to separately consider the vapor and slurry phases due to their different velocities, residence times, and extent of backmixing.

3.2 SRC Experimental Programs

To develop a more comprehensive understanding of backmixing phenomena, and to investigate concepts of interest in the scaleup of an SRC-II dissolver, backmixing experimental and modelling studies were conducted in support of the SRC-II Demonstration Plant. The axial dispersion model was selected as the basis for this work. Backmixing was studied qualitatively and quantitatively on the 12" ID x 25 ft tall cold flow bubble column at GS&TC to determine if the dispersion model could be extended to a column of that height and diameter. Radiotracer injection studies were conducted on the Ft. Lewis dissolver to evaluate flow behavior in an operating environment. In addition to these large column studies, cold-flow laboratory studies were conducted at the University of Pittsburgh to develop a fundamental understanding of how liquid and system properties may affect mixing. Results from these programs are discussed below.

3.2.1 GS&TC Bubble Column Tests

Liquid phase backmixing for the air/water system was studied on a 12" ID x 25' tall plexiglas column. Qualitative tests consisted of visual observation of the column following liquid dye injection at the top or middle of the column.[12] During these tests, the column was operated in a batch liquid mode (gas flow, but no liquid flow). The dispersion and progression of dye through the column was recorded with color photographs. When dye was injected at the top of the column, approximately two minutes were required to achieve equal color distribution throughout the column. For middle injections, upward migration was rapid, but downward migration remained slow, still requiring two minutes to achieve complete backmixing. Radial dispersion of the dye after injection appeared to occur instantaneously. The dye was reported to concentrate axially in distinct zones or "cells", which appeared to be internally well-backmixed. This observation was interpreted to support the hypothesis that large diameter columns operated under turbulent conditions can be characterized by a multiple cell recirculation model (Figure 6).

The qualitative tests were followed by a series of quantitative tests in which caustic tracer solution was injected into the column under co-current continuous flow conditions (liquid and gas flow).[6] Input and output tracer concentration curves were developed by continuous measurement of solution conductivity. The first and second moments of the tracer concentration curves were calculated, resulting in estimates of liquid phase mean residence time and dispersion number. The results of these liquid tracer tests at various gas phase velocities are shown in Table IV. Observed dispersion numbers were significantly lower than predicted values at all gas velocities studied, indicating that backmixing was less complete than was predicted based on the dispersion coefficient correlations in Equation 1.

The results of these cold flow studies suggested that application of the axial dispersion model based on standard literature dispersion coefficient correlations may not adequately describe the extent of backmixing in large reactors. The apparent presence of "circulation cells" observed in the qualitative tests also casts doubt about whether the fundamental dispersion model assumption of a uniform radial velocity profile is met in large bubble columns.

3.2.2 Ft. Lewis Radiotracer Tests

Radiotracer tests were performed on the Ft. Lewis dissolver to study backmixing in an SRC-II reaction environment. Due to the evolutionary nature of this program, the results can only be considered as preliminary. Interpretation of mixing data is complex, and analysis of the results obtained in the reported Ft. Lewis tracer tests indicates that data interpretation precedures needed to progress further. Had the SRC-II Demonstration Plant project continued, additional dissolver tracer studies would have been desireable. Results from the last set of injections in February, 1981, will be discussed here.[13]

Injections of liquid (Br-82) and gas (Ar-41) phase radiotracers were made into the dissolver feed stream or at the middle of the dissolver. Radiotracer concentration was monitored with scintillation detectors located near the dissolver walls at the top and bottom of the vessel, as shown in Figure 8. Detectors were also located at the injection point to confirm that a pulse injection was achieved.

The radiotracer concentration data were analyzed using a method-of-moments technique. Estimates of the first moment (mean residence time) and second moments (variance) were obtained. The dispersion number parameter for the axial dispersion model was calculated based on these estimates and open vessel boundary conditions. This analytical procedure was followed for both liquid and gas phase radiotracer data.

Liquid Radiotracer Results. A typical radiotracer concentration curve is shown in Figure 9. Reported results from the data analysis of the liquid radiotracer injections in February 1981 are provided in Table V.[13] These tests resulted in consistent estimates of mean residence time (about 65 minutes) and dispersion number (0.15).

It is important in analyzing concentration data in this manner that the estimated dispersion model parameters (mean residence time and dispersion number) be substituted into the model and a projected concentration curve generated. This curve must then be compared to the actual data to determine if the estimated model parameters adequately represent actual behavior. This is necessary for two reasons. First, flow behavior which violates the dispersion model assumptions can create skewing or unusual tailing in the curves. Second, well backmixed systems will produce curves with long, extended tails. It is essential that these tails be considered in the analysis of curve data. Either of these factors can produce gross errors in the interpretation of the estimated moments.

Examples of possible concentration curves expected for different dispersion numbers were presented in Figure 5. Referring to Figure 5, it is apparent that dispersion numbers between 0.1 and 0.2 (Table V) are indicative of concentration curves very different from the Ft. Lewis data shown in Figure 9. The actual tracer data appear better represented by a dispersion number greater than 1.0. This apparent failure of the method-of-moments technique to estimate dispersion in this case must be investigated further. The failure to adequately predict dispersion number by the method-of-moments also implies that the mean residence time data shown in Table V are of questionable accuracy.

To study the effect of the concentration curve characteristics on the estimate of mean residence time and dispersion number, the curve in Figure 9 was smoothed as shown in Figure 10. Three possible baselines are apparent from Figure 10. These are shown in Figure 11. Also shown in Figure 11 are the calculated estimates of mean residence time for each baseline based on applying the method-of-moments to the concentration data. Estimates of mean residence time and dispersion number based on the method-of-moments technique applied to the baselines in Figure 11 are shown in Table VI. While estimates of mean residence time varied substantially (31 to 65 minutes), the estimated dispersion numbers for all of the baselines were similar due to the identical curve shapes. Substitution of the estimates of residence time and dispersion number into the axial dispersion model and prediction of normalized concentration curves resulted in the curves shown in Figures 12-14. None of the predicted curves resembled the original concentration curve. The poor fit of the concentration curve data using the method-of-moments estimates of model parameters leads to the conclusion that either the axial dispersion model is inappropriate in describing slurry flow behavior in the Ft. Lewis dissolver or the data curve was incomplete due to cutting off measurement of the tail. Assuming the latter to be true, the Ft. Lewis tracer data can be used to test model parameters derived in other ways.

An alternative means for estimating the dispersion number is to estimate the dispersion coefficient, and use it to calculate the dispersion number. Applying the dispersion coefficient correlations in Equations (1) and (2) to the conditions at Ft. Lewis results in estimated dispersion coefficients of 1219 cm ^{2}/sec and 1379 cm ^{2}/sec, respectively. Based on an estimated gas holdup of 20% of the dissolver volume, and slurry holdup of 80%, the slurry phase mean residence time (slurry volume in the reactor divided by slurry volumetric flowrate) was calculated to be 46 minutes. Applying an average disperson coefficient of 1300 cm ^{2}/sec and a mean residence time of 46 minutes to the axial dispersion model results in the estimated concentration curves illustrated in Figure 15 for the indicated baslines.

The curves in Figure 15, based on a dispersion number of 4.375, visually resemble the tracer data curve more closely than the curves calculated from the method-of-moments analysis, although the fit of the curve tail remains poor. This suggests that backmixing in the Ft. Lewis dissolver was greater than had been indicated by the reported dispersion number data (0.15 in Table V). A dispersion number of 4.375 is indicative of a fairly well backmixed system. This is consistent with perceived high levels of liquid phase backmixing in the Ft. Lewis dissolver, as evidenced by the relatively flat temperature profile throughout most of the dissolver.

Two conclusions are justified from these liquid phase tracer data. First, the slurry phase at Ft. Lewis was well backmixed. The extent of backmixing was in line with dispersion model expectations based on literature correlations for the dispersion coefficient. .Second, the method-of-moments data analysis technique did not provide a reliable estimate of mean residence time or dispersion number for the slurry phase. This appears to have been due to the failure to include the complete tracer curve in the data analysis. Backmixed systems like the Ft. Lewis dissolver produce concentration data curves with extremely long tails, which have a significant influence on the analytical results. (For example, a dispersion number of 4 is characteristized by a concentration curve with an extended tail in which the normalized concentration declines to 1% of its peak value only after more than 30 times the mean residence time has elapsed.) The value of the Ft. Lewis data in validating the use of the axial dispersion model is limited because of the short time frame of the data obtained. It was not possible to determine if significant flow irregularities, such as radial variations in velocity or stagnant zones, were present in the Ft. Lewis dissolver. Future tests of this nature should take care to monitor the entire span of the tracer concentration curve.

Although the high level of backmixing observed at Ft. Lewis is encouraging for scale up, the results of this study are highly empirical. Applicability of the dispersion coefficient relationships shown in equations (1) and (2) to larger diameters is not proven by the Ft. Lewis data. The exponential effect of diameter on dispersion coefficient in those relationships should be of concern for large diameter columns.

Gas radiotracer results. A typical gas phase radiotracer concentration curve is shown in Figure 16. The detector signal returns to the original baseline within the recorded time frame and significant tailing is not evident. Results from the method-of-moments analysis of concentration data from the gas tracer injections are shown in Table VII. The gas phase in the Ft. Lewis dissolver was expected to approach plug flow. Because of this characteristic, injection point and detector location affect the value of the estimated mean residence time, which is not the case under backmixed conditions. The presence of a bottom detector response during the middle injections suggested that either the radiotracer was absorbed into the backmixed liquid phase, or gas bubbles were entrained in the turbulent backmixing of the liquid phase and carried downward with the liquid phase. The low values (0.1) of the calculated dispersion numbers suggested that the gas phase approached plug flow, with only minor backmixing. Referring to Figure 5, a gas phase dispersion number of 0.1 appears to characterize a concentration curve similar in shape to the data shown in Figure 16. This suggests that the method-of-moments produced reliable estimates of dispersion model parameters for the gas phase. The large amount of signal noise in the gas tracer curves made it difficult to create a smoothed curve and develop a comparison of predicted to actual data. Such a step would have indicated the extent to which the dispersion model fit the vapor phase flow in the dissolver. It would also have provided insight into potential gas phase flow irregularities such as channelling.

3.2.3 University of Pittsburgh Bubble Column Studies[4]

A series of cold flow experiments was conducted at the University of Pittsburgh to investigate the fundamentals of bubble column mixing and flow regimes. These tests were carried out on the 6" ID by 11 ft. high continuous cold flow bubble column. Air was used as the vapor phase. Four liquid phases were investigated as shown below. Some measured physical properties of the liquids are shown in Table VIII.

Dilute Alcohol Solutions: Chosen to study the effects of low surface tension, relatively high gas holdup, and hindered bubble coalescence.

Carboxy-Methyl-Cellulose (CMC) Solutions: Chosen to study the effect of viscosity with a non-Neutonian fluid. These solutions exhibited increasingly pseudoplastic behavior with increasing concentration.

Sodium Chloride Solutions: Chosen to study the effect of electrolytic characteristics, which hinder bubble coalescence.

Polyacrylamide (PAA) Solutions: Chosen to study the effect of non-Neutonian viscoelastic behavior on flow regime and mixing.

The transition of the flow regime from bubble flow to churn turbulent flow was studied for each group of liquids. Gas phase drift flux was calculated and plotted as a function of gas holdup. Drift flux was defined as:

$$W_{cd} = U_{og} - h_g(U_{og} + U_{o\ell})$$

where U_{og} = superficial gas velocity (cm/sec)

$U_{o\ell}$ = superficial liquid velocity (cm/sec)

h_g = gas holdup (volume fraction)

W_{cd} = drift flux (cm/sec)

Smoothed results for some of the conditions studied are presented in Figures 17-20. The point at which an abrupt change occurred in the slope of the drift flux versus gas holdup plot was identified as the transition from bubble flow to churn turbulent flow. The results shown in Figures 17-20 indicate that liquid composition played a role in determining the level of holdup at which churn turbulent flow predominated. Figure 17 shows that increased alcohol chain length deferred the onset of churn turbulent flow. Similar results were observed with increasing concentrations of sodium chloride, as shown in Figure 18, and PAA solutions, as shown in Figure 19. Increasing concentrations of CMC solutions had the opposite effect, causing the flow regime transition to occur at lower levels of gas holdup.

Definition of bubble column flow regime is important because the flow regime is a major determinant of the extent and type of backmixing or dispersion that occurs. Quiescent bubble flow can be seen to approach the concept of axial dispersion, with orderly movement of bubbles through the column. Churn turbulent flow, on the other hand, is characterized by intense bubble movement, bubble breakage and coalescence, and physical recirculation which results in cross-sectional velocity gradients. The results in Figures 17 to 20 show that liquid phase properties can cause flow regime transition to occur over a wide range of gas holdup (10-40%). Unfortunately, a sound basis for extrapolating this discovery to the coal liquid/hydrogen system does not exist. It would be desireable to investigate the flow regime transition for coal liquid components.

Backmixing was studied through temperature surveys during continuous addition of heat at the top of the bubble column. The axial temperature profile data were used to calculate thermal dispersion coefficients for the axial dispersion model. Since physical properties were nearly constant through the column, the thermal dispersion coefficients were considered to be comparable to mass dispersion coefficients. Some scatter was observed in the calculated dispersion coefficients, probably due to observed temperature fluctuations in the column resulting from stochastic mixing patterns. However, based on a qualitative review of the data, some trends appeared to be evident .

The bubble flow and churn turbulent flow regimes observed in the drift flux/gas holdup plots appeared to result in distinct behavior in the dispersion coefficients. A general plot of dispersion coefficient versus gas holdup is presented in Figure 21. The bubble flow regime was typically characterized by fairly constant dispersion coefficients. However, as shown in Figure 21, relatively high levels of dispersion were sometimes encountered at very low gas holdup. When this occurred, dispersion would decrease to "normal" levels with only a small increase in holdup. This phenomenon was unpredictable. It occurred with all of the classes of liquids tested, but generally occurred only at conditions of intermediate superficial liquid velocity (5-10) cm/sec) and low superficial gas velocity (2-3 cm/sec). It was speculated that this phenomenon resulted from strong liquid recirculation patterns caused by radial gradients in gas holdup and velocity.

Dispersion coefficients in the churn turbulent flow regime typically exhibited a monotonically increasing trend consistent with steadily increasing levels of turbulence and backmixing. However, at high levels of gas holdup, a decrease in dispersion was sometimes observed as holdup increased further. This phenonemon also was unpredictable.

The dispersion coefficients calculated from the bubble column were compared to coefficients estimated from literature correlations. None of the tested correlations consistently produced reliable (± 10%) estimates of dispersion coefficients. This was not surprising considering the poor reliability of general correlations observed in the gas holdup studies. The literature correlations for dispersion coefficient can be considered to be highly empirical, and reliability for extrapolation to different liquid systems requires validation with experimental data.

Two major conclusions were warranted by the bubble column studies. First, flow regime transition was significantly affected by liquid composition, but a means of predicting the transition for non-tested systems is unavailable. Second, to maximize the level of dispersion or backmixing, it is desirable to operate in the churn turbulent flow regime, which is generally accompanied by high gas velocity and holdup. It is significant to note that very high levels of gas holdup (ca. 40% in a commercial SRC Dissolver) may hinder dispersion.

3.3 Modeling Studies

Mathematical simulation studies of the SRC-II dissolver system were conducted in support of the Demonstration Plant design to study the impact of different levels of backmixing on product yields, temperature profiles, and temperature control. The material balances used in these simulations were developed from either the simplified SRC-II kinetic model or the second order yield correlation models. The kinetic model was based on data obtained on the A-1 continuous stirred tank reactor at GS&TC.[14] The simplified reaction kinetic model is illustrated in Figure 22.[15] The yield correlation models were based on a combined pilot plant data base.[16]

The zero order of the SRC conversion reactions in the kinetic model indicated that flow regime was not a factor in achieving a specific level of conversion at a given mean residence time and temperature profile. (For zero order systems equivalent conversion can be achieved in plug flow or backmixed reactors of equal volume.) The zero order reaction rate suggested that based on reaction kinetics, a commercial SRC-II dissolver design did not have to target a specific level of backmixing as long as the appropriate temperature profile and residence time were provided.

To develop comprehensive energy balances for dissolver simulation, numerous simplifications of backmixing, rates of reaction, and rates of heat generation were necessary. Since detailed information in these areas did not exist, the common approach taken was to either assume an average heat release per unit of dissolver volume or simultaneously solve a series of mass and energy equations in which both reaction products and heat generation were linearly estimated for increments of the dissolver volume. Both of these approaches assumed that the fluid dynamic environment in the dissolver was characterized by the axial dispersion model and a high degree of backmixing. The simulation results showed repeatedly that the SRC-II dissolver could be operated in a thermally controlled manner with hydrogen quench for fine-tuned temperature control because of relatively slow reaction rates and the large amount of thermal inertia of the slurry phase.[17,18,19] The systems studied were characterized by fairly high assumed levels of backmixing, with Peclet Numbers ranging from 0 (perfect backmixing) to 0.5, based on the assumption that high levels of thermal and mass backmixing would be provided in the Demonstration Plant dissolver.

3.4 Impact of Backmixing on Reactor Design

The SRC-II reactor modeling under conditions of less-than-perfect backmixing highlighted the importance of improving the understanding of coal liquefaction reaction chemistry.[20] The lack of a proven dynamic model for hydrogenation necessitate the use of "averaged" or steady state models based on pilot plant data for studying the dynamics of reaction rates and temperature profile in the dissolver. Because these models were developed from backmixed systems, their use in simulation of the Demonstration Plant dissolver reinforced the perception that efficient backmixing was the path to optimum dissolver design. However, two observations from the pilot plant database suggest that efficient backmixing in the dissolver may not be as critical as originally perceived.

The first observation concerned initial hydrogen rates of reaction and rates of heat generation. The correlation models of pilot plant yield data have consistently shown a near-linear relationship between hydrogen consumption and slurry residence time (SRT) over the range of residence times studied (6 minutes to 1.5

hours). Plots of this relationship show that extrapolation to an SRT of zero results in an intercept of 1-2% hydrogen consumption.[16] This suggests that rapid and substantial hydrogenation activity may be occurring at very short residence time in the SRC-II dissolver. Since hydrogen consuming reactions are believed to be the major source of exothermic heat release in the dissolver, a rapid rate of reaction at very short residence time would presumably result in a high level of heat release near the reactor inlet. The rate of heat release per unit of hydrogen consumed in the hydrogenation reactions also has been shown to be non-uniform. Heat balance studies around the P-99 dissolver showed that the average exothermic heat of reaction decreased as total hydrogen consumption increased.[21] This implies that the incremental heat of reaction per unit of hydrogen consumption was continuously decreasing. Average and incremental heats of reaction based on this study are shown in Figure 23. These results suggest that hydrogen comsuming reactions that occur early in the reaction chain are more exothermic than later reactions. This would also result in a large release of exothermic reaction heat near the dissolver inlet, which would decrease the level of thermal backmixing required to achieve the desired dissolver temperature profile.

The second observation which questions the importance of backmixing results from the tests at P-99 with different diameter dissolvers.[22, 23] Dimensions of the dissolvers used in those tests were:

4¼" ID X 20 ft High	($^L/D$ = 56)
6" ID X 10 ft High	($^L/D$ = 20)

The 10 ft high dissolver vessel was the standard vessel used at P-99, and was believed to be fairly well backmixed. The 20 ft vessel was chosen to make the dissolver flow considerably less backmixed. This was successful, as shown by the temperature profiles in Figure 24. The lower average dissolver temperature observed for the tall reactor should have resulted in a heavier product distribution, but that was not the case. The product distribution with the tall dissolver was approximately the same as was observed with the short dissolver. This observation suggests that the existing understanding of the relationship between yield distribution and reactor temperature profile is incomplete; isothermal operation at

855°F, which was a Demonstration Plant design goal, may not be required for the desired level of performance.

Several conclusions are warranted from the backmixing studies. First, the validity of applying the axial dispersion model to large scale bubble columns, in which complex flow non-idealities such as channeling, radial variations in velocity, stagnant zones, and internal recirculation cells may be present, remains unproven. Second, radiotracer data showed the slurry phase in the Ft. Lewis dissolver to be well-mixed and the gas phase to approach plug flow, as expected. However, the slurry phase tracer data were incomplete, and a conclusion about whether the dispersion model characterized the slurry hydrodynamics cannot be reached. Third, the properties of the liquid and gas phases influence flow regime and dispersion characteristics significantly, limiting the usefulness of data obtained on cold flow apparatus in the design of a large coal liquefaction reactor. Fourth, the existing understanding of SRC-II reaction chemistry is limited by the steady state, or "averaged", nature of the pilot plant database. The Demonstration Plant design was believed to be constrained to reproduce the well-backmixed behavior of the pilot plants. Whether such a constraint was necessary is uncertain. It would be desireable in the future to establish a more fundamental understanding of the dynamic reaction chemistry in this system.

Resolution of the design uncertainties in large reactors suggested by these conclusions will not occur until a large scale unit is operated. To deal with these uncertainties in the design of the Demonstration Plant, a number of fallback contingencies were proposed, including dissolver internals (flow redistributors and downcomers) and excess preheater capacity to provide higher dissolver feed temperatures.[24] Internal redistributors would be provided to minimize flow non-idealities. Downcomers would enhance backmixing from the top to the bottom of the reactor. A higher feed temperature would decrease the required level of backmixing to achieve the desired average dissolver temperature. The availability of these contingencies was considered to sufficiently mitigate risks due to hydrodynamic uncertainty, while providing adequate operating flexibility to generate the data required for future reactor design optimization.

Table IV

Liquid Phase Dispersion in GS&TC Bubble Column

Test Number	Liquid Velocity CM/SEC	Gas Velocity CM/SEC	Liquid Estimated Mean Residence Time, Min	Dispersion Number		Ratio Observed to Predicted %
				Observed	Predicted*	
1	3	0	3.84	0.0185	0.0224	83
2	3	2	3.60	0.1538	0.2857	54
3	3	4	3.45	0.1852	0.3448	54
4	3	10	3.04	0.2500	0.4545	55

*Predicted Dispersion Number = $\frac{\text{Axial Dispersion Coefficient}}{\text{(Liquid Velocity) (Length)}}$,

where Axial Dispersion Coefficient = $2.7 \times (\text{Diameter})^{1.4} \times (\text{Gas Velocity})^{0.3}$

Table V

Ft. Lewis Dissolver Liquid Phase Radiotracer Injections

February 1981 Results

	Date	Time	Detector	Estimated Mean Residence Time,Min	Dispersion Number
Inlet Injections	2/23	17:09	Top	63.6	0.145
			Bottom	65.6	0.149
	2/24	20:48	Top	65.4	0.143
			Bottom	63.4	0.154
Middle Injections	2/19	15:07	Top	67.5	0.142
			Bottom	66.9	0.145
	2/23	10.03	Top	71.0	0.130
			Bottom	64.4	0.152
	2/24	16.59	Top	62.7	0.154
			Bottom	62.4	0.154

Table VI

Effect Of Baseline On Interpretation of Liquid Phase Radiotracer Data

	GS&TC Results	Baseline A	Baseline B	Baseline C
Mean Residence Time, minutes	63.6	65.4	56.4	30.9
Dispersion Number	0.145	0.1436	0.1663	0.1624

Table VII

Ft. Lewis Dissolver Gas Phase Radiotracer Injections

February 1981 Results

	Date	Time	Detector	Estimated Mean Residence Time, Sec	Dispersion Number
Inlet Injections	2/20	14.20	Top	58.7	0.092
			Bottom	23.5	0.081
	2/24	16.06	Top	65.3	0.076
			Bottom	26.8	0.165
Middle Injections	2/23	16.25	Top	41.0	0.128
			Bottom	44.8	0.120
	2/24	15.22	Top	26.1	0.131
			Bottom	33.5	0.095

Table VIII

Properties of Liquids Used in University of Pittsburgh Bubble Column Tests

Newtonian Fluids

Alcohols (0.5 Vol%)	Density, gm/cc	Surface Tension, Dyne/cm	Viscostity, cp
Methanol	.9940	69.7	0.83
Ethanol	.9931	68.2	0.83
n-Propanol	.9949	65.7	0.85
n-Butanol	.9932	60.8	0.84
NaCl Solutions			
0.05M	.998	70.50	1.00
0.2M	1.018	72.15	1.22
0.5M	1.045	71.25	1.23
1.0M	1.065	73.50	1.29

Non-Newtonian Fluids

CMC Solutions	Consistency Index, cp	Flow Behavior Index	Relaxation Time, Sec
50ppm	2	1.0	-
500ppm	4.5	1.0	-
1000ppm	7.6	1.0	-
2300ppm	5.98	0.95	-
PAA Solutions			
50ppm	0.97	1.0	0
500ppm	2.56	0.973	.32
1000ppm	3.8	0.948	.50
4000ppm	8.8	0.92	.97

4.0 Mass Transfer

Little is known about mass transfer resistance between the hydrogen-rich vapor phase and the reactive slurry phase in coal liquefaction reactors. Generally, mass transfer resistance becomes a significant design consideration only in systems where the rate of reaction exceeds the rate of mass transfer, leading to reactant starved regions away from the gas-liquid interface. Hydrogen mass transfer resistance in the SRC-II dissolver is worrisome because of the inherently high reactor temperature, which will lead to undersireable thermal cracking reactions in the absence of hydrogen. This concern led to laboratory tests and mathematical simulation studies of mass transfer in the SRC-II dissolver in support of the Demonstration Plant design.

Laboratory studies of mass transfer resistance were conducted on the A-1 CSTR SRC-II pilot plant.[25] Levels of mass transfer resistance were studied by varying the agitator specific mixing energy in the reactor. Formation of coke deposits in the reactor was the primary means of distinguishing conditions of hydrogen starvation. Of the agitator speeds tested (150, 200, 300, 400, 600, and 1000 RPM), coke deposits were only found in three of the seven runs at 200 RPM and in the single run at 150 RPM. The product yield distribution appeared to shift towards heavier products at agitator speeds below 400 RPM, providing further evidence of mass transfer limitations and hydrogen starvation. The mixing energy provided in the A-1 reactor by a 400 RPM agitator speed was estimated to be equivalent to a specific power consumption (P/V) of 1.78 hp/1000 gal slurry.

The level of mixing, as characterized by the specific power consumption, is a major determinant in the mass transfer process in multiphase reaction systems. In the A-1 CSTR, the reactor mixing energy was provided by an externally driven agitator. Mixing energy in a bubble column such as the SRC-II dissolver is provided by the change in potential energy of the vapor phase as it passes through the liquid phase. This can be related to the specific power consumption (P/V) by the following equation:

$$P/V = U_{og}\ \rho\ g\,(1-h_g)$$

Where U_{og} = superficial gas velocity
ρ = liquid (slurry) phase density
g = gravitational constant
h_g = fractional gas holdup.

For an SRC-II dissolver, a specific power consumption equivalent to the 1.78 hp/1000 gal slurry limit established in the A-1 unit would be provided by a superficial gas velocity of approximately 3 cm/sec. The superficial gas velocity in the Ft. Lewis dissolver (3-3.5 cm/sec) and in the P-99 dissolver (1-2 cm/sec) challenged the 3 cm/sec lower limit, without any apparent hydrogen mass transfer limitation problems. This suggests that the 3 cm/sec limit is a conservative basis for design, and the 5-10 cm/sec gas velocities expected in the Demonstration Plant dissolver should result in ample mixing and mass transfer as long as adequate radial distribution of the gas throughout the dissolver can be achieved.

The mathematical simulation studies converted the laboratory mixing power results to a more theoretical basis, and applied the theoretical relationships to develop a comprehensive dissolver model.[26] The overall mass transfer rate in the dissolver was defined as:

$$\text{Mass transfer rate} = (k_\ell\ \underline{a}) \times (\Delta C),$$

where $k_\ell\ \underline{a}$ was the overall mass transfer coefficient and ΔC was the hydrogen concentration gradient between the vapor phase and the slurry phase. The overall mass transfer coefficient $k_\ell\ \underline{a}$ was a "lumped" term which included the specific mass transfer coefficient, k_ℓ , and a measure of the interfacial area available to mass transfer.

Using specific mass transfer coefficient data for the hydrogen/tetralin system, and literature-reported relationships governing the behavior of the overall mass transfer coefficient in multiphase systems, the following equation for the overall mass transfer coefficient in an SRC-II reactor was developed:

$$k_\ell \underline{a} = (1.532 \times 10^{-3})(\exp -2248/T)(P/V)^{0.84}$$

where T is the reactor temperature and P/V is the specific power consumption.

A reactor model was developed by substituting this relationship into the hydrogen mass transfer rate equation, and equating the resulting relationship with the hydrogen reaction rate based on the SRC-II kinetic model. This created a solution in which the hydrogen reaction was limited by the mass transfer rate. The model was tested against hydrogen consumption data obtained during the A-1 mixing tests discussed above. Measured and simulated values of hydrogen consumption are shown in Figure 25. The agreement of the model with experimental data was interpreted to verify the model.

The reactor model was then applied to a bubble column reactor to study conditions under which hydrogen starvation might occur. Estimated hydrogen consumption based on the reactor model at a given specific mixing power (due to superficial gas velocity) was compared to the maximum theoretical hydrogen consumption based on the kinetic model (no mass transfer resistance). The effect of mass transfer resistance was defined as the percentage reduction in hydrogen consumption. Results are shown in Figure 26. At a gas velocity of 1 cm/sec, mass transfer resistance was estimated to result in a 3.7% reduction in hydrogen consumption. At the high velocities expected in the Demonstration Plant dissolver (10cm/sec) the reduction was less than 1% of the maximum theoretical hydrogen consumption.

The sensitivity of this analysis to the value of the mass transfer coefficient was studied by reducing the value of the mass transfer coefficient to 50, 20, and 10% of its theoretical value. Results are shown in Figure 27. Even at a mass transfer coefficient of only 10% of theoretical value, the high gas velocity in the Demonstration Plant reactor would result in only a small (5.5%) reduction in hydrogen consumption. These results suggested that hydrogen mass transfer limitations would not affect the Demonstration Plant dissolver performance as long as effective radial distribution of the gas phase was maintained.

The lack of specific data for overall mass transfer coefficients in coal liquefaction reactors was identified as a major deficiency in development of the reactor model. To overcome this, a program to construct and operate a high pressure-high temperature 6" ID by 30 ft tall experimental bubble column to measure mass transfer coefficients under actual process conditions for the hydrogen/coal liquid system was proposed.[27] This column would also have had the capacity to measure gas holdup and dispersion in an environment approaching that of a coal liquefaction reactor. Operation of such a system would be very desireable for reducing hydrodynamic uncertainty in dissolver scaleup.

5.0 Solids Settling

As discussed above, solids settling has not been considered a major concern in the SRC-II reactor because of the small particle size (1-10 μ) of the residual solids (ash and unreacted coal) remaining after the coal dissolution reactions. Major accumulations of solids in the dissolver did not normally occur during operations at either Ft. Lewis or P-99. The small cone-shaped solids accumulations that did occur near the dissolver inlets at both units presumably were due to the lack of feed distributors. The major accumulations that were observed at P-99 were found after the dissolver had been held at high temperature without slurry or gas feed, and presumably were due to coking.

For scaleup to a large reactor, this experience suggests that an appropriate feed distributor design will mitigate solids accumulation problems, as long as coal type and grind size are not different from the pilot plants' experience. To provide flexibility in the coal grinding and coal slurry mixing circuit and to allow for testing of larger sized coal, the SRC-II Demonstration Plant design included a dissolver solids purge system to remove oversized solids having a terminal settling velocity which would have resulted in net accumulation in the reactor. This concept was successfully tested on the 12" ID by 25 ft tall cold flow bubble column at GS&TC using sand, silica flour, or glass beads as the solids phase in an air/water/solids system.[12] Solids withdrawal from the bottom of the column did not appear to affect hydrodynamic performance. A continuous withdrawal system was recommended over an intermittent system for the Demonstration Plant because of its obvious advantages in consistent flow and less opportunity for settling and plugging.

6.0 Effect of Hydrodynamics on the Demonstration Plant Dissolver Design

For a complex reactor system such as the SRC-II dissolver, there are many trade-offs required to reach an "optimized" design. Desired levels of gas holdup, backmixing, and mass transfer, and prevention of solids settling were aspects of the dissolver design that were all dependent on a common variable, gas velocity. However, high levels of gas velocity produce advantageous effects in some areas, and disadvantageous effects in others. Major trends include:

- High gas velocity leads to high gas holdup, with an attendant reduction in slurry holdup and slurry residence time.
- High gas velocity enhances liquid phase backmixing except at very high levels of gas holdup.
- High gas velocity results in higher mixing power per unit of liquid volume, thereby enhancing hydrogen mass transfer if flow channeling can be avoided.
- High gas velocity enhances solids entrainment in the liquid phase.

An evaluation of these factors, along with economic, safety, mechanical, and future scaleup considerations provided the basis for selecting the size of the Demonstration Plant dissolvers.[24,28] In the analysis of hydrodynamic factors, it was assumed that hydrodynamic behavior in the dissolver was well characterized by the holdup, dispersion and mass transfer models developed from cold-flow data. A maximum-sized dissolver (single vessel per process train) was found to offer advantages in lower capital and operating costs, greater safety, and less complicated plant control due to minimization of redundant high pressure, high temperature systems. The main disadvantages associated with a single dissolver per train design, compared to a multiple vessel design, were identified as higher gas phase holdup (due to higher gas velocity) and greater uncertainty about backmixing and mass transfer (due to the longer reactor length). Additional reactor volume was provided to account for the higher gas phase holdup. Uncertainty in backmixing and mass transfer was addressed by identifying viable fallback contingencies that could be employed if insufficient backmixing or mass transfer were encountered. Reactor internals, such as downcomers to improve vertical mixing, and flow redistributors to prevent channeling were proposed for this purpose. The apparent advantages of the single reactor design coupled with identification of means to deal with its disadvantages, led to its selection as the design basis for the Demonstration Plant.

This conclusion should be reevaluated in light of the experimental results obtained in the radiotracer studies at Ft. Lewis which suggest that the amount of gas holdup to be expected in an SRC reactor operated at high gas velocity may, in fact, be greater than originally anticipated. Estimated levels of gas holdup in the Demonstration Plant dissolver based on GS&TC's original gas holdup correlation, and on a correlation modified to fit the Ft. Lewis holdup data are shown in Table IX. Also shown is the ratio of the modified estimate of holdup to the GS&TC-predicted holdup. These results show that the single dissolver design based on the existing gas holdup correlation would have experienced 23% less slurry holdup than predicted. This would be expected to lead to a significant reduction in distillate yields, and excess vaccum bottoms production. The higher yields of vacuum bottoms would have negatively influenced the overall plant material and energy balances, since the only means of disposing of this material was as gasifier feed. Operating options such as a reduction in coal feedrate or slurry feedrate, both of which amount to derating the plant, would probably have to had to be considered to bring the plant back into balance.

This observation, based on the high gas holdup observed in the Ft. Lewis dissolver, suggests that the dissolver size per train should be reconsidered. The obvious way to reduce the loss of slurry residence time in a single vessel design is to increase height, and thus the volume of the vessel. The implications of such a change on vessel fabrication and cost must be evaluated. It is possible that given the already large size of the single dissolver per train vessel, the prospect of an even larger vessel may have reversed the outcome of the dissolver size evaluation.

Table IX

Impact of High Gas Holdup on Slurry Residence Time

		Ft. Lewis(U_g = 3.4 cm/sec)	P-99 (U_{og} = 1cm/s)	Single Dissolver/Train Demo (U_{og} =12 cm/s)	Parallel Dissolver/Train Demo (U_{og} = 6 cm/s)
Predicted*	h_g	0.104	0.036	0.243	0.167
	h_s	0.896	0.964	0.757	0.833
Observed	h_g	0.20	0.096	0.426	0.281
	h_s	0.80	0.904	0.574	0.718
Slurry Holdup Ratio Observed/Predicted,%		89	94	76	86

*Predicted holdup based on GS&TC gas holdup correlations.

**Estimated Holdup based on equation: $h_g = 0.096 (U_{og})^{0.6}$, which gives observed holdup for Ft. Lewis of 0.20.

7.0 Additional Data Needs

The stochastic nature of hydrodynamic behavior in large bubble columns results in considerable uncertainty in the scaleup to commercial size units from laboratory and pilot plant data. For the SRC-II dissolver, this was exacerbated by the apparent difference in gas holdup behavior relative to the typical aqueous systems studied in laboratory bubble columns. It is doubtful that additional cold flow laboratory bubble column studies would be of much benefit in reducing this uncertainty. However, hydrodynamic scaleup uncertainty could be reduced by operating a laboratory scale bubble column with coal liquids and hydrogen at high temperature, high pressure conditions. The gas holdup and mass transfer response of such a column could then be used to modify existing correlations, increasing confidence in the ability to predict behavior in larger systems. GS&TC proposed a plan for construction and operation of such a unit prior to termination of the SRC -II Project.[27] The proposed bubble column would also have been used to study dispersion in the coal liquid/hydrogen system.

The issues discussed relating to required backmixing and uncertainties in the heat of reaction and hydrogen reaction rates also merit further study. A more fundamental understanding of dissolver thermal and mass backmixing requirements is desireable, particularly for short residence time, "low" temperature reactions occurring near the reactor inlet. Current short contact time coal liquefaction research may provide information to address these topics and to plan future research needs.

Another area in which additional research would be of use in mitigating design uncertainty is the study of design parameters for reactor internals. Effort in this area was initiated with the dissolver downcomer tests at Ft. Lewis, which showed that significant vertical downward slurry flow could be achieved in such a device. However, flow rates could not be measured, and design guidelines for downcomers in large vessels are unavailable. Internal flow redistributors, which might be required to keep radial velocity profiles uniform, also do not have established design guidelines. Since performance of reactor internals should not be specific to system properties, an opportunity exists to develop design guidelines through tests on large scale cold flow systems. Construction of a large air/water bubble column was being considered for this purpose when the SRC-II Project was terminated.

8.0 Conclusions

The following major conclusions about the fluid dynamic behavior of SRC-II reactors are warranted by this review.

- Radiotracer data indicate that gas holdup in the Ft. Lewis dissolver was approximately twice as high as expected. Standard literature-reported gas holdup models, which are based primarily on data from cold flow systems, appear to be inadequate for predicting holdup in an SRC-II reactor. Higher than expected gas holdup in the Demonstration Plant reactor would have adversely affected conversion to distillate products because of reduced actual slurry residence time.

- The Ft. Lewis radiotracer data also indicated that the slurry phase was fairly well backmixed, while the gas phase approached plug flow. Insufficient data were available to determine whether either phase was adequately characterized by the axial dispersion model.

- Cold flow backmixing studies showed that liquid phase properties play a role in flow regime transition. Churn turbulent flow was found to result in a higher extent of backmixing than quiescent bubble flow, but backmixing appeared to peak at some level of gas holdup, beyond which backmixing decreased.

- It is likely that the complex fluid dynamic behavior in large dissolvers will violate the uniform radial velocity profile assumption of the axial dispersion model. However, development of a more appropriate model will have to be based on operating data from a large scale system such as the Demonstration Plant dissolvers. Until such data are obtained, scaleup of large vessel hydrodynamics will remain somewhat speculative.

- The extent of backmixing should not affect levels of conversion in the dissolver as long as the designed operating temperatures can be achieved. Reaction kinetics studies have shown the slurry phase conversion reactions to be zero order with respect to non-distillable hydrocarbons ("SRC"). Backmixing will affect the dissolver temperature profile by influencing direct heat exchange between products and reactants. Bulk slurry mixing will also be a major factor in temperature control. Reactor internals, such as downcomers, have been identified as viable means of influencing overall backmixing behavior. Unfortunately, for a first plant, guidelines for downcomer design do not exist. The Demonstration Plant would have served as a test unit for development of guidelines for future facilities.

- Lack of a fundamental understanding of instantaneous rates of reaction and rates of heat generation may have resulted in too great an emphasis on dissolver backmixing and average temperature. Results from P-99 showed similar product yield distributions under conditions of significantly different dissolver backmixing and average temperature.

- Conversion in the Demonstration Plant dissolver was expected to be limited by reaction rate kinetics, rather than hydrogen mass transfer resistance. The relatively high gas velocity in the dissolver was expected to result in high mixing energy, with attendant high mass transfer rates. Uniform radial velocity profiles would be necessary to assure this. Internal flow redistributors and strategically located quench nozzles were identified as viable means of achieving radial uniformity. The Demonstration Plant dissolvers would have provided guidelines for the design of reactor internals for future units.

- The dissolver number and size evaluation should be reconsidered in light of evidence of higher-than-expected gas holdup. Failure to provide additional dissolver volume may have led to unit derating to achieve a product distribution that could be processed in downstream units.