DEMONSTRATING THE EFFECT OF INTERPHASE MASS TRANSFER

In a Transparent Fluidized Bed Reactor

JEAN SAAYMAN AND WILLIE NICOL
University of Pretoria • Pretoria, South Africa, 0002

Gas-Solid fluidization is a unique and well employed part of the field of Chemical Reaction Engineering and accordingly it is taught in most undergraduate Chemical Engineering programs. Educational experiments employing fluidization are therefore not new to literature; prime examples can be found for adsorption[1] and polymer coating[2] experiments. The catalytic gas-fluidized bed reactor is a classic example of how hydrodynamics can affect reactor performance and it is likely to be one of the first examples for the undergraduate (or early post-graduate) student where classical reaction engineering principles are integrated with complex flow phenomena. It is well established that the contacting between the leaner and denser "phases" can cause severe deviations from the predicted behavior.[3] This is mainly due to the mass transfer resistance between the phases, where most of the reactant has to be transported from the lean phase to the dense (or emulsion) phase that contains most of the catalyst. Most undergraduate textbooks[4,5] focus on the bubbling fluidization regime where the lean phase is present in a bubble form and accordingly bubble-to-emulsion mass transfer is covered to a reasonable degree. These texts also illustrate how the conversions for a relatively fast reaction in the bubbling regime can be significantly less than that predicted by a plug flow (or even perfect mixing) model. To the knowledge of the authors no educational experiment has been published to illustrate the interphase mass transfer principle.

In this paper an experimental setup is presented to visually and experimentally illustrate the effect of interphase mass transfer on a fast chemical reaction in the smooth, bubbling, and turbulent regimes of fluidization. The student will be confronted with major differences in overall conversion between that of the smooth (homogeneous) fluidization regime and the bubbling regime, while the transition from the bubbling to the turbulent regime will illustrate how transfer limitations diminish while only back mixing effects remain. Visual observations of the experiment allow for an intuitive confirmation of the measured results, while the modeling afterwards, based on well developed correlations, will tie the theory to practice.

***Jean Saayman** is a Ph.D. student at the University of Pretoria. He received his B.Eng. degree, as well as his M.Eng. at the same institution. His research interests are in Reaction Engineering, specifically focusing on Fluidized Bed Reactors.*

***Willie Nicol** is a professor in chemical engineering at the University of Pretoria. He received his B.Eng. degree from the University of Pretoria and his Ph.D. from the University of the Witwatersrand. He runs the Reaction Engineering Research Group that focuses on Trickle Bed Reactors and Gas-Solid Fluidization. He has been teaching the undergraduate reactor courses in his department for more than seven years.*

The well established ozone decomposition reaction on iron oxide-impregnated Fluidized Catalytic Cracking (FCC) catalyst is used. The conditions of the suggested experiment were optimized in order to enhance the observation of mass transfer effects. It is suggested that the apparatus should be used for undergraduate demonstrations, while the generated data should be handed to the students in order for them to perform their own interpretations. On a postgraduate level the experiment can be performed by the students themselves. There are different options in terms of the level of interpretation required. For undergraduates a simple Kunii-Levenspiel model[3] or a two-phase plug flow model[6] can be used, while more advanced dispersion modeling coupled with regime transition predictors[7] can be performed by postgraduates.

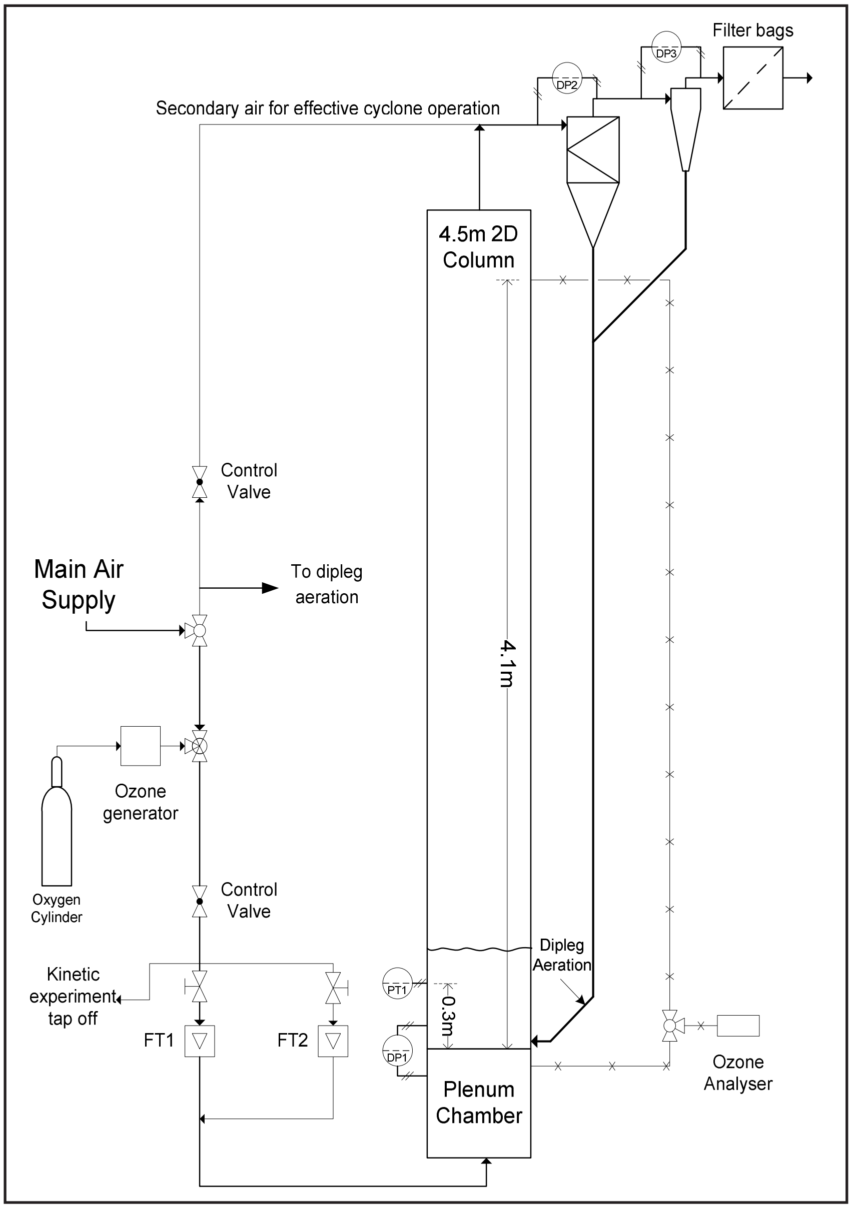

***Figure 1.** Experimental setup.*

BASIC EXPERIMENTAL REQUIREMENTS

There are different options in terms of the complexity of the experimental setup. A transparent two-dimensional fluidized bed is suggested (some laboratories will already have such a setup). The complexity of the column design will depend on the velocity range required. The minimum requirement is a maximum superficial velocity of 0.2 m/s (based on FCC catalyst used in this study). This will allow for comfortable operation in the bubbling regime without significant solid entrainment, thus allowing for a simple solid separation device like a filter bag at the exit. Although this design will not be able to cover the turbulent regime, it will be able to demonstrate the severe interphase mass transfer effect in the bubbling regime. For higher superficial velocities a solids recycle will have to be used by employing a cyclone (or multiple cyclones) and a dipleg (see section entitled "Demo Experimental Apparatus") The column has to be supplied with a measured inflow of air. One will typically require two parallel flow measurement devices, one for the small flow ranges (packed bed and minimum fluidization ranges) and the other for the higher fluidization velocities. An ozone generator (with oxygen supply) and an online ozone analyzer are further requirements. It is preferable to link the ozone reading to a visual display. Lastly, fresh FCC catalyst is required as support, while ferric nitrate is used to prepare the active sites on the catalyst. A high-frequency pressure transmitter is optional, but will be useful for high-velocity experiments where bubbling-turbulent regime transition needs to be characterized.

The main cost contributors of the setup will be the ozone equipment, the Plexiglas column, and the gas flow measurement if an air stream is readily available. For our system the ozone analyzer cost $7,000, while the generator and the detector had a cost of only $2,500. The column used in this study cost $17,000; although a simple system with a less elaborate recycle system will be much less. Different options are available for the flow measurement but $8,000 should be sufficient.

DEMO EXPERIMENTAL APPARATUS

A two-dimensional Plexiglas column with a thickness of 25 mm, width of 0.4 m, and height of 4.5 m was used for the demonstration. The reason for the two-cyclone system in Figure 1 is that the column was designed to operate up to a superficial velocity of 1.2 m/s. A triangular pitch perforated plate distributor with 35x 2 mm holes was used. A porous cloth was placed below the distributor to prevent solids weepage. This assisted in increasing the pressure drop over the distributor to a value greater than the pressure drop over the bed, thus ensuring even gas distribution. The plenum chamber was filled with glass beads to enhance ozone mixing. A high frequency pressure transmitter was installed at a height of 0.3 m, just below the bed surface. The inlet of the sample probes were covered with porous cloth and sealed to ensure a solids-free sampling system. A UV-106 ozone analyzer was connected via a three-way valve to an inlet and outlet sample tube. The ozone generator (Eco-Tec's MZPV-1000) had a maximum output of 1g/hr. The ozone production can be controlled by varying the inlet oxygen flow or by adjusting the intensity of the generator. The total feed (air + ozone generator outlet) concentration varied between 15 and 70 ppm, while the ozone conversion varied between 15 and 99.5%. The exit gas from the reactor was diluted with cyclone gas and released outside the laboratory. Activated carbon absorbers can be used, but the influence of the pressure drop over the absorber on the column pressure should be considered. Health-based standards established by the U.S. government recommend limiting an 8 hr exposure to a maximum ozone concentration varying between 70 – 120 ppb and an immediate danger to life or health limit of 5 ppm.[8] An ozone detector was installed next to the demo experimental setup which would sound an alarm at a ozone level of 100 ppb. Ozone can already be smelled at 20 – 50 ppb, however.[9] Proper sealing and disposal should be ensured.

CATALYST

The FCC catalyst (NEKTOR 366, Grace Davison Refinery Technologies, Europe) has a Sauter mean diameter of 66 µm and exhibited typical Geldart A particle characteristics. The fresh catalyst is mixed with a 10 %(wt) ferric nitrate solution in a weight ratio of 1:1.8. The mixture is well-stirred for 2 hours, followed by decanting of the excess solution. The separated catalyst is dried overnight at 95 °C and then calcinated at 475 °C for 2 hours.[10] The required active site (Fe_2O_3) will form on the catalyst according to the following reaction:

$$\mathrm{Fe}\left(\mathrm{NO}_3\right)_3.\mathrm{nH2O} \rightarrow \frac{1}{2}\,\mathrm{Fe}_2\mathrm{O}_3 + 3\mathrm{NO}_2 + \frac{3}{4}\mathrm{O}_2 + \mathrm{nH}_2\mathrm{O} \qquad (1)$$

A fume hood or oven extraction system is required to remove the formed NO_2 gas. For the demo apparatus 5 kg of catalyst was prepared.

The reaction is known to be first order with respect to ozone at oxygen concentrations less than 50% and water concentrations less than 4%.[11] The demonstration catalyst was found to rapidly deactivate for the first 2.5 hours of operation, after which the activity remained constant for 10 hours. The volumetric rate constant (based on volume of solid) for the stable activity period was found to be 0.7 s^{-1}. Deviations from this activity (for different FCC supports) will still illustrate the principles of the demonstration (see

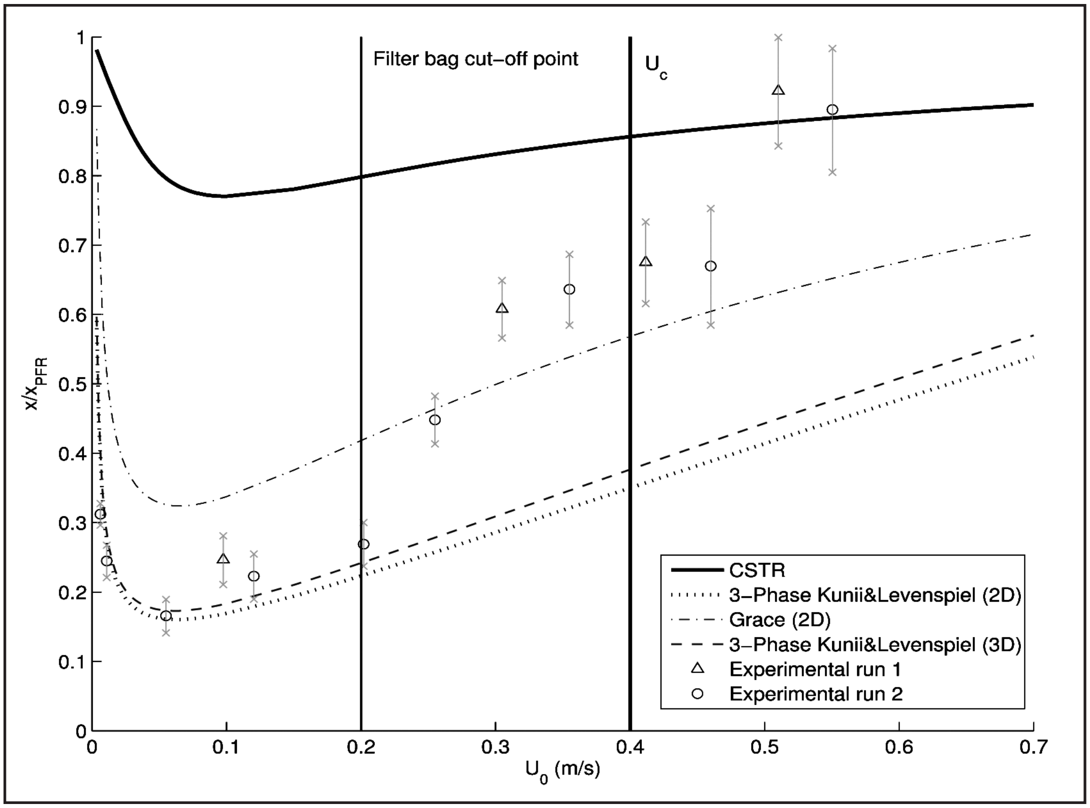

***Figure 2.** Experimental data and theoretical models.*

Figure 3). The rate constant of a specific catalyst batch can be determined from the bubbling regime measurements by using the Kunii-Levenspiel three-phase plug flow model [with 2D correction –see Eqs. (6) and (7)]. The accuracy of this model for the two-dimensional column was confirmed by using a rate constant that was independently determined in a separate fixed bed reactor. It is suggested that the rate constant should be established before the demonstration experiment, in order to supply the students with the kinetic information required for their own analysis.

RESULTS

The steady state conversions at different superficial velocities are represented in Figure 2. In order to illustrate the major deviation from plug flow performance the y-axis is normalized with respect to the maximum (or PFR) conversions. It is interesting to note that the first data point (at u_0 = 3.5mm/s) is at the maximum conversion. At this point the velocity is just beyond that of minimum fluidization and still within the smooth or homogeneous fluidization regime (u_{mf} = 3.1 mm/s and u_{mb} = 6.3 mm/s). The conversion in the smooth fluidization regime was found to be very similar to that of the packed bed and for practical purposes ideal plug flow can be assumed. Upon bubble formation there is a drastic drop in conversion (at u_0 = 6.3 m/s the conversion is 31%) and from the theoretical CSTR solution on Figure 2 it is clear that the major difference cannot be attributed to mere mixing effects.

During observation the students will intuitively understand the major deviation in conversion, due to the bubble bypassing the emulsion (or catalyst bed). This will be a good time to address the importance of interphase mass transfer and the distribution of feed gas between bubble and emulsion flow. This should be done before increasing the velocity to the extent where the x/x_{PFR} values start to increase (in order to clearly observe distinct bubbles rising in the bed).

The gradual recovery in the reactor performance with an increase in the superficial velocity will not be clearly observed in the conversion measurements due to the drop in the theoretical plug flow conversion with an increase in throughput. Accordingly the turning behavior in Figure 2 will only be observed when plotting the relative conversion. On a visual level, however, the severity of bubble-dense phase interaction at higher velocities will be clearly observed.

Figure 3 gives the expected results for catalysts with a higher/lower activity than that of the demonstration catalyst. It is evident from the graph that the demonstration can be performed at higher/lower catalyst activities.

INTERPRETATION OF THE RESULTS

The interpretation should center on the graphical representation of the data and predictive models in the suggested format of Figure 2. For undergraduate students a simple two- or three-phase plug flow with exchange model will be sufficient.

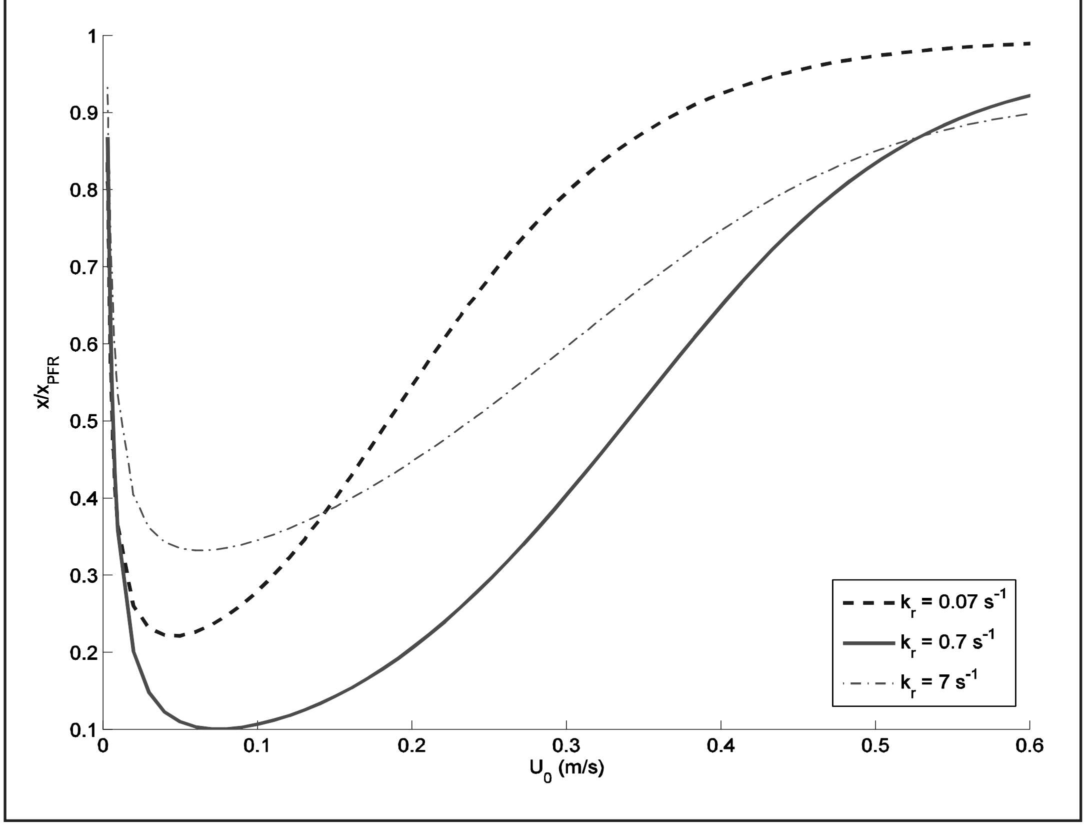

Figure 3. *Predicted reactor performance for different catalyst activities using the Thompson, et al., transitional model*[7] *in conjunction with the Kunii-Levenspiel mass transfer coefficient for 2-phase flow.*

The Kunii-Levenspiel three-phase model can be written as the following ordinary differential equations[5] (see textbook for more details):

$$u_b \frac{dC_{i,b}}{dz} = f_b R_i\left(\mathbf{C_b}\right) - K_{bc}\delta\left(C_{i,b} - C_{i,c}\right) \tag{2}$$

$$u_c \frac{dC_{i,c}}{dz} = f_c R_i\left(\mathbf{C_c}\right) + K_{bc}\delta\left(C_{i,b} - C_{i,c}\right) - K_{ce}\delta\left(C_{i,c} - C_{i,e}\right) \tag{3}$$

$$u_e \frac{dC_{i,e}}{dz} = f_b R_i\left(\mathbf{C_e}\right) + K_{ce}\delta\left(C_{i,c} - C_{i,e}\right) \tag{4}$$

$$C_i = u_b C_{i,b} + u_c C_{i,c} + u_e C_{i,e} \tag{5}$$

Where the reaction rate, $R_i(\mathbf{C_J})$, is a function of the species in the relevant phase. An area correction should be made to the volumetric mass transfer coefficients to account for the two dimensional bubbles so that:

$$K_{bc,2D} = \frac{2}{3} K_{bc,3D} \tag{6}$$

$$K_{ce,2D} = \frac{2}{3} K_{ce,3D} \tag{7}$$

The distribution of catalyst for the demo example was chosen to be $f_b = 0.005$; the bubble wake fraction of the model was chosen to be 0.4 and the bubble diameter used was 8.5 cm. Due to the first-order kinetics an analytical solution for the model is possible, but it is easier to solve the set of ordinary differential equations numerically. The basic Kunii-Levenspiel approach is to assume zero gas flow in the emulsion and cloud phases and thus Eqs. (3) and (4) will reduce to algebraic equations. The shortest method to solve the formulation is to assign small velocity values (0.1% of u_b) to the cloud and emulsion velocities, specify the inlet concentration of reagent in all three-phases, and use a simple ordinary differential equation solver. The cloud and emulsion concentration will reach its steady state values within the first few integration steps, while the final solution will be very close to the analytical solution. The solution, in the format of three concentrations as a function of bed height, has the added advantage of graphically representing the concentration gradients as a function of bed height.

A two-phase plug flow approach will give the following two differential equations:

$$u_b \frac{dC_{i,b}}{dz} = f_b R_i\left(\mathbf{C_b}\right) - k_{be}\delta\left(C_{i,b} - C_{i,e}\right) \tag{8}$$

$$u_e \frac{dC_{i,e}}{dz} = f_e R_i\left(\mathbf{C_e}\right) + k_{be}\delta\left(C_{i,b} - C_{i,e}\right) \tag{9}$$

$$C_i = u_b C_{i,b} + u_e C_{i,e} \tag{10}$$

The mass transfer correlation for two-dimensional bubbles of Sit and Grace[12] can be used:

$$K_{be} = \frac{2}{3}\left(0.4\ u_{mf} + 2\sqrt{\frac{D_m \varepsilon_{mf} u_b}{\pi d_b}}\right) \tag{11}$$

Alternatively the Kunii-Levenspiel model can be converted to a two-phase model by ignoring the cloud phase and by obtaining a single mass transfer coefficient given by:

$$K_{be} = \frac{K_{bc} K_{ce}}{K_{bc} + K_{ce}} \tag{12}$$

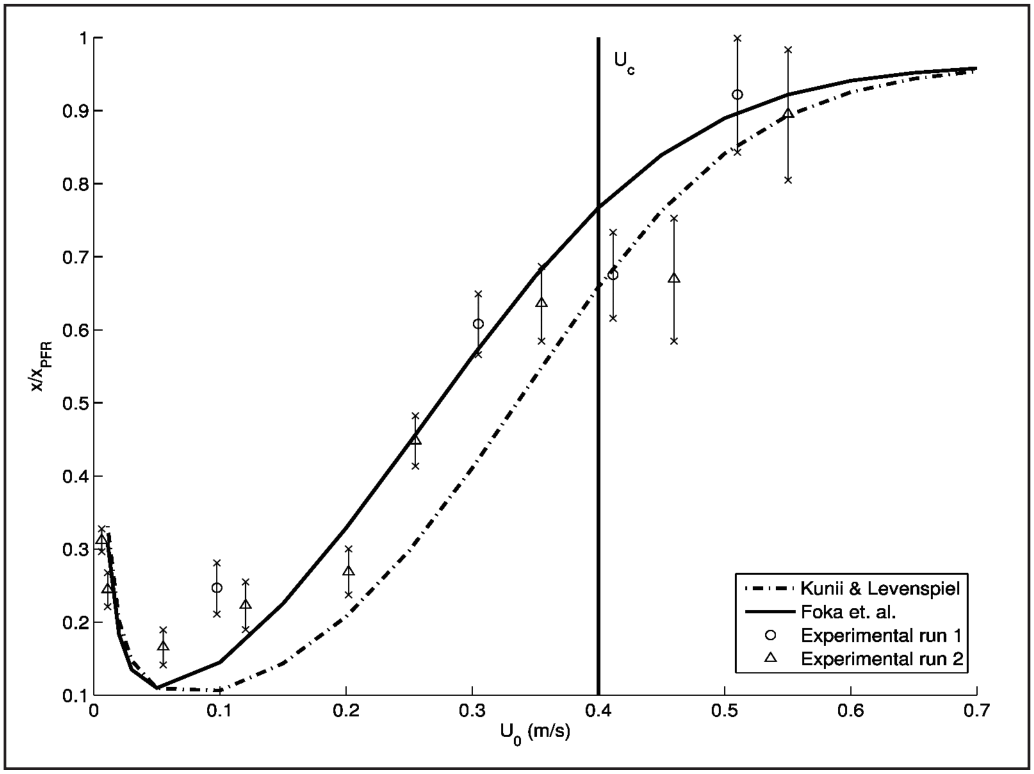

Figure 4. *Data prediction over the entire velocity range using the Thompson model (1999) with different 2-phase mass transfer coefficients. Foka, et al.,*[14] *gives good agreement.*

A similar approach to that of the three-phase model can be used to solve the formulation and students will be able to compare the two types of plug flow models. For the two-phase model represented in Figure 2 the catalyst distribution was chosen to be $f_b = 0.0355$. It is evident from Figure 2 that both models give a reasonable fit for the lower velocity ranges, but underpredict the performance at higher velocities where the bed starts exhibiting properties of turbulent fluidization. More advanced students can follow the approach by Thompson, et al.,[7] where the transition between the bubble and turbulent regimes is modeled using probabilistic averaging. The transition velocity u_C* is required in this model and can be determined from pressure fluctuation readings.[13] This transitional two-phase model employs axial dispersion in both phases and achieves an adequate prediction of the data over the complete velocity range, as can be seen in Figure 4.

TRIALS AS PART OF A POSTGRAD COURSE

The described experiment has been used as part of a postgraduate course on reactor hydrodynamics. Before the demonstration experiment, the students were exposed to the two- and three-phase approach to modeling fluidized beds. The example in the Levenspiel textbook[5] was used as a base case scenario to verify the numerical solutions of both models. This provided the students with the necessary tools to predict conversions in the bubbling flow regime. This was all performed prior to the demonstration. The demonstration itself was a great success in terms of confirming the governing principle of interphase mass transfer. Most students were keen to test the results against their already developed models and were surprised at the accuracy of their prediction in the bubbling regime. The observed deviation at higher velocities provided a platform for the lecture on the turbulent regime. From the student feedback the general consensus was that the demonstration (accompanied with the analysis of the experimental results) greatly assisted their understanding of fluidized bed hydrodynamics.

CONCLUSION

This demonstration experiment is an ideal tool for illustrating the effect of interphase mass transfer in a fluidized bed reactor. The student is directly exposed to the reaction rate reduction effect of the bubbles in the bed. The experiment in combination with the theoretical interpretation provides an ideal platform for developing an integrated understanding of the subject. Trials with postgraduate group proved to be very successful in terms of student feedback and test results.

NOMENCLATURE

C_i	Gas concentration of species I (kmol/m^3)
D_m	Gas diffusion coefficient (m^2/s)
d_b	Bubble diameter (m)
K_{bc}	Bubble-Cloud mass transfer (s^{-1})
K_{ce}	Cloud-Emulsion mass transfer (s^{-1})
K_{be}	Bubble-Emulsion mass transfer (s^{-1})
k_r	Reaction rate constant based on volume catalyst (s^{-1})
u_b	Bubble phase velocity (m/s)
u_{br}	Single bubble rise velocity (m/s)
u_c	Cloud phase velocity (m/s)
u_C^*	Minimum turbulent velocity 1 (m/s)
u_e	Emulsion phase velocity (m/s)
u_{mb}	Minimum bubble velocity (m/s)
u_{mf}	Minimum fluidization velocity (m/s)
u_o	Operating velocity (m/s)
z	Height in reactor (from distributor) (m)

Subscripts

b	Bubble phase (Low density phase)
c	Cloud phase
e	Emulsion phase (High density phase)
mf	Minimum fluidization

Greek letters

ε	Gas volume fraction
f	Solids volume fraction (1-ε)
δ	Phase volume fraction

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