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Improving the Conversion in Fluidised Beds with Secondary Injection

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IMPROVING THE CONVERSION IN FLUIDISED BEDS WITH SECONDARY INJECTION

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ABSTRACT

The effect of secondary injection on the performance of a fluidised bed reactor has been studied. A modified Kunii and Levenspiel model was used to predict the effect on conversion and indicates that the reduction in bubble size caused by secondary injection results in a significant increase. This effect was confirmed experimentally, although the model appears to underestimate the experimental values.

INTRODUCTION

The mass transfer of a reactant from the bulk fluid to the catalyst in a bubbling fluidised bed is severely hindered because a large portion of the gas flow is in the form of bubbles. The reactant gas must diffuse through the bubbles and into the dense phase before it can reach the catalyst. As such, much of the gas bypasses the catalyst bed entirely. The result of the poor gas-solid contact throughout the bed is a low conversion and poor selectivity.

To improve the performance of a bubbling fluidised bed the size of the bubbles must be reduced. Using secondary gas injection, whereby a portion of the total gas flow is injected into the reactor via a fractal injector (Figure 1a), results in a reduction of the bubble size by 50% or more. Furthermore, the total volume of the bubbles is reduced (1, 2). These results indicate that a much better gas-solid contact is achieved, which should result in a higher conversion. The purpose of the current work is to directly study the effect of secondary injection on the conversion in a bubbling fluidised bed. Firstly, predictions of the effect using a reactor model are presented. Secondly, the results of preliminary conversion experiments using ozone decomposition (equation (1)) as a test reaction are reported. Ozone decomposition is often used as a test reaction because it has some favourable characteristics (3-5). Ozone is easy to detect at very low concentrations, thus temperature and volume changes due to reaction are negligible. It is simple to generate and the reaction kinetics are typically close to first-order.

$$2O_3 \rightarrow 3O_2 \tag{1}$$

REACTOR MODELLING

The purpose of modelling the effect of secondary injection is to determine how the conversion is dependent on the bubble size. These results will be compared with the experimental data. The reactor model used is the fine-particle bubbling bed model proposed by Kunii and Levenspiel (6, 7). The assumptions inherent in this model are: bubbles, cloud, and emulsion can be modelled as separate phases; bubbles are spherical and follow the Davidson model for bubble behaviour (i.e., they travel faster than the emulsion gas and are surrounded by thin clouds); the wake of the bubbles is considered to be part of the cloud; bubble size is constant throughout the reactor; and the flow through the bubble phase is so much larger than the flows through the other phases that the latter flows can be ignored.

The model has been modified to include the flow through the emulsion phase because it is not negligible compared to the flow through the bubble phase for the total gas flow rate used in this study ($4\times Q_{mf}$). The assumption of constant bubble size has also been removed by using the Darton equation (8) to predict the bubble size along the height of the reactor. This relation has been shown to be accurate in standard fluidisation columns (9). We must assume, however, that it will still be valid with secondary gas injection and the presence of internals.

It is not possible to implement the radial distribution of the secondary injection points in this one-dimensional axial model. Therefore, we assume that the fractal injector can be modelled as a series of levels at which the secondary gas is uniformly introduced into the bed. In addition, even though previous experiments have shown that secondary injection causes an increase in the flow through the emulsion phase (2), it was conservatively assumed that the emulsion phase remains at minimum fluidisation conditions throughout the reactor and that all of the secondary gas goes directly into the bubble phase. A schematic description of the model is shown in Figure 1b. Each phase also contains a reaction term (not shown). These modifications to the original K-L model result in a system of differential and algebraic equations that must be solved numerically. The general scheme is, firstly, to solve the system of equations up to the first injector level. Secondly, to adjust the boundary conditions to take into account the fresh secondary gas, and to continue the integration up to the next injector height, repeating this process until the final bed height is reached. Since the bed height depends on the bed porosity, which, in turn, depends on bubble size and flow rate (both of which are changing with height), iteration must be performed until the solution converges.

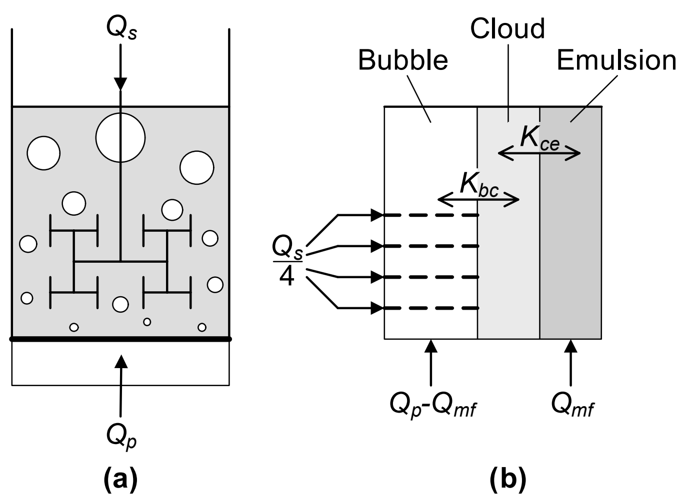

Figure 1: Schematics of the fluidized bed and fractal injector; (a) experimental setup; (b) model configuration

To take the effect of secondary injection on the bubble size into account, the Darton equation is multiplied by a bubble diameter reduction factor, β, as shown in equation (2). This factor is always between 0 and 1 and depends on the amount of injected secondary gas. Its value is determined from experiments, which will be discussed later. For example, if the bubble diameter with secondary injection is 25%

smaller, then β is equal to 0.75. If β is known as a function of height then it can be replaced by $\beta(h)$ in equation (2). Here, $\beta(h)$ was not known, so it was assumed that the values measured halfway up the bed were the average values for the reactor. The parameter A_0, the area of the distributor plate per orifice, is unknown but is very small for porous distributors. Therefore, A_0 was neglected in this study.

$$d_b = \frac{0.54\left(U_0 - U_{mf}\right)^{0.4}\left(h + 4\sqrt{A_0}\right)^{0.8}}{g^{0.2}} \cdot \beta \tag{2}$$

A minimum bubble diameter, $d_{b,min}$ = 1.3 cm, had to be defined because the model would not converge at very small values. The model uses the result of equation (2) or $d_{b,min}$, whichever is greater at the current height in the bed. It should be noted that d_b is the average bubble size at that height. The rest of the model follows the development of Kunii and Levenspiel (6, 7). The steady-state material balances for the reactant in each of the phases, assuming first-order reaction, are:

$$\frac{dC_{A,b}}{dh} = \frac{-1}{\left(\delta \cdot U_b\right)} \cdot \left[\delta \cdot K_{bc} \cdot \left(C_{A,b} - C_{A,c}\right) + f_b \cdot k \cdot C_{A,b}\right] \tag{3}$$

$$0 = -\delta \cdot K_{bc}\left(C_{A,b} - C_{A,c}\right) + \delta \cdot K_{ce}\left(C_{A,c} - C_{A,e}\right) + f_c \cdot k \cdot C_{A,c} \tag{4}$$

$$\frac{dC_{A,e}}{dh} = \frac{-1}{\left(1-\delta\right) \cdot U_{mf}} \cdot \left[-\delta \cdot K_{ce}\left(C_{A,c} - C_{A,e}\right) + f_e \cdot k \cdot C_{A,e}\right] \tag{5}$$

This method of predicting the effect of a reduced bubble size on the conversion is general enough to be applied to modelling other techniques that decrease the bubble size throughout the reactor.

MODEL RESULTS & DISCUSSION

All parameters in the model, such as Q_0, Q_s, U_{mf}, β, bed mass, number and placement of injectors, etc., were chosen to match the experiments, which are described below. The reaction is assumed to be first order with the ozone concentration, while the reaction rate constant, k, is unknown and is used as an adjustable parameter. The modelling was carried out with and without secondary injection. An example of the calculated concentration profiles and bubble diameters for a total flow rate, Q_0, of $4 \times Q_{mf}$ is given in Figure 2. In this particular case, the calculated conversions are 62.9% for the case without secondary injection and 68.7% for the case with $Q_s = 2 \times Q_{mf}$ and $\beta = 0.62$. These results indicate that a strong relationship exists between the conversion and the bubble size in a fluidised bed reactor. It can be seen that, with secondary injection, the concentration in the bubble phase is lower, while the concentration in the emulsion phase is higher than in the normal bed. This change in concentration profiles indicates that mass transfer to the dense phase has increased, which results in a higher conversion for sufficiently high values of k.

The relationship between the decrease in bubble size (with increasing Q_s) and the relative increase in conversion (X_s/X_0) is confirmed when the case with $\beta = 1$ for all flow conditions is compared to the case with the experimentally determined β's (Figure 3). When $\beta = 1$ for all flow conditions and low to moderate values of k, the conversion changes very little. For high values of k the mass transfer is not fast enough to keep the catalyst supplied with reactant. The conversion decreases with increasing Q_s in this case because the reactant injected higher in the bed has less time to transfer to the emulsion phase. When the bubble size reduction is taken into

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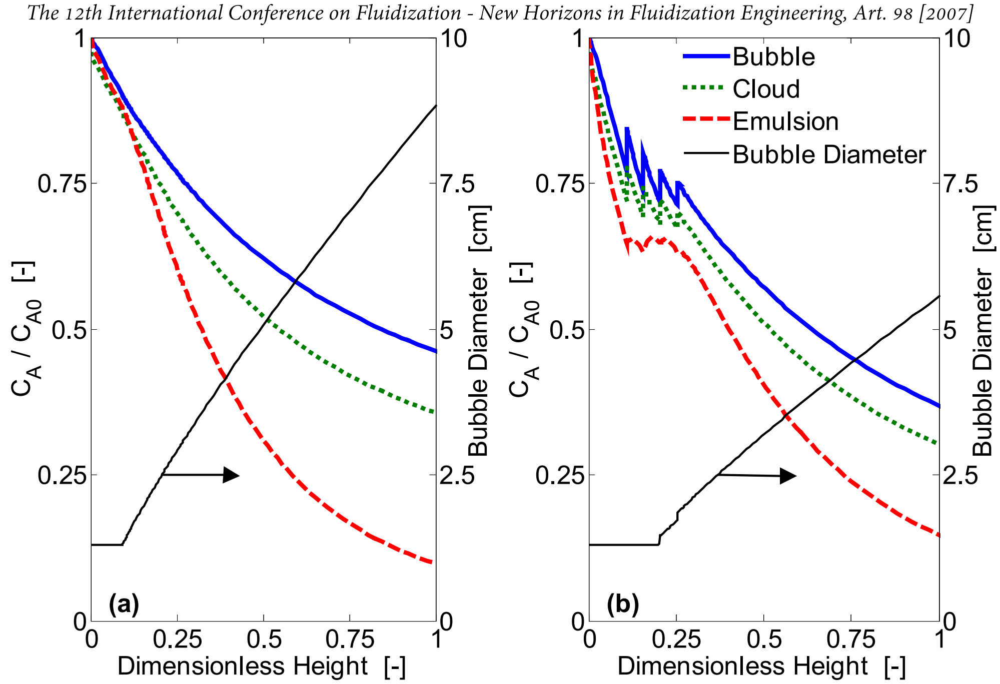

Figure 2: Concentration profiles and bubble diameters predicted by the modified K-L model with $Q_0 = 4 \times Q_{mf}$, $k = 1$ $m^3_{gas}/(m^3_{solid} \cdot s)$, $d_{b,min} = 1.3$ cm; (a) no secondary injection; (b) $Q_s = 2.0 \times Q_{mf}$, $\beta = 0.62$

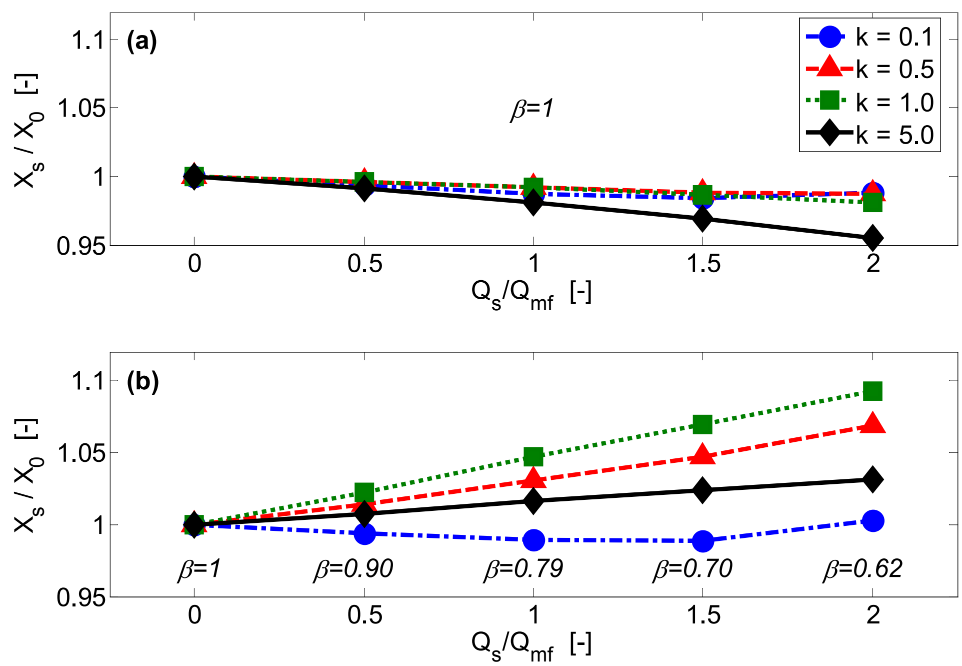

Figure 3: The relative change in conversion, X_s/X_0, as a function of Q_s for $Q_0 = 4 \times Q_{mf}$ and various k; (a) with $\beta = 1$ for all flow conditions; (b) with β determined from experiments for each flow condition. k has units of $m^3_{gas}/(m^3_{solid} \cdot s)$.

account ($\beta < 1$) the conversion increases significantly (when k is greater than 0.1) with increasing Q_s and decreasing bubble size. The change in conversion is small when k is low because the reaction is kinetically limited; therefore an improvement in the mass transfer will have little effect. The increase in conversion when k is very high is also small because the absolute conversion at $Q_s = 0$ is already high, and is difficult to further increase. As a result, the biggest relative increases in conversion are seen at intermediate reaction rates. These results are only taking the reduction in bubble size into account but are neglecting the increase in emulsion phase flow that also occurs with secondary injection (2). Thus, an even higher conversion is expected in experiments.

EXPERIMENTAL

Experiments were conducted in a 20 cm wide × 1.5 cm deep quasi-2D column with a porous plate distributor. The lowest level of the fractal injector was at 6 cm and the highest at 14 cm. The injector configuration is as shown in Figure 1a. The bed mass consisted of 40 g of 1 wt% iron-impregnated Al_2O_3 particles diluted with 855 g of the same non-impregnated particles to give a settled bed height of 40 cm. The particle size was 250-300 μm and the particle density was approximately 1339 kg/m^3, which is in the A/B border region of the Geldart chart. Ozone was generated by an OAS Coolflow O_3 generator and mixed with air to produce the desired flow rate. The ozone concentrations were analyzed with an INUSA 2000 O_3 analyzer with a range of 0-100 ppm$_v$ and an accuracy of 0.1 ppm$_v$. The temperature of the feed gas and the cabinet in which the column was located were heated to 55°C. The relative humidity was monitored (but not regulated) and stayed within the range of 1-2% over the course of these experiments. A constant flow was drawn off the feed gas line to analyze the initial ozone concentration. By switching a set of valves the product concentration was sampled. Both sample lines had mass flow controllers to control the sample flow rates to 1.8 L/min. For the secondary gas injection experiments the feed gas was split into primary and secondary streams using needle valves and a calibrated rotameter to monitor the flow. The ozone concentration in the feed was in the range of 60-70 ppm$_v$, with the exact value depending on the back-pressure on the O_3 generator, which was typically less than 0.5 bar(g).

The method of determining bubble sizes from pressure fluctuations proposed by van der Schaaf *et al.* (10) and validated by Kleijn van Willigen *et al.* (11) was used to estimate the bubble size reduction caused by secondary injection. The standard deviation of the incoherent portion of a pressure fluctuation-time series measured in the bed at high frequency (in this case, 400 Hz) is directly related to the size of the bubbles passing the pressure sensor. Typically a calibration factor (usually obtained from video analysis) is required to determine an absolute bubble size with this technique, but for our purposes here, only the relative change in bubble size with respect to the case without secondary injection is required, so calibration was not needed. For more information regarding this technique, the reader is directed to (10) and (11). Kistler type 7261 piezoelectric pressure transducers and Kistler type 5011 amplifiers were used to measure the pressure fluctuations at three locations – the reference sensor located immediately above the distributor plate, and two others at 19 cm and 30 cm above the distributor. The pressure transducers were connected to sample ports in the side of the bed at these locations by 10 cm long × 4 mm inner diameter copper tubes, well within the probe size recommendations proposed by van Ommen *et al.* (12).

The feed concentration and pressure fluctuations were measured simultaneously over a period of five minutes for each flow condition. The sampling valve was then switched, and the product concentration was measured simultaneously with the pressure fluctuations for an additional five minutes.

EXPERIMENTAL RESULTS AND DISCUSSION

The behaviour of β with increasing secondary injection for $Q_0 = 4{\times}Q_{mf}$ is shown in Figure 4 for two measurement positions. The 19 cm position is 5 cm above the topmost level of the fractal injector. It shows that β decreases significantly with increasing values of Q_s. The bubble size reduction at the 30 cm probe position, which is more than twice the height of the fractal injector, is still very large. The β's observed at 19 cm were used in the modelling discussed above.

The conversion results are presented in Figure 5 for $Q_0 = 4{\times}Q_{mf}$. The error bars are the 95% confidence intervals. Although the uncertainty is quite large, there is a definite indication that conversion increases with increasing Q_s. This trend shows that secondary injection has a much greater effect than the presence of the internals. The relative increase in conversion is as high as 14%, which confirms that the conversion size depends on bubble size. These results need to be reproduced and the uncertainty in the data needs to be decreased. The fractal injector has not been optimized; future designs may yield even better results.

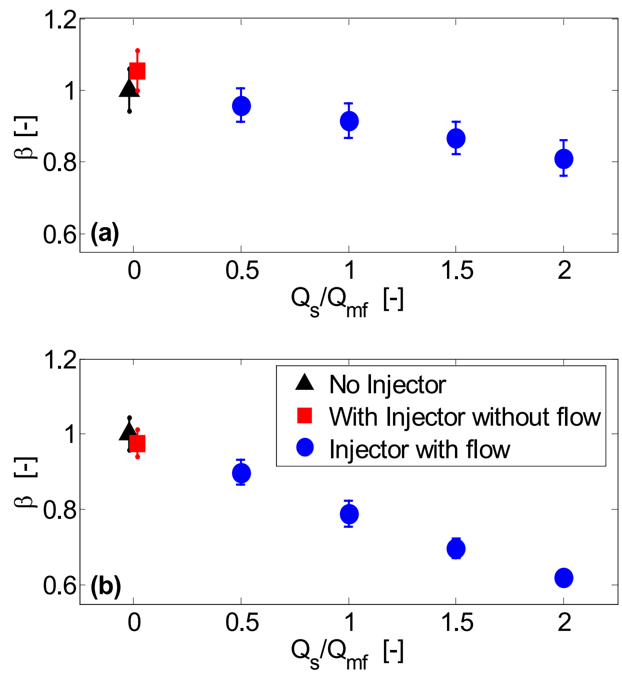

Figure 4: β as a function of Q_s at $Q_0 = 4{\times}Q_{mf}$; (a) measured at *h* = 30 cm; (b) measured at *h* = 19 cm. Error bars are 95% confidence intervals.

The model predictions are also presented in Figure 5. The value of k that gave the same conversion as the experimental result at $Q_s = 0$ was used ($k = 0.29$ $m^3_{gas}/(m^3_{solid}{\cdot}s)$). A large relative increase in conversion with decreasing bubble size was expected, given that this is an intermediate value of k. The model predicts higher conversions with increasing Q_s, but underestimates the absolute values and the rate of increase when compared to the experimental data. This is an indication that only taking the decrease in bubble size into account is not sufficient. Therefore the increase in emulsion phase flow caused by secondary injection should also be included in the model.

The benefit of secondary injection at an industrial scale is expected to be even larger than in this laboratory-scale reactor. The effect will be greater because the bubbles grow much larger, so the potential to increase the mass transfer between the phases is much higher.

CONCLUSIONS

A modified version of the Kunii and Levenspiel model that incorporates emulsion phase flow and bubble growth has been used to predict the effect of secondary injection on the conversion in a bubbling fluidised bed reactor. The results indicate that the conversion increases because secondary injection reduces the bubble size, which results in an improved mass transfer. Experiments were also performed using ozone decomposition as a test reaction. These results also indicate that the conversion increases, while the bubble size decreases, with increasing secondary gas. The model predicts a positive trend in the conversion, but consistently underestimates the experimental values and rate of increase. The model should predict the data better by including an increase in the emulsion phase flow.

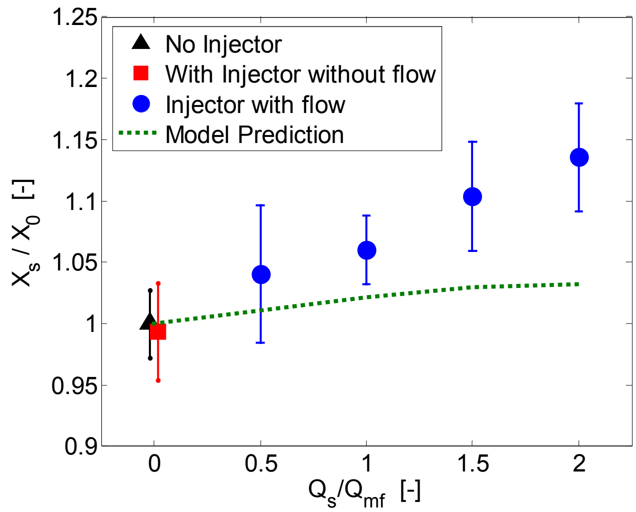

Figure 5: The relative change in conversion as a function of Q_s; $Q_0 = 4 \times Q_{mf}$. The model consistently underestimates the conversion. In the model, k = 0.29 $m^3_{gas}/(m^3_{catalyst} \cdot s)$. Error bars are 95% confidence intervals.

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NOTATION

A_0	Area of distributor plate per orifice, [m^2]
$C_{A,i}$	Concentration of reactant in phase *i*, [mol/m^3]
C_{A0}	Initial concentration of reactant, [mol/m^3]
d_b	Bubble diameter, [cm]
$d_{b,min}$	Minimum bubble diameter allowed, [cm]
f_i	Solids volume fraction for phase *i* (bubble, cloud, or emulsion), [m^3_{solid}/m^3_{bed}]
g	Acceleration due to gravity, 9.8 [m/s^2]
h	Current height in the bed, [m]
k	First-order reaction rate constant, [$m^3_{gas}/(m^3_{solid} \cdot s)$]
K_{bc}	Interchange rate coefficient between bubble and cloud, [$m^3_{gas} / (m^3_{bubble} \cdot s)$]

K_{ce} Interchange rate coefficient between cloud and emulsion, [m^3_{gas} / (m^3_{bubble}·s)]
Q_{mf} Minimum fluidisation volumetric flow rate, [m^3/s]
Q_0 Total volumetric flow rate, [m^3/s]
Q_p Primary volumetric flow rate that enters the bed via the windbox, [m^3/s]
Q_s Secondary volumetric flow rate that enters via the fractal injector, [m^3/s]
U_b Bubble rise velocity in a bubbling fluidised bed, [m/s]
U_{mf} Minimum fluidisation velocity, [m/s]
X_0 Conversion of the reactant without secondary gas injection, [-]
X_s Conversion of the reactant with secondary gas injection, [-]
Greek
β Bubble diameter reduction factor, [-]
δ Bubble fraction, [m^3 of bubble / m^3 of bed]

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