Hydrodynamics of a Bitumen Upgrader

B. Özüm
L. Lewkowicz
T. Cyr
Alberta Research Council
Devon, Alberta, Canada

M. Oğuztöreli
Petro Simulator Systems Inc.
Edmonton, Alberta, Canada

Bubble columns are used extensively in industrial processes when liquid phase reactions are relatively slow and extensive gas-liquid mass transfer is needed (Deckwer, 1986). Bubble columns have the advantage of large liquid hold-up (large liquid residence time), large interfacial area-mass transfer rates, and ease and flexibility of operation. However, their design is often complicated because of the lack of information regarding their hydrodynamics. All commercial bubble columns are designed on the basis of empirical correlations which are developed mainly for air-water or air-oil systems operating at atmospheric pressure (Pavlica and Olson, 1970; Kelkar and Shah, 1984; Cichy and Russell, 1969; Mashelkar, 1970; Nicklin, 1962; Hughmark, 1967; Hsu and Dudukovic, 1980; Hikita et al., 1980; Shah et al., 1982; Guy et al., 1986). Estimation of hydrodynamic parameters, such as gas hold-up, gas- and liquid-phase axial dispersion, and interfacial area-mass transfer coefficients, from these correlation equations, requires values for the physical properties of gas and liquid at the system's operating temperature and pressure. In most cases, it it difficult to measure physical properties such as density, surface tension, diffusivity and viscosity. The measurements become even more impractical for high temperature-high pressure reactors, especially for heavy oil and/or coal-heavy oil slurry hydrogenation processes. Therefore, experimental investigations are required to understand the bubble column hydrodynamics.

Tracer techniques have been applied to study the residence time distributions in chemical reactors (Danckwerts, 1953; Nauman, 1981; Aris, 1982; Dudukovic, 1986). However, very limited data have been published dealing with tracer studies of high temperature-high pressure reactors, probably due to the experimental difficulties associated with high pressure operations (Bickel and Thomas, 1982; Panvelker et al., 1982; Nalitham and Davies, 1987). The objective of this work is to study the hydrodynamics of a laboratory scale bubble column reactor which is being used at Alberta Research Council to upgrade bitumen, heavy oil, and pitch by means of catalytic and noncatalytic hydrogenation processes at about 420–480°C temperature, and 10–30 MPa pressure. A radioactive tracer technique is employed for the simultaneous estimation of several reactor hydrodynamic parameters, such as gas hold-up, liquid- and gas-phase Peclet numbers, and interfacial area-mass transfer coefficient.

Experimental

The hydrocracking of bitumen residue was carried out in a continuous upflow tubular reactor system. The reactor was made of a 316 stainless steel tube of 25 mm internal diameter and 670 mm length, designed for up to 500°C temperature and 35 MPa pressure. To perform tracer studies, a tracer injection system was added at the bottom inlet of the reactor, Figure 1. The injection system consisted of a 5 cm^3 volume high-pressure fitting connected with two hand operated valves.

Two radioactive isotopes, iodine (^{131}I) and xenon (^{133}Xe), (purchased from the Edmonton Radiopharmacy Center) were used to trace the liquid and gas phases, respectively. ^{131}I was covalently bound to a high boiling compound dissolved in the liquid phase. The half-life of ^{131}I is 8.05 days and it radiates at 0.364 MeV. ^{133}Xe is an inert radioactive gas which has a half-life of 5.27 days and radiates at 0.081 MeV. The tracer injection system was purged with helium and then loaded with about 3 cm^3 of a heavy distillate fraction. Following that, ^{131}I was added in the form of 0.1 cm^3 heavy distillate solution, and then ^{133}Xe gas was added in 0.1 cm^3 helium. The typical charge of the radioactive tracers for one tracer experiment was 1.2×10^{-9} g of iodine (150 μ Ci) and 2.1×10^{-9} g of xenon (400 μ Ci). Preparation of the isotopes, monitoring of the tracers during runs, and radioactive waste disposal were performed by Terabecquerel Tracers Radiotracer Consultants.

Correspondence concerning this paper should be addressed to Dr. Baki Ozum, Coal and Hydrocarbon Processing Dept., Alberta Research Council, Bag 1310, Devon, Alberta, TOC 1EO, Canada.

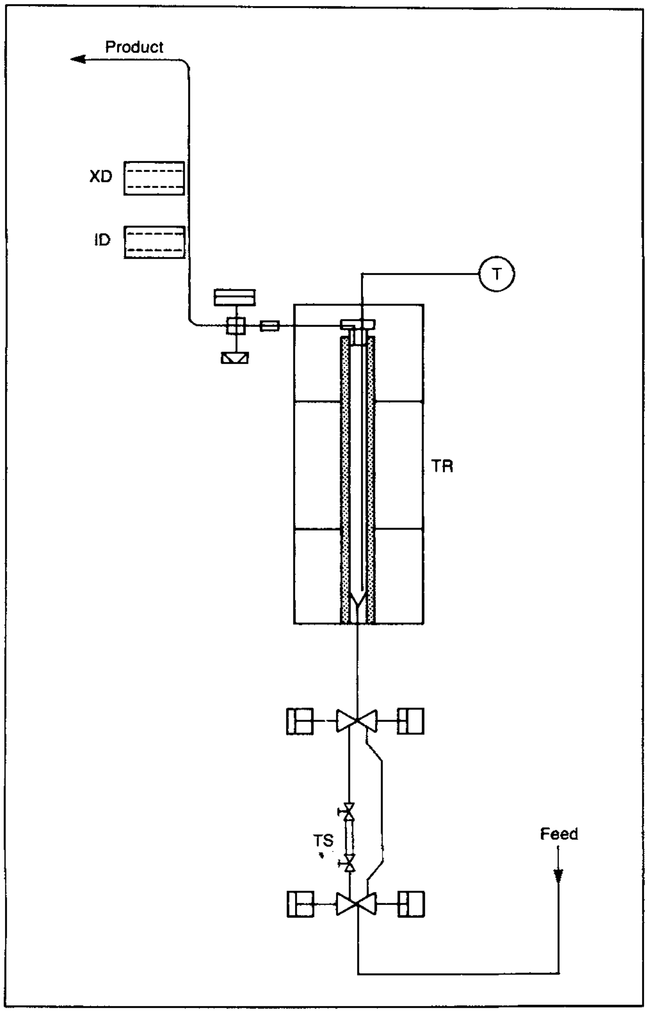


Figure 1. Schematic of bitumen upgrading reactor for tracer studies.

XD = xenon detector, *ID* = iodine detector, *T* = thermocouple, *TS* = tracers sample, *TR* = tubular reactor.

Feedstock for the hydrocracking experiments was Cold Lake Vacuum Bottom, with an initial boiling point (IBP) of 430°C. This was obtained from the ESSO Strathcona Refinery, Edmonton, Alberta. Tracer experiments were performed at a fixed reaction temperature of 455°C and hydrogen pressure of 17.5 MPa. Different flow patterns in the reactor were obtained by varying the liquid (*LHSV*, 1.2–4.0 h^{-1}) and gas (8.0–28.0 *SLPM*) velocities. In a typical experiment the system was operated under steady-state conditions for a few hours before tracers were injected. The time required for the tracers to reach the reactor inlet was less than 6 s. The isotopes in the effluent from the reactor were simultaneously monitored by two sodium iodide solid scintillation detectors connected to a chart recorder. The data was recorded in either 6 or 30 s time intervals, depending on the radiation energy of the tracers and the relative change in detected levels.

Model Equations

In formulating the applied tracer technique, the hydrodynamics of the reactor were assumed to be independent of the chemical reactions. Radial homogeneity in gas and liquid phase compositions, and temperature uniformity along the reactor were assumed. Differential mass balances for the instantaneous tracer concentrations along the reactor length were formulated using a dispersion model with interfacial mass-transfer.

In this study, ^{131}I and ^{133}Xe radioactive isotopes were employed to trace liquid- and gas-phase behaviors. Under the experimental conditions, ^{131}I remained in the liquid phase, while ^{133}Xe dissolved from the gas phase into the liquid phase. If subscripts 1 and 2 represent ^{131}I and ^{133}Xe, and ℓ and g represent the liquid and gas phases, respectively, the dimensionless tracer balance equations become (Levenspiel and Bischoff, 1963):

$$\frac{\partial C_{1,\ell}}{\partial t_\ell} + \frac{\partial C_{1,\ell}}{\partial x} = \frac{1}{Pe_\ell}\frac{\partial^2 C_{1,\ell}}{\partial x^2} \tag{1}$$

$$\frac{\partial C_{2,\ell}}{\partial t_\ell} + \frac{\partial C_{2,\ell}}{\partial x} = \frac{1}{Pe_\ell}\frac{\partial^2 C_{2,\ell}}{\partial x^2} + \frac{K_m a L}{\epsilon_\ell v_\ell}\left(\frac{C_{2,g}}{H} - C_{2,\ell}\right) \tag{2}$$

$$\frac{\partial C_{2,g}}{\partial t_g} + \frac{\partial C_{2,g}}{\partial x} = \frac{1}{Pe_g}\frac{\partial^2 C_{2,g}}{\partial x^2} - \frac{K_m a L}{\epsilon_g v_g}\left(\frac{C_{2,g}}{H} - C_{2,\ell}\right) \tag{3}$$

with the dimensionless distance, x, and dimensionless times, t_ℓ and t_g:

$$x = \frac{X}{L}; \quad t_\ell = \frac{v_\ell t}{L}; \quad t_g = \frac{v_g t}{L} \tag{4}$$

The boundary conditions at the inlet of the reactor are (Danckwerts et al., 1976):

$$C_{1,\ell} - \frac{1}{Pe_\ell}\frac{\partial C_{1,\ell}}{\partial x} = C^*_{1,\ell} \tag{5}$$

$$C_{2,\ell} - \frac{1}{Pe_\ell}\frac{\partial C_{2,\ell}}{\partial x} = C^*_{2,\ell} \tag{6}$$

$$C_{2,g} - \frac{1}{Pe_g}\frac{\partial C_{2,g}}{\partial x} = C^*_{2,g} \tag{7}$$

and at the outlet:

$$\frac{\partial C_{1,\ell}}{\partial x} = \frac{\partial C_{2,\ell}}{\partial x} = \frac{\partial C_{2,g}}{\partial x} = 0 \quad \text{at} \quad x = 1 \tag{8}$$

The reactor is initially void of tracer. A tracer slug, C^*, is injected at the inlet over the period $0 < t < t_0$, where t_0 is the injection period.

$$C_{1,\ell} = 0,\ C_{2,\ell} = 0,\ C_{2,g} = 0 \quad \text{at} \quad t = 0 \tag{9}$$

The model equations are a system of coupled linear differential equations of the boundary value type. The problem is to estimate the model parameters such as ϵ_ℓ, Pe_ℓ, Pe_g and $K_m a$, which provide the best fit to the experimental data.

Numerical Solution

The numerical solution to the model equations was generated using finite differences on a mesh-centered grid. The reactor was partitioned into N elements or blocks. The differential molar balance equations were spatially integrated over the finite volume elements, and then discretized using central differences and arithmetic means. The resulting difference equations were integrated over finite time steps using the trapezoid rule, giving a Crank-Nicolson temporal discretization (Crank, 1956) of the molar balance equations.

The system of algebraic difference equations are 3×3 block tridiagonal, and Thomas's algorithm (Ozum et al., 1986) can be used to generate a solution economically. The iodine tracer equation can be solved independently, whereas the xenon equations are coupled and must be solved simultaneously.

Numerical and analytical solutions of the effluent concentration for the iodine equation were compared, using a constant injection source, $C^* = 1$, at $Pe_\ell = 1$ and $Pe_\ell = 10$, respectively, for varying time steps. The analytical solution was obtained using a Laplace transform method. The numerical solution ($N = 21$) approaches the analytical solution as $\Delta t \rightarrow 0$, for the Peclet numbers of interest.

The tracer slug is approximated by a square pulse. The inlet is modeled more rigorously by assuming a thin mixing zone where the tracer, entering the reactor as a plug flow, encounters a highly dispersive environment. The tracer within the injection line flows as a plug, with Peclet numbers several orders higher

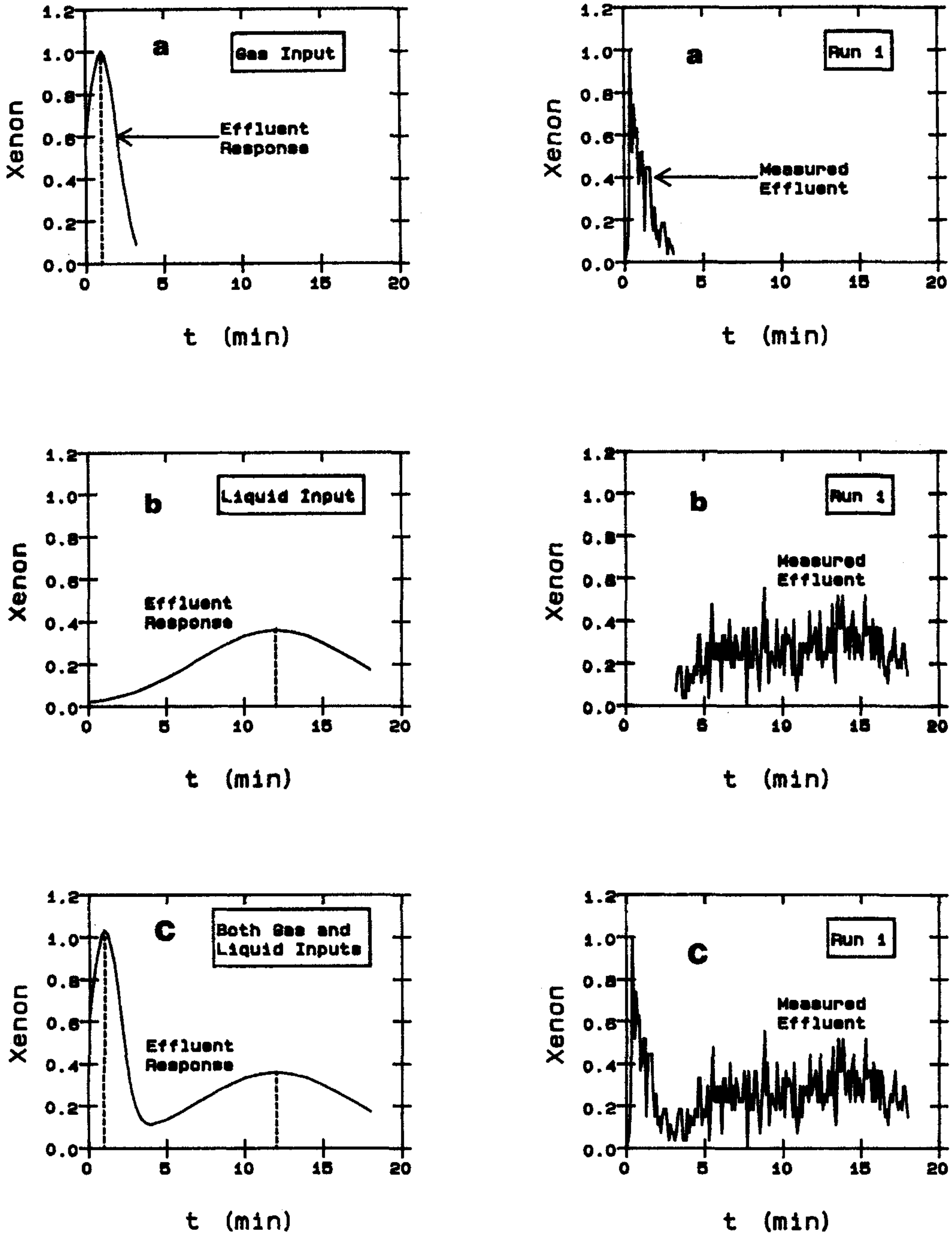
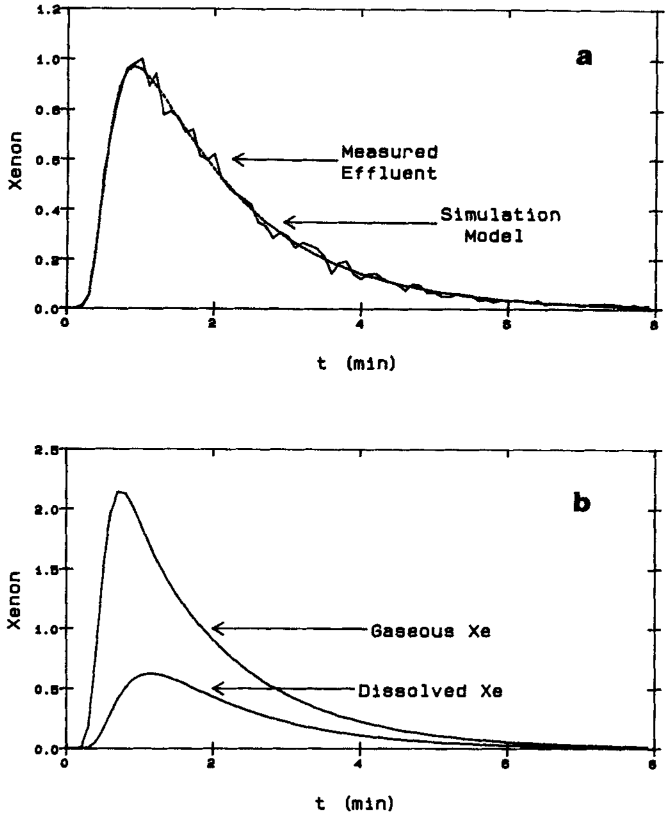


Figure 2. Xenon effluent due to injected: *a* = gaseous xenon; *b* = dissolved xenon; *c* = both gaseous and dissolved xenon.



a: parameter estimation using effluent data
b: simulated xenon gas and liquid fractions

Figure 3. Effluent data for Run 5.
LHSV = 4.0 h^{-1} and H_2 = 8 *slpm*.

than that in the reactor. To account for the discontinuity in diffusive properties between tubing and reactor mediums, the injected concentration is averaged between the concentration upstream in the injection line and the current concentration downstream at the reactor inlet.

Iodine measured in the effluent comes directly from the liquid phase, whereas the xenon effluent has contributions from both liquid and gas phases, since the scintillation detectors cannot differentiate between dissolved and gaseous species.

An injection concentration of $C^* = 1$ is assumed and effluent concentration histories generated numerically. The simulated

Table 1. Tracer Injection Data Set*

	v_g cm/s		
v_l cm/s	1.91	3.35	6.70
0.0229		Run 1 τ_l = 60 s τ_g = 3 s	
0.0476		Run 2 τ_l = 30 s τ_g = 3 s	
0.0762	Run 5 τ_g = 6 s	Run 3 τ_l = 20 s τ_g = 20 s	Run 4 τ_l = 20 s τ_g = 20 s

Reactor dimensions: r = 2.54 cm; L = 68.6 cm
Experimental conditions: T = 455°C; P = 17.0 MPa

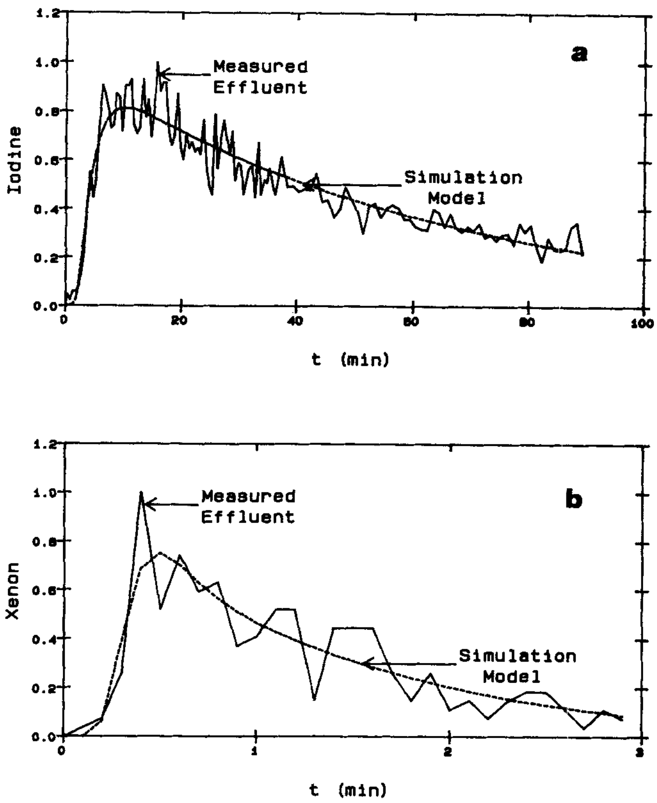


Figure 4. Iodine (a) and xenon (b) effluent fit for Run 1.
LHSV = 1.2 h^{-1} and H_2 = 14 *slpm*.

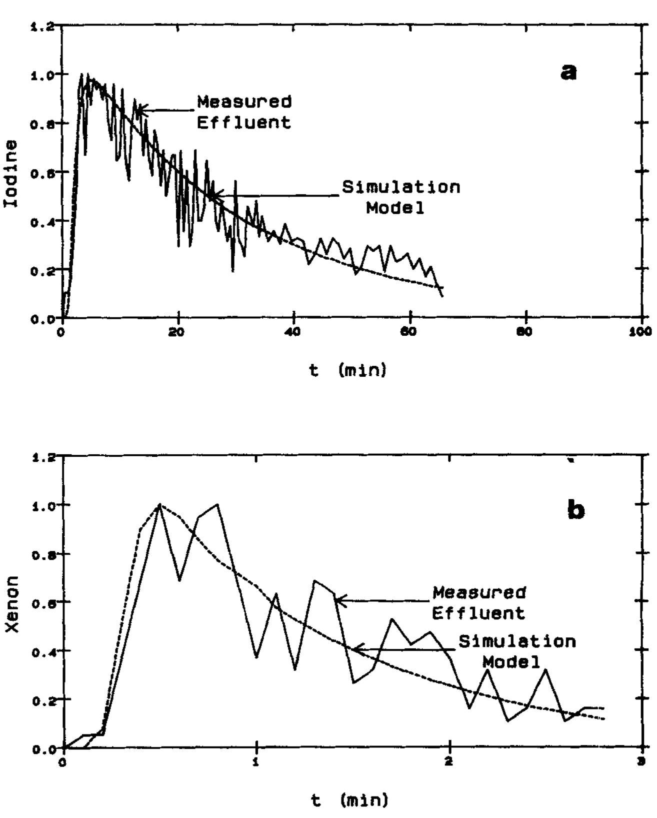


Figure 5. Iodine (a) and xenon (b) effluent fit for Run 2.
LHSV = 2.5 h^{-1} and H_2 = 14 *slpm*.

and measured effluent concentrations are normalized by assuming equal areas under the curves, and scaled by the maximum concentration in the measured effluent. The tracer slug is injected into the reactor over a time interval with a pulse width, τ. The injection pulse widths for liquid, τ_ℓ, and gas, τ_g, are generally different, depending on the near-equilibrium volumes present in the injection bomb and the two-phase flow rates. The pulse widths are not known and are treated as discrete variables in the numerical solution. They are adjusted manually to establish the best coincidence between measured and calculated peaks in the effluent.

The mean square deviation between measured and simulated effluent concentrations is calculated over M data points in time. The model parameters (Pe_ℓ, Peg, ϵ_ℓ, $K_m a$, H) are estimated using the downhill simplex method (Press et al., 1986) to minimize the mean square deviation between experimentally measured and numerically simulated concentrations of iodine and xenon in the effluent.

Results and Discussion

The initial tracer experiments had both iodine and xenon in the tracer bomb prior to their injection into the reactor. Iodine and xenon effluent concentrations were measured at four different operating conditions. Analysis of effluent xenon suggested that significant quantities of xenon had dissolved into the liquid phase within the tracer bomb prior to injection, producing long tails similar to that seen in the effluent iodine. As the ratio of gas to liquid flow rates increase, a bimodal distribution emerges with two separate peaks, the first due to the injection of gaseous xenon and the second due to the injection of xenon dissolved in the iodine-liquid mixture, Figure 2.

A separate tracer experiment, injecting only xenon gas into the reactor, was carried out, Figure 3. A higher concentration of tracer was injected, giving less fluctuation in the measurement of effluent concentrations. Observed xenon levels in the effluent disappeared shortly after injection, supporting the premise that the concentration tails which had appeared in the previous experiments were in fact a result of dissolved xenon gas prior to injection. Figure 3a shows the simulated xenon effluent concentration which best fit the data in Run 5. Figure 3b shows the gaseous and dissolved xenon fractions of the simulated effluent, with gaseous xenon accounting for most of the detected radiation energy.

The most relevant information with which to estimate the gas-phase hydrodynamic parameters from the previous experiments, were contained in the first few minutes of the effluent xenon history. Fewer data points were used to fit runs at higher liquid flow rates, since the effluent xenon arising from that injected in solution obscured the effluent from that injected strictly as gas, in several experiments. Parameters estimated with higher certainty from data sets 1 and 5, were used with runs 2, 3 and 4, as fixed quantities. Table 1 lists the data used for hydrodynamic parameter estimation. Figures 4–7 show the simulated iodine and xenon effluent concentrations which best fit the experimental data for runs 1 to 4. Table 2 summarizes the estimated parameters.

In the present study, process variables such as v_ℓ, v_g and reactor pressure were restricted because of our primary interest in catalytic hydrocracking of heavy oils. Thus the reactor hydrodynamics could not be investigated extensively to provide regression equations for ϵ_ℓ, Pe_ℓ, Pe_g and $K_m a$ as functions of physical parameters (density, viscosity, surface tension) and operating

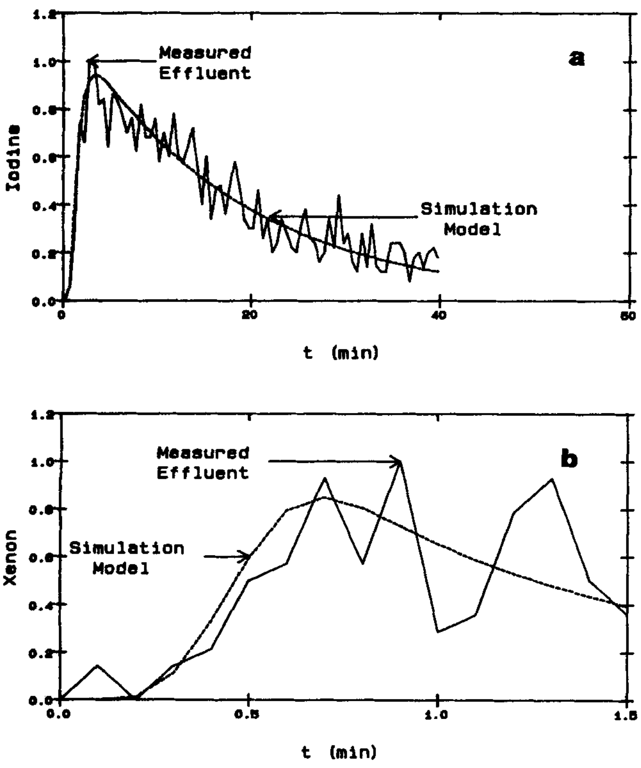


Figure 6. Iodine (a) and xenon (b) effluent fit for Run 3.
LHSV = 4.0 h^{-1} and H_2 = 14 *slpm*.

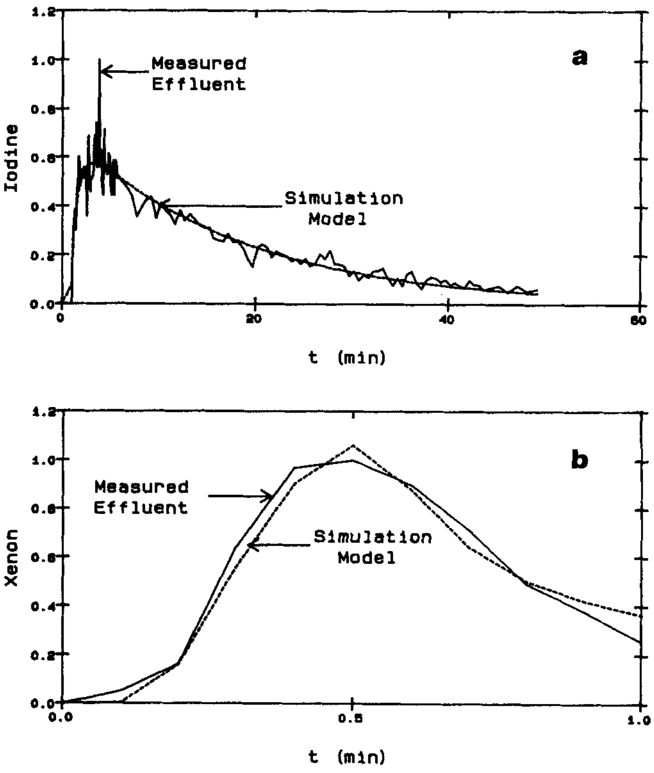


Figure 7. Iodine (a) and xenon (b) effluent fit for Run 4.
LHSV = 4.0 h^{-1} and H_2 = 28 *slpm*.

Table 2. Estimated Reactor Parameters

Run	v_l cm/s	v_g cm/s	Pe_l	ϵ_l	Pe_g	$k_m a$ s^{-1}	H
1	0.0229	3.35	0.67	0.73	8.4	0.019	2.6
2	0.0476	3.35	0.70	0.73	8.3	0.020*	2.6*
3	0.0762	3.35	0.74	0.72	8.0	0.020*	2.6*
5	0.0762	1.91	0.77	0.73	7.1	0.020	2.6
3	0.0762	3.35	0.74	0.72	8.0	0.020*	2.6*
4	0.0762	6.70	0.71	0.72	9.6	0.020*	2.6*

*Preset with fixed values

conditions (pressure, gas and liquid velocities). However, predictions for ϵ_ℓ, Pe_ℓ, Pe_g and $K_m a$, Table 2, are comparable with the experimental measurements of Clark and Foster (1987), Idogawa et al. (1987) and the reported values of Lee et al. (1978). Clark and Foster (1987) applied a neutron absorbing tracer technique to study the hydrodynamics of a paraffin-wax filled container operating at 350°C temperature and 12 MPa pressure, and superficial gas velocities ranging from 1.5 cm s^{-1} to 7 cm s^{-1}. Their measured values for ϵ_g were in the range of 0.05 to 0.35. Idogawa et al. (1987) measured the bubble size and gas hold-up using two electric resistivity probes. Their measured values for ϵ_g were as high as 0.15 in the dispersed jetting region. Lee et al. (1978) used published correlation equations for ϵ_ℓ, Pe_ℓ, Pe_g, and $K_m a$. For the dissolver section of a solvent refined coal process, they predicted $Pe_\ell = 0.98$, $Pe_g = 4.66$, $\epsilon_g = 0.06$, and $K_m a = 0.0553\ s^{-1}$.

The discrepancy between the predictions of this study and others published may originate from the differences in the accuracy of experimental techniques and from the differences in the physical conditions. Peclet numbers in all of these studies are in the same range, while gas hold-up values differ. Gas hold-up measurements using a probe may contain experimental errors, especially at high pressures, where the probe may influence the flow pattern of smaller bubbles. The second source of error in gas hold-up may come from variations along the reactor height due to coalescence. Our predicted values for the gas hold-up is the average, over the reactor volume.

In this study, xenon and iodine isotope tracers were used to identify the hydrodynamics of a two-phase flow tubular reactor. The reactor was operated at 17 MPa, 455°C and had a continuous feed of both liquid and gas streams. Hydrodynamic parameters were estimated using a simulation model to fit the tracer effluent data. The estimated mean values were $Pe_\ell = 0.72$, $Pe_g = 8.3$, $\epsilon_g = 0.27$ and $K_m a = 0.020\ s^{-1}$. The Henry's constant for xenon at the reactor operating conditions was also estimated using the simulation model ($H = 2.6$), and was found to be in good agreement with that predicted using an equation of state. Gas hold-up, calculated independently, using elapsed time to the maximum xenon counts registered at the effluent, was in the same range as the model predictions.

Acknowledgment

The authors gratefully acknowledge the support of AOSTRA/ARC Hydrocarbon Upgrading Program under technical monitoring by Drs. C. Hsi and R. T. Bailey of AOSTRA. The experiments and product characterization work were diligently performed by ARC Coal and Hydrocarbon Processing Department Technical Staff: H. O. Kretschmer, K. Badree, E. Fitzpatrick, and B. Doherty. Preparation and measurement of radioactive tracers were performed by J. Mercer and S. Hunt of Stuart Hunt and Associates, Ltd., Edmonton, Alberta.

Notation

a = gas-liquid interfacial area per unit reactor volume, cm^{-1}
C = concentration, g cm^{-3}
H = Henry's constant
K_m = mass transfer coefficient, cm s^{-1}
L = reactor length, cm
$LHSV$ = liquid hourly space velocity, h^{-1}
M = number of data points
N = number of grid elements
Pe = Peclet number
$SLPM$ = standard liters per minute, l min^{-1}
t = time, s
t_g = dimensionless time ($t_g = v_g t/L$)
t_ℓ = dimensionless time ($t_\ell = v_\ell t/L$)
v = velocity, cm s^{-1}
X = distance from reactor inlet, cm
x = dimensionless distance

Greek letters

ϵ = hold-up
τ = injection pulse width

Subscripts and superscripts

g = gas
j = specie
k = phase
ℓ = liquid
1 = iodine
2 = xenon
$*$ = inlet

Literature Cited

Aris, R., "The Scope of R.T.D. Theory," *Residence Time Distribution Theory in Chemical Engineering*, ed., A. Petho, and R. D. Noble, Verlag Chemie, Weinheim (1982).

Bickel, T. C., and M. G. Thomas, "Catalyst Deactivation in the H-Coal Coal Liquefaction Process: I. Catalyst Residence Time Distribution," *Ind. Eng. Chem. Proc. Des. Dev.*, **21**, 377 (1982).

Clark, K. N., and N. R. Foster, "Application of Neutron Techniques to Studies of Reactor Fluid Dynamics," *Chem. Eng. J.*, **34**, 35 (1987).

Cichy, P. T., and T. W. Russell, "Reactor Model Parameters," *Ind. Eng. Chem.*, **61**(8), 15 (1969).

Crank, J., "Mathematics of Diffusion," Oxford Clarendon Press, (1956).

Danckwerts, P. V., "Continuous Flow Systems: Distribution of Residence Times," *Chem. Eng. Sci.*, **2**(1), 1 (1953).

Danckwerts, P. V., and E. A. Mahlmann, "Boundary Conditions of Liquid Phase Reactors with Axial Dispersion," *Chem. Eng. J.*, **11**, 19 (1976).

Deckwer, W. D., "Design and Simulation of Bubble Column Reactors," *Chem. Reactor Des. and Tech.*, ed., H. I. de Lasa, NATO ASI Ser., (110), 411 (1986).

Dudukovic, M. P., "Tracer Methods in Chemical Reactors. Techniques and Applications," *Chem. Reactor Des. and Tech.*, ed., H. L de Lasa, NATO ASI Ser., (110), 107 (1986).

Guy, C., P. J. Carreau, and J. Paris, "Mixing Characteristics and Gas Hold-Up of a Bubble Column," *Can. J. Chem. Eng.*, **64**, 23 (1986).

Hikita, H., S. Asai, K. Tanigawa, K. Segawa, and M. Kitao, "Gas Hold-Up in Bubble Columns," *Chem. Eng. J.*, **20**, 59 (1980).

Hsu, Y. C., and P. Dudukovic, "Gas Hold-up and Liquid Circulation in Gas-Lift Reactors," *Chem. Eng. Sci.*, **35**, *135 (1980)*.

Hughmark, G. A., "Hold-up and Mass Transfer in Bubble Columns," *Ind. Eng. Chem. Proc. Des. Dev.*, **6**(2), 218 (1967).

Idogawa, K., K. Ikeda, T. Fukuda, and S. Morooka, "Formation and Flow of Gas Bubbles in a Pressurized Bubble Column with a Single Orifice or Nozzle Gas Distributor," *Chem. Eng. Comm.*, **59**, 201 (1987).

Kelkar, B. G., and Y. T. Shah, "Hydrodynamics and Axial Mixing in a Three-Phase Bubble Column. Effects of Slurry Properties," *Ind. Eng. Chem. Pros. Des. Dev.*, **23**, 308 (1984).

Lee, M. H., J. A. Guin, and A. R. Tarrer, "A Dispersion Model for the Solvent Refined Coal Process," *Ind. Eng. Chem. Proc. Des. Dev.*, **17**(2), 127 (1978).

Levenspiel, O., and K. B. Bischoff, "Patterns of Flow in Chemical Process Vessels," *Advances in Chemical Engineering*, Academic Press, New York, 95 (1963).

Mashelkar, R. A., "Bubble Columns," *British Chem. Eng.*, **15**(10), 1297 (1970).

Nalitham, R. V., and O. L. Davies, "Residence Time Distribution Studies in a Multiphase Reactor Under High Temperature and Pressure Conditions," *Ind. Eng. Chem. Res.*, **26**, 1059 (1987).

Nauman, E. B., "Residence Time Distributions and Micromixing," *Chem. Eng. Commun.*, **8**, 53 (1981).

Nicklin, D. J., "Two-Phase Bubble Flow," *Chem. Eng. Sci.*, **17**, 693 (1962).

Ozum, B., M. N. Oguztoreli, M. P. duPlessis, and M. Oguztoreli, "Isothermal Axial Dispersion Reactors in Coal Liquefaction Hydroprocessing," *Chem. Eng. Commun.*, **44**, 287 (1986).

Panvelker, S. V., J. W. Tierney, and Y. T. Shah, "Backmixing in a SRC Dissolver," *Chem. Eng. Sci.*, **37**(10), 1582 (1982).

Pavlica, R. T., and J. H. Olson, "Unified Design Methods for Continuous-Contact Mass Transfer Operations," *Ind. Eng. Chem.*, **62**(12), 45 (1970).

Press, W. H., B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, "Numerical Recipes, The Art of Scientific Computing," Cambridge Univ. Press (1986).

Shah, Y. T., B. G. Kelkar, S. P. Godbole, and W. D. Deckwer, "Design Parameters Estimations for Bubble Column Reactors," *AIChE J.*, **28**(3), 353 (1982).

Manuscript received June 6, 1988, and revision received Feb. 23, 1989.