Distributed Secondary Gas Injection via a Fractal Injector

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A Nature-Inspired Approach to Improving Conversion in Fluidized Bed Reactors

Proefschrift

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Summary


The conversion in bubbling fluidized bed reactors is suppressed because the interphase mass transfer and gas-solid contact in bubbling fluidized bed reactors are often poor. Most of the gas is present in the form of bubbles, which have low surface-to-volume ratios and are nearly devoid of catalyst particles. The chaotic behaviour of the bubbles is difficult to predict and can change with reactor size, making scale-up very difficult. The work in this thesis presents a novel approach to overcoming these difficulties in bubbling fluidized beds.

Nature uses branching, fractal structures, which greatly facilitate mass transfer in natural systems, such as trees and lungs. These structures scale easily, which is a very important feature as the organism grows. This approach can also be applied to fluidized beds. A fractal injector was developed for both quasi 2-D and 3-D beds to distribute a portion of the total gas flow throughout the fluidized bed. To determine the effect of this distributed secondary gas injection on the properties of a gas-solid fluidized bed, the study is split into four topics: the effect on the hydrodynamics of the fluidized bed, the mechanisms leading to the observed changes in the hydrodynamics, the residence time and macroscopic mixing of the gas, and the influence on the performance of the reactor.

Experiments on both 2-D and 3-D systems were performed to determine the bubble size and behaviour to characterize the bubble phase hydrodynamics. This was accomplished with spectral decomposition of pressure fluctuation-time series as well as video analysis in the quasi 2-D bed. It was found that, in both cases, the bubble size decreases significantly with increasing secondary injection at a constant total flow rate. It was also discovered that even with constant primary flow rates and increasing secondary flow rates (and thus increasing total flow rates) most of the secondary gas does not contribute to the bubble phase. An analysis of the number of bubbles with height revealed that there are more bubbles present with secondary injection, but that these bubbles are smaller. This result is an indication that the bubble coalescence is being hindered and the bubble behaviour is being controlled. Since the bubble size is decreasing and the number of bubbles is increasing, it could be expected that the bubble fraction is increasing because the smaller bubbles rise with a lower velocity and stay in the bed longer. The opposite was found to be true, however; the bubble fraction actually decreases with secondary injection. It was concluded that the secondary gas tends
to help break up existing bubbles, prevent bubble formation, and hinder bubble coalescence by forcing more gas through the dense phase and imposing a dynamic structure on the hydrodynamics. This greatly improves gas-solid contact.

Computational fluid dynamics simulations of small fluidized beds with single injection points were used to gain insight into the mechanisms behind the reductions observed in both the bubble size and bubble fraction, and to study the influence of secondary injection on the properties of the dense phase. From these simulations it was determined that the bubbles tend to be smaller because there is less primary gas, and the secondary gas does not contribute to bubble growth. An analysis of the average dense phase porosity revealed that a greater amount of gas flows through the dense phase above the injection point, as evidenced by the increase in the dense phase porosity. This effect shows that the secondary gas stays in the dense phase and hinders bubble formation and growth. It was deduced that secondary injection breaks up particle clusters and gives particles more energy, resulting in the (partial) collapse of the bubbles and an increase in the expansion of the dense phase. Since more gas is present in the dense phase, there is less gas available for the bubble phase and the bubble fraction decreases. Most of the observed decrease in bed height is due to the decrease in the bubble phase volume. These results provide additional evidence for improved gas-solid contact.

The influence of distributed secondary gas on the residence time and macroscopic mixing of the gas was measured experimentally using a tracer pulse response. A methodology was developed that facilitated the interpretation of the experimental data. It was found that the average residence time of the gas tends to decrease with increasing secondary gas injection. This can partially be explained by the observed decrease in the bed height, which effectively makes the reactor volume smaller. Note that the gas-solid contact time is more important than the overall residence time for heterogeneous reactions. The decrease in residence time is small compared to the expected increase in contact time. The back-mixing of the gas in the reactor is also found to decrease. This increase in plug flow behaviour is beneficial for positive order reaction kinetics because it maintains a high concentration gradient in the reactant, which is the driving force for the reaction to proceed.

The preceding results indicate that the mass transfer and gas-solid contact in a bubbling fluidized bed are increasing. These outcomes imply that the conversion of a mass transfer-limited reaction should increase. Conversion experiments using ozone decomposition as a test reaction were carried out to directly measure the influence of distributed secondary gas injection on the performance of a bubbling fluidized bed reactor. The results of these experiments demonstrate that the conversion increases with secondary gas injection,
achieving the main goal of this project. A maximum was observed in the conversion results as a function of increasing secondary gas injection. At higher secondary gas velocities, the gas may be channelling, which could be responsible for the decrease in conversion via increased gas bypassing. We should expect that using wider injection outlets, or more of them, will prevent this effect. A simple two-phase model was developed to predict the outcome of the conversion experiments. The model did not include mechanisms for the increase in the dense phase porosity or the decrease in bubble fraction, which were observed in the experiments, because it was not known how these parameters change as a function of height in the presence of secondary injection. It was found that the model could adequately predict the experimental results only when an increased interaction between the phases is assumed via an increase in local micromixing around the injection levels. This model was applied to the production of maleic anhydride, which is a much more complex reaction scheme that includes consecutive and side reactions. The model predictions indicate that both the production and the yield of maleic anhydride increase with secondary injection. These results indicate that distributed secondary gas injection significantly enhances the performance, as measured by the conversion and selectivity, of industrially useful reactions. It is concluded that, although there are still challenges to be overcome, distributed secondary gas injection has great potential for application in industrial bubbling fluidized beds and may, in fact, increase the relevance of such reactors for new applications. Some aspects of applying this technology in industry are discussed.
Samenvatting


De conversie in een fluïde bed in het bellenregime wordt beperkt doordat de stofoverdracht en het contact tussen het gas en de deeltjes vaak slecht zijn. Het meeste gas is als bellen in de reactor aanwezig. Dit zorgt voor een kleine oppervlakte-volume verhouding. De bellen zijn arm aan katalysator deeltjes en het contact is dus slecht. De chaotische beweging van de bellen is moeilijk te voorspellen en hangt af van de afmetingen van de reactor. Dit maakt het opschalen van fluïde bedden erg moeilijk. In dit proefschrift wordt een nieuwe manier om deze problemen op te lossen voorgesteld.

De natuur maakt gebruik van vertakte fractale structuren, zoals bomen en longen, die zorgen voor een goede stofoverdracht en een hoge oppervlakte-volume verhouding. Het opschalen van dit soort structuren is makkelijk, wat belangrijk is als de boom of long groeit. Dit idee kan ook op fluïde bedden toegepast worden. Een fractale injector is ontwikkeld voor zowel 2-D als 3-D systemen om een deel van het totale gasdebiet op verschillende hoogtes in het bed te introduceren. Om het effect van deze secondaire gasinjectie op het gedrag van het fluïde bed te bepalen, richt deze studie zich op vier aspecten: het effect op de hydrodynamica, de mechanismen die zorgen voor dit effect, de verblijftijd en menging van het gas in de reactor, en de invloed op de conversie en selectiviteit van de reactor.

Om de grootte van de bellen en hun gedrag te bepalen zijn experimenten in 2-D en 3-D systemen uitgevoerd. Dit is door middel van spectral decomposition van drukfluctuaties en video analyse in het 2-D systeem gedaan. Uit de resultaten blijkt dat de belgrootte afneemt met hogere volumes van secondaire injectie bij gelijkblijvend totaal debiet. Uit experimenten met een constante primaire gasstroom en stijgende secondaire injectie bleek verder dat het secondaire gas niet in bestaande bellen terechtkomt. Een analyse van het aantal bellen als functie van de hoogte toonde dat er meer bellen waren, maar dat zij kleiner waren. Dit resultaat is een indicatie dat coalescentie van bellen gehinderd wordt. Men zou verwachten dat de fractie bellen stijgt, omdat de verblijftijd van kleinere bellen langer is. Dit gebeurt echter niet; de fractie van bellen neemt af met toenemende secondaire injectie. Daarom moet er minder gas in het totale belvolume aanwezig zijn. Dat betekent dat er dus meer gas in de dichte fase is. Hieruit wordt de conclusie getrokken dat de bellen door de secondaire injectie worden opgebroken, de vorming en coalescentie van bellen worden gehinderd, en dat meer gas door de dichte fase gestuwd wordt. Secondaire injectie creëert een soort
Om inzicht te krijgen in de mechanismen verantwoordelijk voor de boven genoemde effecten zijn computational fluid dynamics simulaties van kleine bedden met één injectie punt gedaan. Ook zijn simulaties gebruikt om het effect van secondaire injectie op de dichte fase te bepalen. De resultaten tonen dat de bellen kleiner zijn doordat er minder primair gas is en dat het secondaire gas niet aan de groei van bestaande bellen bijdraagt. Een analyse van de gemiddelde porositeit van de dichte fase toonde dat er meer gas in de dichte fase is boven het injectiepunt. Dit effect, samen met het feit dat er minder bellen boven het injectiepunt in deze kleine systemen zijn, betekent dat het secondaire gas in de dichte fase geïntroduceerd wordt en daar ook blijft en dat belvorming en groei worden gehinderd. Uit de simulatieresultaten is verder afgeleid dat clusters van deeltjes afgebroken worden en dat de deeltjes meer energie krijgen, wat zorgt voor kleinere bellen en meer gas in de dichte fase. De toegenomen hoeveelheid gas in de dichte fase heeft tot gevolg dat er minder gas beschikbaar is voor de bellen, waardoor de fractie bellen afneemt. De hoogte van het bed gaat omlaag, wat vooral veroorzaakt wordt door de afname van het totale volume van bellen. Deze resultaten geven dus meer aanwijzingen voor een verbeterd contact tussen het gas en de deeltjes.

De invloed van secondaire gasinjectie op de verblijftijd en de menging van het gas in een fluide bed is door middel van een tracer pulse response bestudeerd. Een methode is ontwikkeld om de interpretatie van de data te vergemakkelijken. Uit de resultaten blijkt dat de verblijftijd van het gas licht afneemt als de secondaire gasinjectie toeneemt. Een mogelijke verklaring voor dit fenomeen is dat de hoogte van het bed afneemt en het effectieve volume van de reactor dus minder is. De contacttijd tussen het gas en de deeltjes is belangrijker voor de effectiviteit van de reactor dan de verblijftijd voor heterogene reacties. De vermindering van de verblijftijd is klein in vergelijking met de toename van de contacttijd. De macro-menging van het gas neemt af. Dit is gunstig omdat de conversie in buisreactoren (zonder gasmenging) hoger is dan in gemengde reactoren. De gradiënt in de concentratie van de reactant is hoog in dit geval en dit is de drijvende kracht voor de reactie.

Bovengenoemde resultaten tonen dat de stofoverdracht en het contact tussen gas en deeltjes verbeterd worden met secondaire gasinjectie via een fractale injector. Dit impliceert dat de conversie in een fluide bed zal stijgen. Om dit te testen zijn experimenten uitgevoerd met ozondecompositie als testreactie. Uit de resultaten van die experimenten blijkt dat de conversie inderdaad stijgt wanneer de fractale injector in gebruik is. Deze stijging is groter dan het effect van alleen de structuur van de fractale injector. Het belangrijkste doel van dit
project is dus bereikt. In de trend van conversie tegen volume van secondaire gasinjectie is een maximum aanwezig. Bij hogere waarden van het secondaire gasdebit treedt mogelijk kanaalvorming op omdat de snelheid van het gas te hoog is. Het valt te verwachten dat dit fenomeen verdwijnt als de injectiepunten groter worden of als meer injectiepunten aanwezig zijn om de snelheid van het gas te verminderen. Een eenvoudig twee-fase model is ontwikkeld om de conversie te voorspellen. Dit model houdt geen rekening met de toename van de porositeit in de dichte fase of de afname van de belfractie, die tijdens de experimenten waargenomen zijn, omdat we geen informatie over die factoren als functie van de hoogte hebben. Het model kon de experimentele data alleen beschrijven wanneer een toegenomen interactie tussen de bellen en de dichte fase aangenomen wordt via een locale menging van het gas in de bellen en dat in de dichte fase ter hoogte van de injectiepunten. Dit model is toegepast op de productie van maleïnezuuranhydride, een relevante industriële reactie – een vrij complexe reactie waarbij ook nevenreacties en volgreacties optreden. De resultaten van het model tonen dat de conversie en selectiviteit van industriële reacties toenemen met hogere volumes van secondaire gasinjectie. Er kan worden geconcludeerd dat, hoewel er nog uitdagingen zijn om op te lossen, secondaire gasinjectie via een fractale injector een groot potentieel heeft in industriële fluide bedden in het bellenregime en dat de toepasbaarheid van dit reactor type zal stijgen. Verscheidene aspecten van industriële toepassing van een fractale injector zijn beschreven.
To my family
&
To Tamara
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Fluidized beds are very often used in the chemical industry. One of their biggest applications is in fluid catalytic cracking (FCC), whereby heavy oils are upgraded to lighter hydrocarbons to make such products as gasoline and diesel fuel. Nearly every refinery uses a fluidized bed somewhere. Fluidized beds are also used extensively in the production of bulk chemicals, polymers, coal and biomass gasification, as well as physical processes, such as drying and coating, particularly in the pharmaceutical industry. Fluidized beds have been in operation in industry for over 80 years and there exists a vast knowledge of heuristics and empirical correlations to describe the fundamentals of fluidized bed operation, yet still so little is understood about the fundamental physics that describe the behaviour of these multiphase reactors. There are many hydrodynamic regimes in which fluidized beds operate, and each has its own set of advantages and disadvantages. This work focuses on bubbling fluidized beds.

In gas-solid bubbling fluidized bed reactors the inter-phase mass transfer is often poor because most of the reactant gas in the reactor is in the form of bubbles. These bubbles are almost entirely devoid of catalyst particles, thus the reactant must transfer from the bubble into the surrounding dense phase before it can react. This extra step limits the gas-solid contact, which is of the utmost importance in heterogeneously catalyzed reactions, and leads to a lower conversion with respect to fixed bed reactors where this extra mass transfer resistance does not occur.

Bubbling fluidized beds also suffer from difficulties in scaling a laboratory- or pilot-scale reactor up to an industrial installation. These difficulties arise because the bubble behaviour, which plays a major role in the overall hydrodynamics of the system, is chaotic and scale-dependent. For example, two reactor columns operated at exactly the same conditions, but with one larger than the other, will exhibit different hydrodynamic behaviour because the bubble behaviour is different.

The poor gas-solid contact and difficult scale-up are the main reasons why bubbling fluidized beds have found relatively few applications in the chemical industry.
circulating fluidized beds are more often used because bubbles, *per se*, do not exist in these hydrodynamic regimes where the gas flow is much higher. There are large drawbacks of these regimes, however. Firstly, the contact time between gas and solid is very short because of the very high gas velocities. Secondly, attrition of the particles and wear of the equipment (reactor walls and internals such as heat exchanger tubes) is much worse than in bubbling fluidized beds because the particles travel faster and impact with much more force. Thirdly, it is much more difficult to keep fine particles, which contribute to the quality of the fluidization and the over performance of the reactor, in the process. Recycle streams or large reactors can be used to overcome the first problem, whereas additional maintenance is required to monitor wear, which increases operating and material costs, plus possibly requiring additional down-time. The use of series of cyclones is often required to capture the fines to return them to the bed, but these are also subject to wear. In this case, there is still some loss of particles because the cyclones are not 100% efficient.

If the bubbles that occur in a bubbling fluidized bed can be made smaller they will have a larger surface to volume ratio, which means better mass transfer to the dense phase and improved reactant-catalyst contact. By controlling the bubble behaviour the hydrodynamics become much less dependent on the system size. If bubble size and bubble behaviour can be made to be more controllable and predictable in bubbling fluidized beds then conversion and scalability would both increase. In controlling the bubble size, optimum conditions can be obtained such that the mass transfer is improved, while still meeting the particle mixing and heat transfer requirements of the process; these properties are typically enhanced by the presence of bubbles. With these improved characteristics, bubbling fluidized beds may become attractive for more applications, while also requiring smaller reactors, decreasing compressor costs, and reducing wear, since the gas flow rates are lower. This scenario could be considered a sort of process intensification and lead to a more sustainable process.

The work presented in this thesis describes how distributed secondary gas injection via a fractal injector can be used to reduce the bubble size and control the bubble behaviour in gas-solid bubbling fluidized beds. It will be shown that the gas-solid contact is greatly improved because of the reduction in bubble size and also because of a reduction of the total volume of gas in bubbles. This enhanced gas-solid contact leads directly to an increase in conversion of a mass transfer-limited heterogeneously catalyzed reaction. It is also shown that secondary gas injection can also lead to an increase in product selectivity, which, in systems with complicated reaction networks, is often more important than conversion. The distributed nature of the secondary gas injection is shown to impose a structure on the hydrodynamics, which hinders bubble coalescence and increases control over the bubble
behaviour. This increased control is promising in terms of improving the scalability of bubbling fluidized beds.

1.1. Outline of the Thesis

In this thesis the distributed secondary gas injection is discussed in four areas: the effects on the hydrodynamics, the mechanisms responsible for the change in hydrodynamic behaviour, the residence time and mixing of the gas, and the performance of the reactor. Each of these is described in a separate chapter.

Chapter 2 discusses the effect of distributed secondary gas on the bubble size and behaviour in a 2-D bubbling fluidized bed. It is shown that the bubble size decreases considerably with increasing secondary gas flow. Although the number of bubbles also increases, it is found that the total volume of gas present in the form of bubbles decreases. Bubble coalescence is also reduced, even well above the fractal injector, indicating that the bubble behaviour is being controlled. These results are discussed and it is argued that the gas-solid contact is improved.

Chapter 3 details the use of computational fluid dynamics (CFD) to determine the mechanism behind the reduction in bubble size and how this is linked to the dense phase hydrodynamics. It is shown that bubbles are smaller with secondary gas for several reasons, including the initial bubble volume is lower because there is less gas just above the distributor, and bubbles tend to be broken up by the secondary gas and re-absorbed by the dense phase. It is shown that the secondary gas tends to stay in the dense phase, causing the dense phase to expand and reducing the amount of gas available for the bubble phase and reducing the bubble fraction. It is concluded that, although the study uses very small simulation domains, the gas-solid contact is improved.

Chapter 4 considers the effect of gas injection via a fractal injector on the residence time and macroscopic mixing of the gas in a 2-D bubbling fluidized bed. The results of residence time distribution (RTD) experiments are discussed. It is found that, although a decrease in average residence time is not expected based on a simple model, the average residence time tends to decrease slightly with increasing secondary gas flow. Contact time is much more important than residence time in a heterogeneously catalyzed reaction, but the residence time can be considered the upper limit of contact time. Possible reasons for the decrease are discussed. The gas is also found to behave in a more plug flow-like fashion with secondary gas. This is a positive benefit because the decrease in back-mixing implies a stronger concentration gradient, which is the driving force for positive order reactions.
Chapter 5 discusses the effects of distributed secondary gas injection on both the hydrodynamics and performance in more realistic 3-D bubbling fluidized beds. Although there are significant physical differences between 2-D and 3-D reactors, the effects of secondary gas injection are shown to be qualitatively the same in both cases. The results of conversion experiments indicate that distributed secondary gas injection via a fractal injector increases the conversion significantly. A simple model based on two-phase theory is developed and applied to a more complex reaction, where it predicts that both the conversion and selectivity improve with secondary gas injection.

1.2. Background on Fluidization

Fluidized beds are very common in the chemical and process industries. In concept, fluidized beds are not so different from packed or fixed beds – only the gas flow is higher and there is space above the particle bed inside the reactor walls. In a fixed bed reactor the reactant gas percolates through a randomly packed bed of catalyst particles (Figure 1-1a). As the gas velocity is increased a critical point will be reached where the drag force exerted on the particles equals their weight. The particles then start to move around in the gas stream and the particle bed expands; the superficial gas velocity at this point is called the minimum fluidization velocity, $U_{mf}$. This hydrodynamic regime is known as incipient or minimum fluidization (Figure 1-1b). A further increase in gas velocity results in a change of the hydrodynamic regime, depending on the particle properties of size and density. Geldart [1] classified particles into different groups based on their size and density. For group A particles, a further increase in gas velocity causes the bed to homogeneously expand (Figure 1-1c), whereas with group B particles a further increase in velocity causes the formation of regions devoid of particles, called bubbles or voids, that rise through the bed (Figure 1-1d). Group A particle beds will also exhibit this behaviour but only when the gas velocity reaches a second critical point called the minimum bubbling velocity, $U_{mb}$. In group B, $U_{mb}$ equals $U_{mf}$. Increasing the gas velocity further may result in slugging behaviour depending on the aspect ratio of the column (Figure 1-1e & f) and eventually lead to a transition into the turbulent regime (Figure 1-1g) and on to pneumatic transport (Figure 1-1g), where all of the particles are simply blown out of the column.

The Geldart classification is shown in Figure 1-2. Group C powders are very small and cohesive. Strong interparticle forces dominate their behaviour and they are difficult to fluidize. Group D particles are very large and are known for their spouting behaviour. These particle types are not dealt with in this thesis. Group A and B particles are characterized by the drag force exerted by the gas flow being the dominant mechanism for particle motion and
behaviour, although interparticle forces still play an important role for group A. A and B particles are most often used in the chemical industry because of the ease and quality of their fluidization. Group A powders typically exhibit a maximum bubble size as they rise through reactor, whereas in group B particles do not. In the work presented in this thesis more focus is placed on group B because the effect of distributed secondary injection is expected to be larger than for group A. It will be shown, however, that considerable gains can be made even with the use of secondary gas injection with group A powders.

![Fluidization regimes](image)

**Figure 1-1: Fluidization regimes with increasing superficial gas velocity. Adapted from [2].**

Fluidized beds are often used in industry, despite their lower conversions compared to fixed beds, because they have excellent heat transfer and pressure drop properties. Both of these effects are related to the particle mobility in fluidized beds that does not exist in a fixed bed. The excellent heat transfer makes fluidized beds ideal for use with highly exothermic reactions to have temperature uniformity and to avoid hot-spot formation, which can cause runaway behaviour or decrease the lifetime of the catalyst. The low pressure drop characteristics mean that much smaller catalyst particles can be used than in a fixed bed, which effectively eliminates internal mass transfer resistances and increases the effectiveness factor of the catalyst. The solids mobility also makes solids handling much easier and allows
catalyst replacement on-line. This property means that a fluidized bed reactor can operate continuously even in situations where a fixed bed reactor would have to be shut down to replace the catalyst inventory.

![Geldart classification of particles based on their density and diameter. Adapted from [2].](image)

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1.3. Bubbling Fluidization

The focus of this project is on improving the performance of bubbling fluidized bed reactors and, as such, an important question is why bubbles form in the first place. It has been postulated that the fluidization will remain homogeneous until the gas velocity is increased to a critical point; each incremental increase in gas up to this critical point causes the dense phase to expand a little bit more to allow the extra gas through [3]. After the critical point,
all extra gas will form bubbles because the dense phase cannot expand further and keep all of the particles at their terminal velocities. It has been surmised that this inability to expand further is related to the gas flow around the particles or interparticle forces. A second theory states that bubbles form because of energy dissipation caused by inelastic collisions between the particles [4,5]. The particles lose energy and tend to cluster together, which causes voids to form between clusters. These void spaces then propagate into bubbles. In a certain sense these two theories are similar. The dense phase cannot expand beyond the critical velocity because the tendency for the particles to cluster is too strong due to the increased dissipation during the collisions of faster particles. One approach to reduce the bubble size and prevent bubble formation is to break up these particle clusters by giving the particles more energy. One way to achieve this injection of energy is in using distributed secondary gas injection via a fractal injector.

1.4. Distributed Secondary Gas Injection via a Fractal Injector

Bubbles are a hindrance to mass transfer in gas-solid fluidized beds. Very few catalyst particles are contained within them so the reactant gas must transfer into the dense phase. The surface area of the bubble limits the mass transfer because it does not increase at the same rate as the bubble volume, i.e., the surface to volume ratio decreases as bubbles grow. This limitation results in low mass transfer rates and poor gas-solid contact. Nature has solved similar mass transfer problems, for example, in lungs and trees where high mass transfer rates are required to sustain life (Figure 1-3a). These organisms achieve high rates of mass transfer by using hierarchical branching structures that are highly scalable. This concept inspired the idea for the fractal injector (Figure 1-3b), which is to distribute a portion of the total feed gas into the reactor in a distributed way to improve the gas-solid contact and increase the mass transfer by using an internal device that is inherently scalable [6]. The fractal structure has two benefits, the first is the scalability, and the second is the need for only one additional flow of gas aside from the primary gas entering the reactor though the windbox. This flow is then split evenly to each injection tip. The uniformity of flow through the fractal injector is made possible by the fact that the path length to each injection point on the fractal is exactly the same. In the absence of a significant change in static pressure, the flow rates of gas through each injection point will be exactly the same. In larger-scale reactors, the change in the static pressure will be significant, so the pressure drop over the injection tips will have to be much larger than the static pressure different to ensure an even distribution of the secondary gas through the injector. A higher pressure drop over the tips was included in the design and construction of the 3-D injector used in this work. This was achieved by attaching porous metal disks to the injection points. The pore size in the disks determines the magnitude of the pressure drop and can be tailored to the desired secondary
flow rates. This design also prevented particles from blocking the outlets, thus maintaining flow uniformity. For the 2-D injector, this design was not required because there are far fewer outlets. This means that the flow rate and pressure drop through each tip are considerably higher. Coupled with the small static pressure difference due to the small scale, the 2-D design was sufficient to ensure uniform flow without additional components.

![Figure 1-3: (a) a lung with the hierarchical structure of the bronchus, bronchi, and bronchioles, adapted from [7]; (b) a photograph of a 3-D fractal injector prototype](image)

The fractal injector used in the 2-D portions of this study is based on an 'H'-shaped repeating unit, see Chapter 2 for a schematic. It also has a fractal dimension of two, which is for reasons of simplicity. This value implies that if the fractal were grown infinitely (by adding an infinite number of generations), the structure would be area-filling, which is not desirable from a reactor point-of-view, but (quasi-) 2-D reactors have no application in industry. This structure is used because of its simplicity. The injector used in the 3-D experiments is based on three half-'H's, i.e., an 'H' split vertically in half. The three halves are joined at the horizontal tube and placed 120° apart. This structure is shown in Figure 1-3b. This structure is only 2.6-dimensional, which means that it will not fill the reactor volume as the number of generations approaches infinity. This fact is important because, as a reactor is scaled-up, the injector will never exceed a particular volume fraction. This means lower material costs, as well as leaving sufficient space for the bed mass. The fractal injectors used in this work used approximately 1.7% and 6.5% of the reactor volume for the quasi-2-D and 3-D reactors, respectively. It should be noted that the fractal structures used in this work are only first designs; no structural optimizations have been performed. Indeed, it is one of the purposes of this work to lay the foundation of knowledge that will allow future optimization of the
structure. This optimum configuration is very likely going to depend on the reaction as well as the shape of the fluidized bed column in which the fractal injector is to be applied.

1.5. Notation

- $U_{mf}$: Minimum fluidization velocity, [m/s]
- $U_{mb}$: Minimum bubbling velocity, [m/s]
- $\rho_g$: Gas density, [g/cm$^3$]
- $\rho_s$: Solids density, [g/cm$^3$]
- $d_p$: Particle diameter, [μm]

1.6. References

2. The Influence of Secondary Gas Injection on the Hydrodynamics

In the quest to improve the conversion in gas-solid bubbling fluidized beds it is best to quantitatively determine if a new technique can reduce the bottleneck that is causing the poor performance. In other words, does distributed secondary gas injection reduce the size of the bubbles in a bubbling fluidized bed? This chapter answers this question and further discusses the effect of secondary injection on the hydrodynamics in the fluidized bed. Written in co-operation with Dr. Kleijn van Willigen, this work studies the effects of both secondary gas injection and, separately, electric field-enhanced fluidization, two techniques that have shown promise in imposing dynamic structures on fluidized beds.

This work presents results of bubble size measurements in quasi 2-D fluidized beds of glass beads using both spectral decomposition of pressure fluctuations and video analysis. The outcome of this study is that both techniques reduce the bubble size significantly, with distributed secondary effect having a greater effect at higher gas velocities. The number of bubbles is also determined as a function of height and found to increase, which implies that, since the bubbles are also smaller, bubble coalescence is being hindered. The bubble fraction was calculated based on the video analysis and was found to decrease, despite the fact that an increase in the number of small bubbles should increase the bubble fraction. It was concluded that the difference in the volume of the bubble phase must be taken up by the dense phase. These results imply that the mass transfer is improving because of the smaller bubbles, while the gas-solid is also being directly improved through an increased gas flow through the dense phase.

This chapter was previously published as:

2.1. Abstract

Structuring fluidized beds can increase the conversion and selectivity, and facilitate control and scale-up. Two methods for introducing a dynamic structure into gas-solid fluidized beds are compared based on their overall hydrodynamics: electric field enhanced fluidization and distributed secondary gas injection by a fractal injector. It is shown that, under various conditions, these systems lead to significant decreases in bubble size and bubble hold-up and to an increase in the number of bubbles. It was found that the electric field enhancement can lead to homogeneous fluidization at lower flow rates, and the distributed secondary flow leads to smaller bubbles at higher flow rates.

2.2. Introduction

Two common reactor types for heterogeneously catalyzed gas phase reactions are the packed bed and the fluidized bed. Fluidized beds couple short intraparticle diffusion lengths to good heat transfer, but suffer from chaotic bubble behaviour [1], leading to back-mixing, fluid bypassing, and particle-fluid separation problems [2]. Packed beds show much less back-mixing and have virtually no catalyst attrition and separation problems, but have longer diffusion lengths that can only be overcome by an unacceptably large pressure drop. Moreover, they are sensitive to flow maldistribution that can lead to problems such as poor catalyst contact, hot-spot formation and runaway behaviour [3]. In the past few years, much effort has been devoted to the development of reactors in which the catalyst material is present in a static, structured way, e.g., monolith and Katapak® reactors [4]. However, for reactions with large heat production and/or fast catalyst deactivation, it is often advantageous to use a mobile catalyst [2]. In these cases, fluidized beds are preferred, despite the disadvantages of chaotic bubble behaviour and the difficulty of scaling fluidized beds from lab-scale to pilot- and industrial-scale. Just as for packed bed reactors, the structuring of fluidized beds is interesting from the point of view of process intensification, to facilitate scale-up and control, and to improve performance.

In this paper, we will show that it is possible to manipulate the hydrodynamic structure of fluidized-bed reactors, thereby increasing the number of degrees of freedom for the designer and helping to intensify the process. This is achieved by manipulating the interparticle forces and particle-fluid interactions to obtain the desired fluidization behaviour for a given application. Two methods of structuring gas-solids fluidized beds are presented and compared: imposing an electric field and secondary injection of gas. By using these non-conventional ‘active’ internals, we introduce a dynamic structure into the fluidized bed, leading to better control over the hydrodynamics of the system (especially the bubbles). The
contact of the gas in bubbles with the solid catalyst particles is often poor, and when the
catalyst itself is sufficiently active, the mass-transfer from bubble to emulsion is the rate-
limiting step. Therefore, our goal is to control the bubble behaviour and decrease the
average bubble size in a structured manner. A decrease of the bubble diameter by a factor
four can increase the conversion in a fluidized bed as much as 2.5 times, and is therefore well
worth investigating [5, 6].

Three cases are discussed and compared: the base case of a column with no active internals,
a column using electric field enhanced fluidization (EF), and a column with secondary gas
injection by a fractal injector (FI). Using both pressure fluctuation analysis and video analysis
of the quasi 2-D column, we attempt to discern the effect of these improvements on the
hydrodynamics and bubble behaviour of bubbling fluidized beds.

Electric Field Enhanced Fluidization (EF)

One method to reduce bubble size is the application of an AC electric field to a fluidized bed
of semi-insulating particles. In the presence of a relatively low intensity electric field, the
particles (i.e., glass particles) become polarized, leading to attractive or repulsive forces.

The degree of polarisation, \( P \), of particles with a diameter \( d_p \) in a fluidized bed dictates the
magnitude of the interparticle forces, and is a function of the electrical conductivity, \( \sigma_e \) and
the dielectric constants of particle and continuous phase (\( \varepsilon_p \) and \( \varepsilon_c \)), as well as the electric
field strength, \( E_0 \).

\[
P = f(d_p^3, \varepsilon_p, \varepsilon_c, \sigma_e(RH), E_0)
\]  

(2.1)

The conductivity of the system is strongly influenced by the relative humidity, RH, of the
fluidizing gas.

The influence of small variations in interparticle forces on fluidization behaviour has been
shown both experimentally (e.g., liquid bridges [7], magnetic forces [8], electric polarisation
forces (e.g., [9, 10]), and in discrete element models (e.g., [11]). The electrical forces thus
induced by the electric field should be large enough to decrease the formation and growth of
bubbles, but small enough to allow the free movement of particles, i.e., the fluidity of the
system must be preserved. The oscillation of the AC fields has the advantage over constant
(DC) electric fields that fixation of particles or defluidization is unlikely.
In practice, the electric fields are introduced in the bed by stringing thin wires through the column (cf. Figure 2-1a), and alternately, both horizontally and vertically, driving these with an AC potential or grounding them. This creates a strongly inhomogeneous field in both the horizontal and vertical directions in the column.

![Figure 2-1: Two ways of structuring gas-solids fluidized beds with active internals: (a) imposing an AC electric field and (b) secondary (fractal) injection of gas (Cheng et al. 2001).](image)

Secondary Injection of Gas using a Fractal Injector (FI)

The number of degrees of freedom available to optimize the fluidized bed hydrodynamics increases when part of the gas is injected at various other locations inside the bed rather than only feeding the gas via the bottom [12]. This is possible as long as enough “primary” gas ($Q_p$) is injected from the bottom in order to maintain fluidization ($Q_p > Q_{mf}$), while an injector distributes the remaining “secondary” gas ($Q_s$) into the bed. This way, the amounts of gas distributed over the reactor space can be optimally dosed to control both hydrodynamics and reactor performance. Rising gas, depleted of reactants, is continuously replenished with fresh feed. Simultaneously, the bubble size can be controlled, as less primary gas (fraction of primary gas to total gas flow, $Q_p/Q_0$) leads to smaller bubbles initially, while fresh feed blown into the reactor at various locations (fraction $Q_s/Q_0$) tends to break up existing bubbles or blow particles apart, leading to an emulsion phase of higher void fraction. Unstable emulsions take time to break up into equilibrated phases, and it is this delay that is exploited. The effects of using secondary gas injection are: increased gas-solid contact due to a higher-than-usual emulsion phase void fraction; smaller, more slowly rising bubbles; and the ability to increase yields and selectivities of chemical processes by a distributed feed. In principle, each injection point could be fed by a separate tube, but it is more useful and practical to connect all injection points by a hierarchical, tree-like fractal structure (cf. Figure 2-1b). This gives intrinsic scalability and ensures a uniform access to the smallest branch tips – the outlets. The optimal fractal injector design will depend on the application.

In this paper, we will compare the application of electric fields to the fractal injection of secondary feed, as well as to the baseline cases of a column with inactive internals and a
column without internals altogether. The advantages and disadvantages of these two methods of structuring fluidized beds on the hydrodynamics and mass transfer of these systems will be discussed.

2.3. Experimental

Both columns (EF and FI) were built as similar as possible. By removing the fractal injector from its column, measurements could be conducted in a column without internals. The two quasi-2D Plexiglas columns, 20 cm × 1.5 cm × 80 cm, were fitted with 5 piezo-electric pressure transducers, Kistler type 7261, at 1, 10, 20, and 30 cm above the sintered metal porous distributor, and in the plenum [13]. The pressure drop was measured over the lowest 20 cm of the columns with a Validyne DP15-28. A data acquisition system (LMS-Difa) recorded all measurements at 200 Hz and provided outputs to control the mass flow controllers. The relative humidity (RH) at 1 atm of the fluidizing air was controlled at either 2% or 40% at 30ºC. Baseline measurements were conducted in the column without internals and in the columns with internals but with those internals inactive. The higher RH allowed for enough static charge dissipation that particles did not stick to the walls. The mono-disperse glass beads, \( d_p = 550 \mu m \) with a density of 2400 kg/m\(^3\) (Geldart B), were dried in an oven before use, and fluidized at least overnight when the RH was set to 40% before measurements were conducted. The settled bed height was 40 cm. The columns were operated within a cabinet controlled at 30ºC. A digital video camera (25 fps, 576 × 720 pixels) was set up with a viewing window on the column covering an area that spanned from 10 to 40 cm above the distributor. This viewing window was below the bed surface to prevent blinding of the camera by the backlight behind the column.

Electric Field Enhanced Fluidized Bed (EF) Set-up

The lower 20 cm of the column were fitted with thin wire electrodes. The wires were threaded through the front and rear of the column at a vertical pitch of 1.25 cm and a horizontal pitch of 2.2 cm. In the horizontal plane, they were threaded diagonally relative to the column walls, so that the nodes of highest field strength are in the centre of the column. The wires were alternately grounded and driven at a potential. The porous metal distributor was also grounded. Frequencies ranging from 1 to 160 Hz (sine wave) and maximum field strengths from 2.4 to 7.2 kV/cm were applied using a Trek 20/20c high voltage amplifier. The LMS-Difa DAQ, besides recording all measurements, served as the signal generator. At least 51200 data points (4.26 min) were measured at every combination of flow rate, field strength, and field frequency. At all the measured field frequencies, a measurement series consisted of a baseline measurement (0 kV applied potential), the range of field strengths,
The Influence of Secondary Gas Injection on the Hydrodynamics

followed by a second base measurement. The superficial velocities, as multiples of the minimum fluidization velocity, ranged from 1.5 to 3.5 × \( U_{mf} \) in increments of 0.5 × \( U_{mf} \).

**Fractal Injector Fluidized Bed (FI) Set-up**

A fractal injector, consisting of 16 uniformly spaced injection points, was constructed from 3 and 6 mm stainless steel tubing and brass connections. Excluding the main feed stem, the fractal injector had the dimensions: 15.6 cm wide by 7.4 cm high, and was centrally positioned in the column at a height of 10 cm above the distributor plate. The highest row of injection points is at approximately 14 cm, and the lowest row at approximately 6 cm. Therefore, the maximum bed height in contact with the fractal injector is somewhat less (~6 cm) than the EF column. The air fed through the fractal injector is heated but not humidified due to equipment limitations. It is not possible to add enough extra humidity to the primary airflow to make up for this difference and, thus, the humidity of the primary flow was maintained at its normal level (i.e., either the dry plant air or the 40% RH humidified air, depending on the experiment). As a result, the experiments with increasing secondary flow rate unavoidably had decreasing levels of humidity, but never to a level that particle adhesion to the walls or the injector was visible. Experiments were conducted with varying \( Q_s/Q_p \) ratios. The total superficial velocities (and therefore flow rates) ranged from 1.5 to 3.5 × \( U_{mf} \) in increments of 0.5 × \( U_{mf} \). At every total flow rate \( (Q_s+Q_p) \) corresponding to a superficial velocity higher than 1.5 × \( U_{mf} \), \( Q_s \) was increased in steps corresponding to 0.5 × \( U_{mf} \) but always with a minimum \( Q_p \) corresponding to 1.5 × \( U_{mf} \). At least 204,000 data points (17 min) were measured at every combination of flow rates. Each set of flow conditions always contained a baseline experiment with no secondary flow.

**Data Analysis**

The analysis of pressure fluctuations is an attractive method to characterize the hydrodynamic behaviour of fluidized beds because the fluctuations are closely associated with properties of the bubbles. Using the pressure probes described earlier, time-series of pressure fluctuations were measured at various heights in the column. A technique proposed by van der Schaaf et al. [13] was used to decompose the time series into a variance of the pressure time series that is associated with the size of bubbles passing the probe (the incoherent variance, \( \sigma_{IOP}^2 \)) and a variance associated with other processes such as the formation, eruption, and coalescence of bubbles (the coherent variance). For more details the reader is referred to [13]. This method requires measurement of pressure fluctuations in the plenum in addition to the height under consideration. The incoherent variance has been shown to be a good quantitative descriptor of the average bubble size at a certain height in a
The influence of secondary gas injection on the hydrodynamics of a fluidized bed, although a calibration of this value (for example, using video analysis or optical probes) is required to determine absolute bubble sizes [10]. The measure of bubble size (defined as frontal area of the bubble – and, thus, volume for a fixed thickness of the column) derived from pressure fluctuations is theoretically determined by the vertical dimension of the bubble and averaged over long time spans. It does not give information about the total bubble hold-up, or about the number of bubbles. In this study, we are interested in the reduction of average bubble size due to the electric field or fractal injector, and therefore, only consider the ratio of the $\sigma_{IOP}^2$ in the EF or FI system to the $\sigma_{IOP}^2$ at normal conditions (baseline with inactive internals).

The second analysis method employed for this comparative study is the use of digital video images. Although not applicable to long experiments (typically only measurements of a few minutes can be properly analysed because of the processing time), video analysis cannot only distinguish the changes in bubble size, like pressure fluctuation analysis, but can also distinguish the changes in the bubble frequency, which pressure fluctuation analysis cannot. The bubble hold-up can also be determined from video analysis. The video analysis was used as a complementary measurement method only for those settings considered most interesting (i.e., the largest positive influence on the bubble size) based on the pressure fluctuation analysis.

Video analysis over the bed height stretching from 10 to 40 cm was performed for a series of experiments over all flow rates with the most optimal electric field frequency and strength for the EF set-up and the most optimal primary/secondary flow ratio for the FI set-up. For every experiment, 3000 frames (2 min) were recorded. The analysis was carried out in Matlab™, and consisted of filtering out the background image and the fractal injector stem, then filtering with a median filter and thresholding. The post-processing allows determination of the average bubble size, the bubble frequency, and the bubble hold-up as functions of height.

In this study, the bubble size is defined as the area of the face of the bubble in the pseudo-2D column, which implies that bubbles in these columns are essentially voids stretching directly from the front to the back.

2.4. Results

Minimum Fluidization

The minimum fluidization velocity was determined for all set-ups (column without internals, column with wires, column with fractal injector) using pressure drop measurements at both
The Influence of Secondary Gas Injection on the Hydrodynamics

low and elevated RH. The minimum fluidization velocity determined at low RH with the fractal injector present deviated significantly because of adhesion of particles to the walls and the injector due to static charges. For the other cases, the values for $u_{mf}$ were reproducible and found to be $u_{mf} = 21 \pm 1$ cm/s. The column without internals and the column with wires at low RH were less susceptible to particle clinging, perhaps because of small variations in (adsorbed) moisture or age of the particles (attrition), and, therefore, have a more stable minimum fluidization velocity.

**Pressure Fluctuation Analysis**

The pressure fluctuation analysis method was used to find the most optimal strength and frequency of the electric field and the optimal $Q/Q_p$ ratio for the fractal injector for the conditions studied. For the EF system, the ratio of the average bubble size under the influence of various strengths to the base case was studied at superficial velocities of 1.5 to $3.5 \times u_{mf}$. The change in bubble size was determined at 20 and 30 cm above the distributor over the whole range of electric field strengths and frequencies, both for the low and elevated relative humidity. Fig. 2 shows the ratio of the bubble size as a function of field strength and frequency to the mean of the base measurements at 20 cm before and after the electric field was switched on. As expected, low field intensities (i.e., less than 4 kV/cm) lead to virtually no change in average bubble size, but at higher field strengths the change in bubble size is very significant.

It has been predicted that the interparticle force increases significantly as the RH increases [10,14]. As stronger interparticle forces lead to a larger decrease in bubble size, we therefore expect that at a higher RH the bubble size ratio becomes smaller. This is confirmed in the right-hand column of Figure 2-2, where the bubble size at, for example, $3.5 \times u_{mf}$ is decreased by 39% at 20 cm, compared to 28% for the low RH experiment. As the field strength increases, the effect on bubble size also increases, but a dependence on the field frequency is also seen. Especially at the higher RH, lower frequencies lead to larger bubble size decrease, but one must be careful not to defluidize – DC or very low frequency AC fields may gridlock the particles. With increasing flow rate, the net effect of the electric fields becomes smaller, and the effect wanes above the electrified region. The optimal electric field frequency was chosen at 10 Hz on the basis of the data presented in Figure 2-2, although the results at 5 Hz were slightly better. This was done because low frequencies may lead to particle agglomeration, and the difference in EF efficiency between 5 and 10 Hz was small enough to warrant the choice for higher frequency. The results at optimal frequency and field strength (7.2 kV/cm) are summarized in Table 2-1.
Figure 2-2: Ratio of bubble size with applied electric field and without field, as determined by pressure fluctuation analysis at 20 cm above the distributor. (a) 2% RH and (b) 40% RH. The flow rate increases from top (1.5 \times u_{mf}) to bottom (3.5 \times u_{mf}). Each subplot shows the bubble reduction ratio (cf. the colour scale) as a function of field strength (linear scale) and frequency (logarithmic scale).

The pressure fluctuation analysis was also used to estimate the changes in average bubble size in the FI system. This was done at bed heights of 20 and 30 cm over the full range of total flow rates and \( Q_d/Q_P \) ratios at both humidity levels.

Figure 2-3 shows the effect of increasing the \( Q_d/Q_P \) ratio at the various total flow rates. It is apparent from the graph that at any total flow rate the bubble size based on incoherent variance decreases with increasing \( Q_d/Q_P \) ratio. This trend is consistent at both bed heights, but is slightly less pronounced at the higher height due to bubble coalescence, i.e. the effect of the secondary injection is beginning to wane as the bed tries to return to its equilibrium state. The largest change in bubble size (represented by lower numbers in Table 2-1 and Figure 2–3) always occurs at the highest secondary flow rates and also at the highest total flow rates.

Due to the inconsistent humidity levels, as was mentioned earlier, the effect of moisture could not be determined quantitatively. When the secondary flow stream was at its highest, the lowest RH of the combined stream (when humidified) was 17%, compared to 2% for the dry case. However, it will be shown later on the basis of bubble hold-up that there is some
influence on the results that is attributed to the relative humidity and how the RH is controlled.

Table 2-1: Ratios of bubble size with most optimal EF and FI to bubble size with passive internals, as determined by pressure fluctuation analysis ($\sigma_{IOP}^2$).

<table>
<thead>
<tr>
<th>Superficial velocity [ $\times u_{mf}$]</th>
<th>EF optimal frequency</th>
<th>$\sigma_{IOP}^2$ ratio (30 cm)</th>
<th>$\sigma_{IOP}^2$ ratio (20 cm)</th>
<th>FI optimal $Q_f/Q_p$ ratio</th>
<th>$\sigma_{IOP}^2$ ratio (30 cm)</th>
<th>$\sigma_{IOP}^2$ ratio (20 cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>5 Hz</td>
<td>.24</td>
<td>.08</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>2.0</td>
<td>5 Hz</td>
<td>.63</td>
<td>.43</td>
<td>0.5/1.5</td>
<td>0.73</td>
<td>0.49</td>
</tr>
<tr>
<td>2.5</td>
<td>10 Hz</td>
<td>.68</td>
<td>.57</td>
<td>1.0/1.5</td>
<td>0.71</td>
<td>0.42</td>
</tr>
<tr>
<td>3.0</td>
<td>5 Hz</td>
<td>.69</td>
<td>.59</td>
<td>1.5/1.5</td>
<td>0.62</td>
<td>0.36</td>
</tr>
<tr>
<td>3.5</td>
<td>5 Hz</td>
<td>.76</td>
<td>.61</td>
<td>2.0/1.5</td>
<td>0.51</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Figure 2-3: Effect of increasing the ratio of secondary to primary flow on the incoherent variance, when using the set-up with fractal injector, as a function of total flow rate. The $\sigma_{IOP}^2$ are a measure for bubble size based on pressure fluctuation analysis and are reported here in simplified arbitrary units. Measurements carried out at 40% RH.

Video Analysis

Video analysis was used to determine average bubble size, frequency, and hold-up in the EF and FI systems at the most optimal settings, over the full range of flow rates. This was done at 40% RH. Figure 2-4 shows the ratios of average bubble size and the bubble frequency as
a function of height for the EF system. As already shown by the pressure fluctuation analysis, the ratio of bubble size with and without electric field decreases, and this is most prominent in the electrified region. In the region above the electrodes, the bubble size at low flow rates stays low, but at higher flow rates, bubbles grow quickly. Nevertheless, within the electrified region, the bubble size is 10-60% smaller and up to 35% smaller above the wires.

The effect of the electric field on the bubble frequency is shown in Figure 2-4b, again as a ratio of bubble frequency with and without applied field. At low flow rates, the bubble frequency within the electrified region is decreased significantly. This is because bubbles are either non-existent or are too small to be detected by the video camera. There is also an oscillation in the bubble frequency due to the direct effect of the field on the bubbles. The number of bubbles in the region above the electrodes is increased by 10-70%, depending on flow rate. The emulsion phase can no longer contain as much gas as it is forced to in the electrified region, and thus many small bubbles are formed. As visually observed during experiments and confirmed by the lack of bubbles, at the lower flow rates almost homogeneous fluidization is achieved in the electrified region.

The video analysis results for each total flow rate using the best $Q_g/Q_p$ ratios in the FI system are shown in Figure 2-5. Above the internals, it is apparent that the bubble size is smaller and the bubble frequency higher, when compared to the baselines. Just as for the pressure signal analysis, the bubble size ratio decreases with increasing flow rate, while the number of bubbles increases with increasing flow rate. This means that the FI system is more efficient at higher flow rates. Bubble size reductions are all in the range of 15-55% when measured at the same heights as in the pressure signal analysis. The bubble size ratios increase slightly with increasing height due to bubble coalescence while the system tries to return to its equilibrium state. This is corroborated by the slight decrease in bubble frequency over the same region. The fact that the bubble frequency ratio never returns to unity implies that bubble coalescence is delayed by the use of the fractal injector and that a maximum bubble size is not reached (as is expected with Geldart B particles). Results within the region containing the fractal injector are difficult to interpret, as the total gas throughput is changing in this region.
2.5. Discussion and Comparison

Both of the systems presented here were designed to improve bubbling fluidized bed efficiency and both are inherently scalable. In the design of both internals, however, there is much room for optimization: the spatial distribution of injection points for the fractal injector, and the electrodes in the EF system for highest average field density, as well as an extension of the electrodes to the whole bed height. It should be noted, however, that the introduction of internals into a fluidised bed can be problematic due to attrition. The lifetime of the wires of the EF column is obviously lower than the sturdier fractal injector design, but, on the other hand, the volume density of the wires is much lower than the volume the fractal injector occupies (EF: 0.008%, FI: 1.67%). In addition, the electric field may be introduced using (adaptations of) existing internals or electrodes that are more robust.

Figure 2-6 compares the average bubble sizes determined by pressure fluctuation analysis for all different systems: a column without any internals, a column fitted with electrodes, and a column fitted with the fractal injector. Data are compared with both passive and active internals, at elevated RH. The base lines at 30 cm are not significantly different. At 20 cm,
The influence of the (passive) fractal injector breaking up bubbles is seen to be significant, causing an estimated 12% bubble size reduction at the highest flow rate. The influence of the wires on bubble behaviour in the EF system is not discernable. When active, both systems are able to reduce bubble size considerably, as already shown in Table 2-1. The EF system is more effective at the lower flow rates; the FI system gives a larger bubble size reduction at the higher flow rates.

At this point it is most interesting to compare the bubble hold-up of both systems because of the large influence on the effectiveness of the system. A larger amount of gas in the bubble phase means less contact between catalyst particles and gas, usually reducing conversion. Conversely, when the average bubble size decreases, and the average number of bubbles in the system increases, an equal or lower bubble hold-up means an increase in the emulsion phase flow (as larger bubbles rise more quickly than small ones, which leads to a lower hold-up). The changes in bubble hold-up of the EF and FI systems are compared in Figure 2-7. It is again clear that the EF system is most efficient within the electrified region, leading to a large decrease in bubble hold-up in the lower 20 cm of the column, especially at low flow rates. The bubble hold-up in the same region in the FI column appears to decrease the most...
at *high* flow rates (large secondary flow), but this is because the total flow at this point is much lower than the reference situation, in which the total flow is all primary flow.

![Graph showing mean $\sigma_{IOP}$ at 30 cm vs. total superficial velocity](image)

In the region of 20 to 30 cm above the distributor, the influence of the electric fields quickly decays - the bubble hold-up is 90-100% of the baseline values, with some overshoot at the highest flow rate. However, the FI appears to maintain its effect by keeping the bubble hold-up to 80-90% of the baseline values. This difference in bubble hold-up is high, and the increase in emulsion flow may contribute only part of the decrease. A more detailed study of the influence of the changes in RH on bubble size, and a better experimental control of RH, are required to get a more accurate measure of the increase in emulsion flow. In all, the results of the bubble hold-up analysis show that the height to which the EF or FI internals extend may be optimized for the desired decrease in hold-up.
The Influence of Secondary Gas Injection on the Hydrodynamics

Figure 2-7. Comparison of the improvement in bubble hold-up in the EF (left) and FI (right) systems. The vertical lines indicate the top of the internals. The EF and FI internals both decrease bubble hold-up and increase emulsion phase flow. The electric field has only limited influence on the region above the electrodes, while the FI shows a longer lasting effect. A decrease in bubble hold-up, combined with more and smaller (slower travelling) bubbles, implies an increase in emulsion phase flow.

At first thought, one may expect the mean residence time of gas in the FI column to be shorter than the baseline case because a portion of the gas is injected higher in the column. However, this is not necessarily the case. In fact, it is expected that the mean residence time will either remain unchanged or only decrease slightly [12,15]. Even if there is a slight decrease in residence time, it is mitigated by the improved gas-solid contact resulting from the injection of gas directly into the emulsion phase, the increased driving force for mass transfer between the bubble and emulsion phases, and the increased fraction of gas in the emulsion phase. In the EF system, the reduction of bubble size and increased flow in the emulsion phase are expected to result in an increased residence time. Detailed residence time distribution measurements will be measured in future work. In both systems, the amount of back-mixing is expected to decrease, leading to more plug flow-like behaviour. Since the mass transfer from the bubble to the emulsion phase is typically the rate-limiting step in chemical conversions, it will depend on the rate of mass transfer and the rate of reaction how the combination of changes in residence times and bubble sizes will affect the conversion and selectivity of the system using the electric field enhanced fluidized bed or the distributed secondary gas injection system.
2.6. Conclusions

Both the electric field enhanced fluidized bed and the column with distributed secondary injection by using a fractal injector have been demonstrated to redistribute gas to smaller bubbles and to the emulsion phase. Both systems lead to an increase in particle-gas contact but differ in the mechanism by which this is achieved. In the comparison between electric fields and secondary injection, we find that the reduction of bubble size by the fractal injector is larger at higher flow rates, while the electric fields can force homogeneous fluidization at lower flow rates. Based on the smaller bubble size, the introduction of dynamic structures by both systems is expected to yield significant increases in conversion and selectivity. However, their different influences on the residence time distributions mean that the optimum choice will differ from application to application. It remains for future experimental work that includes chemical reactions to demonstrate how the changes in bubble size and residence time can be used to the greatest advantage.

2.7. Notation

\( d_p \) particle diameter, m
\( E_0 \) electric field strength, V/m
\( P \) dipole moment, C m
\( Q \) gas flow, m\(^3\)/s
\( u \) superficial velocity, m/s

\( \varepsilon_c \) relative dielectric constant of air, -
\( \varepsilon_p \) relative dielectric constant of a particle, -
\( \sigma_e \) electrical conductivity, S
\( \sigma^2_{IOP} \) incoherent variance, Pa\(^2\)

Subscripts
\( \text{mf} \) total fluidizing gas flow
\( \text{mf} \) minimum fluidization
\( p \) primary
\( s \) secondary
2.8. Acknowledgements

F. Kleijn van Willigen and J.R. van Ommen thank C.M. van den Bleek and J. van Turnhout for their long-term support. D. Christensen and M.-O. Coppens thank the Dutch National Science Foundation, NWO, for support via a Young Chemist award (NWO/Jonge Chemici).

2.9. References


3.

Modeling the Mechanisms behind the Effects of Secondary Gas Injection

In order to determine the mechanism behind the bubble size reduction witnessed with distributed secondary gas injection, discrete particle simulations were carried out to determine the local effects of secondary gas injection, which cannot be easily determined from experiments. From the simulations, the effect of secondary injection on the distribution of the gas in the bubble and dense phases could be determined.

The results of the simulations show that the average bubble size and the bubble fraction decrease with secondary injection. These results agree with the outcome of the experiments presented in the previous chapter. It was discovered that bubbles tend to be smaller with secondary gas injection because the primary flow is less, which causes a smaller initial bubble size, and more importantly, the secondary gas does not contribute to bubble growth. To determine why the secondary gas does not increase the bubble size, the average porosity of the dense phase was calculated and was found to increase above the injection point. The increased dense phase porosity and the decreased number of bubbles observed above the injection point mean that the gas stays in the dense phase and does not contribute to bubble growth or formation within the flow rates and domain sizes studied here. It is conjectured that the mechanism for the bubble size reduction is that the secondary gas breaks up clusters of particles and gives them additional energy. These effects result in the (partial) collapse of the bubbles and an expansion of the dense phase. The additional gas in the dense phase limits the amount of gas available for the bubble phase, thus both the bubble size and bubble fractions decrease. These effects result in an improved gas-solid contact.

This chapter has been accepted for publication as:

3.1. Abstract

Experiments have shown that distributed secondary gas injection via a fractal injector in fluidized beds can significantly reduce the bubble size, and may also decrease the bubble fraction. In order to gain insight into the distribution of the gas between the phases and the mechanisms behind these effects simulations of small bubbling fluidized beds with one or two secondary gas injection points were carried out using a discrete particle model. Although the systems are very small, so that wall effects cannot be excluded, the model predicts that the bubble size and bubble fraction both decrease with secondary gas injection, while the gas flow through the dense phase increases. The secondary gas tends to stay in the dense phase, which limits the amount of gas available to form bubbles and is the main contributor to the decrease in the bubble size and fraction. The gas-solid contact improves as a result.

3.2. Introduction

The conversion of mass transfer-limited reactions in bubbling fluidized bed reactors is suppressed because much of the reactant gas is in bubbles, which have very low solids (catalyst) content. As a result, the gas-solid contact is poor and the gas must move into the dense phase to react, which is a slow process when the bubbles are large. The chaotic behaviour of the bubbles also makes scale-up of these fluidized beds very difficult.

Similar mass transfer problems are avoided in nature because organisms use scale-independent branching networks to improve contact, as seen in trees and lungs (Figure 3-1a). Using this concept, we have developed a fractal injector to inject a portion of the total gas feed throughout the volume of the reactor (Figure 3-1b). The fractal nature of this device ensures that it can be very easily scaled-up. Previous lab-scale experimental studies on this method of secondary gas injection have shown that the bubble diameter can be reduced by more than 30% [1,2], while video analysis of quasi-2D columns demonstrated a similar decrease in bubble fraction [2]. A smaller bubble has a higher surface-to-volume ratio, which facilitates mass transfer from the bubble interior to the dense phase, and the gas flowing through the bubble cannot bypass as much of the catalyst bed as in a larger bubble. Smaller bubbles also rise more slowly [3], which increases the length of time they stay in the reactor and the likelihood that a given element of gas will transfer into the dense phase. The lower bubble fraction means that less gas is present in the form of bubbles. This result, coupled with a decreased bubble size, and thus bubble rise velocity, suggests that more gas flows through the dense phase. The end result is improved gas-solid contact.
Initial conversion experiments using ozone decomposition as a test reaction show a significant increase in conversion [4], which supports the conclusions of our hydrodynamic studies. However, we do not have a fundamental understanding of the mechanisms that bring these effects about, which is required to optimize the fractal injector for various reacting systems. The work presented here has two main objectives. The first objective is to gain insight into the distribution of the gas between the phases and, in particular, to determine the effect that the presence of secondary gas has on the dense phase. The second objective is to determine the mechanisms behind the bubble size reduction and reduced bubble fraction that we see experimentally. To meet these objectives local properties need to be studied, which are difficult to determine experimentally. However, numerical simulations are becoming a viable tool for quantifying these small-scale phenomena because of increasing computational power. Using computational fluid dynamics (CFD) hydrodynamic properties anywhere in the simulated fluidized bed, at any time, can be determined within the spatial and temporal resolution of the simulation. The following hydrodynamic properties were calculated from the simulation results: bubble size, bubble rise velocity, bubble positions, bubble fraction, and local porosity profiles. Movies were also made to obtain qualitative information about the fluidization behaviour.

In this study we have chosen to use the discrete particle model (DPM) because it allows us to determine how secondary injection influences the local porosities, which are affected by the particle-particle interactions. The model is briefly explained in the following section, followed by details on the simulated systems, conditions, and analysis techniques. The results of the

![Figure 3-1: (a) schematic detailing the branching structure inside a lung, adapted from [5]; (b) photograph of a fractal injector constructed in our laboratory](image)
simulations are presented in terms of the influence of secondary injection on the bubble and dense phases. A tentative mechanism is proposed that describes these effects.

3.3. Discrete Particle Modeling

CFD modeling of granular flows, such as fluidization, enables us to determine properties that are either difficult to determine accurately experimentally because of the influence of the measurement probe on the flow behaviour [6], or for which the experimental methodology is too expensive or does not yet exist. There are various CFD approaches employed for modeling fluidized beds [7]. These include, in increasing order of scale: the Lattice Boltzmann model, the discrete particle (Eulerian-Langrangian) model, the two-fluid (Eulerian-Eulerian) model, and phenomenological models. The Lattice Boltzmann model is typically used to model the smallest flow phenomena in the most detailed fashion, such as the drag force exerted by a fluid on individual particles. The phenomenological models typically only capture the very large-scale flow phenomena, such as bubble flow patterns. The other two models lie in between these two extremes, and are most useful for studying the phenomena of interest in this study, namely local porosities and local bubble behaviour. In the two-fluid model, the particle suspension is treated like a continuum; particle motion and local porosities are averaged out to form a continuous flow field. The discrete particle model (DPM) considers each particle as a discrete entity, allowing us to study particle-particle interactions and non-averaged local porosities. For the purposes of this study, DPM was deemed the most suitable because the local representation of the properties being studied is more detailed than that of the two-fluid model.

The code used in this study is called *MultiFlow*, developed by Van Wachem and co-workers at Chalmers University [8]. The implication of calculating numerical solutions over a continuous flowing medium, i.e., the Eulerian phase, is the need to discretize the domain over which the equations are solved. A grid is therefore superimposed on the simulation domain, and the equations governing the continuous phase are linearized for each grid cell. The fluid phase properties are determined by solving the Navier-Stokes equations, including volume fraction and source terms, which represent the particulate phase. Finer grids tend to give more accurate results, but calculation time increases.

Since Geldart B particles are used in the simulations for this study, interparticle forces, such as the Van der Waals force, viscous energy dissipation, added particle mass, and lubrication forces are neglected because they are much smaller in magnitude and do not play a significant role in the net force on the particles [9]. The result is that the forces on the particles are limited to collision forces, drag forces, and gravity.
Particle-particle and particle-wall collisions are modeled through a soft-sphere approach [10], which is able to deal with dilute and dense granular systems, in contrast to the hard-sphere approach, which is mainly valid for dilute systems [11]. The soft-sphere approach models the particle interactions by a repulsive force that depends on the amount of particle-particle overlap. This overlap represents the local deformation of the particles due to the interaction. This approach is often referred to as the spring-dashpot-slider model, and it involves kinetic and rotational energy exchange between colliding elements, as well as energy losses due to damping and frictional forces. This is described extensively by Tsuji et al. [12].

As a consequence of the soft-sphere approach a single collision needs to be described by multiple particle time-steps. The particle time-step, $\Delta t_p$, is therefore a function of the collision time, $t_c$, and the number of time-steps to describe a collision, $K$, according to:

$$\Delta t_p = t_c / K$$

(3.1)

The collision time can be estimated by regarding the elemental (particles or walls) kinetic energies before the collision and the collision properties. During the collision kinetic energy is stored in the form of elemental overlap, as in a spring. Transferring all kinetic energy into elastic spring energy according to the non-linear Hertzian contact theory gives an estimate of the maximum elemental overlap for a collision. This is an estimate because friction and rotational energies are not taken into account. Integration and rewriting of the terms leads to:

$$t_c \approx u_{rel}^{-0.2} \times \left(1.25 \times m_{rel} \times E^{-1} \times d_{rel}^{-0.5}\right)^{0.4}$$

(3.2)

where the collision time depends on the relative elemental velocity, $u_{rel}$, the relative mass, $m_{rel}$, the collision elasticity, $E$, and the relative elemental diameter, $d_{rel}$. The motion of each individual particle is calculated by using Verlet’s scheme [13] with a variable time-stepping routine to solve Newton’s equations of motion.

The Wen and Yu [14] relation is used in this work to calculate the drag force because it is valid over a broader range of conditions than another well-known relation, the Ergun equation [15]. For more details regarding CFD and DPM, the reader is referred to the literature, e.g. [6,16].

### 3.4. Simulation Approach

DPM models are very calculation-intensive. As a result, we are limited in the system size for which simulation runs will still provide sufficient data to obtain statistically significant results in a reasonable amount of time. It is not yet possible to model an entire lab-scale column with a complete fractal injector with the DPM model using today’s computers, within an acceptable timeframe. However, we have chosen to study several small 3D domains with
only one or two secondary injection points present; these are shown in Figure 3-2. All simulations are carried out with a total gas flow rate nearly twice the minimum fluidizing flow rate \(Q_{mf}\). The secondary gas flow rate is varied, keeping the total flow rate constant, to study how the fraction of secondary gas influences the hydrodynamics of the system. The particles used in all simulations are spherical with a diameter of 500 μm and a density of 2200 kg/m³ (Geldart B). The coefficient of restitution is 0.97, the friction coefficient is 0.10, the Young modulus is \(5 \times 10^5\) Pa, and the Poisson ratio is 0.25. The wall properties are identical to the particle properties. The fluidizing gas is air with constant properties (293 K, 1 atm). The gas time step is constant at \(1 \times 10^{-4}\) s, and the particle time step automatically adjusts itself to ensure that there are always 40 time steps per particle collision. The minimum fluidization velocity at these parameter settings was determined to be 22.1 cm/s. This is approximately 20% higher than the value standard correlations predict, indicating that wall effects may be influencing the fluidization behaviour, since the systems studied here are very small.

Figure 3-2: Simulation domains modeled; (a) small bed, (b) wide bed with 1 injection point, (c) wide bed with 2 injection points, and (d) tall bed. The size of the injection points are not to scale. Each domain is 3-dimensional and has a depth of 0.4 cm.

Table 3-1 lists the settings used in the various simulations, where \(Q_p\) is the primary (windbox) volumetric flow rate and \(Q_s\) is the secondary (injection point) volumetric flow rate, both presented as multiples of \(Q_{mf}\).

Three different domain sizes are simulated. The purpose of the small bed is to study the effect of the amount of secondary gas on the hydrodynamics of the system over relatively long times to obtain better statistics of bubble events. The purpose of the wide bed is
twofold. Firstly, the intention is to study the width of the region of influence of an injection point with less effect from the walls by using a single off-centre injection point. The off-centre position was chosen because it allows a larger portion of the bed on one side of the injection point to be less affected by either the walls or the injection point. Secondly, the intention is to study the interaction between two injection points. Both of these cases in the wide bed are simulated in two ways. One is to maintain the same \( Q_s/Q_{mf} \) value used in the small bed with the highest \( Q_s \). The other is to use the same secondary gas velocity used in the small bed with the highest \( Q_s \). In the small bed, these flow conditions are the same, but in the wide bed these flow conditions differ from each other because \( Q_{mf} \) is larger (larger cross-sectional area). As a result, under these flow conditions the total flow rate is slightly less than \( 2 \times Q_{mf} \). These simulations allow us to gain insight into whether \( Q_s \) or \( U_r \) has a greater impact on bubble size. The third domain is a tall bed. These simulations are intended to study the height of the region of influence of an injection point.

**Table 3-1: Simulation Settings**

<table>
<thead>
<tr>
<th>Sim. ID</th>
<th>Domain Size [cm³] (w×d×h)</th>
<th>( Q_p/Q_{mf} )</th>
<th>( Q_s/Q_{mf} )</th>
<th># Inj. Points</th>
<th>Settled Bed Height [cm]</th>
<th># Particles</th>
<th>Sim. Length [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Small Bed</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3×0.4×10</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>43 000</td>
<td>20.0</td>
</tr>
<tr>
<td>2</td>
<td>3×0.4×10</td>
<td>1.875</td>
<td>0.125</td>
<td>1</td>
<td>4</td>
<td>43 000</td>
<td>20.0</td>
</tr>
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<td>3×0.4×10</td>
<td>1.8125</td>
<td>0.1875</td>
<td>1</td>
<td>4</td>
<td>43 000</td>
<td>20.0</td>
</tr>
<tr>
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<td>0.25</td>
<td>1</td>
<td>4</td>
<td>43 000</td>
<td>20.0</td>
</tr>
<tr>
<td><strong>Wide Bed</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>0</td>
<td>0</td>
<td>4</td>
<td>65 000</td>
<td>16.0</td>
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<tr>
<td>6</td>
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<td>1.75</td>
<td>0.3036</td>
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<td>65 000</td>
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<td>65 000</td>
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<tr>
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<td>1.75</td>
<td>0.3036</td>
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<td>4</td>
<td>65 000</td>
<td>12.0</td>
</tr>
<tr>
<td>9</td>
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<td>65 000</td>
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<td>4</td>
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<td>10</td>
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<tr>
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<td>0</td>
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<td>65 000</td>
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<tr>
<td><strong>Tall Bed</strong></td>
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<td></td>
<td></td>
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<td></td>
</tr>
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<td>1</td>
<td>6</td>
<td>65 000</td>
<td>6.4</td>
</tr>
</tbody>
</table>

The limiting factor in choosing the size of these domains is calculation time. The wide and the tall beds have nearly 50% more particles and calculation times nearly twice as long per simulated second. Larger domains, although highly desirable to limit wall effects, are not yet feasible.
For the narrow beds (both short and tall), the single injection point is always centred at a height of 2 cm in the bed and at the centre of the horizontal plane. For the wider bed cases with only 1 injection point, it is located at a height of 2 cm, and 1.5 cm from the left wall, i.e., at 1/3 of the width. For the wider bed cases with two injection points, these are located at a height of 2 cm and at distances of 1.5 cm from each side of the bed, i.e., at 1/3 and 2/3 of the width.

The injection point is modelled as a local refinement of the grid to allow for a smaller injection area than the surface of one normal grid cell. The top surface of the cube is assigned a gas velocity to mimic the injection point. The other five sides of the injection cube are defined as walls. Since the system is so small, we do not include other tubes associated with the fractal injector. This omission is justified because experimental work has shown that the reduction in bubble diameter caused by the physical structure is only about 5%, which is very small compared to the entire effect of secondary injection [2]. The injection point gas velocity is always higher than the distributor gas velocity because the area of the injection point is a very small fraction of that of the bottom distributor.

The simulations conducted in each domain have the same grid configuration. The only difference occurs in the simulations with secondary gas where a local grid refinement is necessary to include the injection point. The simulations of the wider beds do not have exactly the planned flow rates because of an oversight. The velocities are the desired values, but the secondary volumetric flow rates are slightly higher than desired because the injection point is slightly larger than in the small bed. The result is that simulations 6 and 8 have a total flow of 2.05×Qmf instead of 2×Qmf and the Qd/Qmf values are slightly larger than the Qd/Qmf value used in simulation 4, the value originally intended for these wide bed simulations. Furthermore, simulations 7 and 9 have a total flow rate of 1.95×Qmf instead of 1.91×Qmf. The increases in flow are small, however, and are not expected to affect the results significantly. This small difference in the flow rates was corrected in simulations 10-12; these simulations are used to gain more insight into the influence of secondary gas on the dense phase in the wide bed.

3.5. Verification and Validation

Verification and validation are very important concepts in CFD work, as multiphase CFD is far from proven technology. Verification is the process by which the solution of the model is shown to be mathematically correct, while validation is the process by which the model is shown to sufficiently describe reality, most often by comparing the results to experimental data. It is extremely difficult to verify multiphase CFD models because of the complexity of
the systems, and verification can often only be achieved for trivial cases. Thorough validation of the model is also difficult to achieve, particularly in the cases where models are used because experiments are too difficult to perform accurately. Grace and Taghipour [17] discuss the verification and validation of fluidization models in detail. In the present study, we are trying to determine local properties that cannot be obtained accurately from experiments, e.g. the local porosity. We cannot claim that we have validated this particular model, although the concept of the discrete particle model and the relations (both theoretical and empirical) contained therein have been well tested and accepted in the literature. To at least attempt to address this issue, we have compared our model results to well known empirical correlations for two hydrodynamic properties: bubble size and bubble rise velocity. Figure 3-3 shows the comparison between the simulated average bubble size results for the cases of the small and wide beds without secondary injection and the Darton equation [18], given below:

\[ d_b = 0.54(U_0 - U_{mf})^{0.4}\left[h + 4\sqrt{A_0}\right]^{0.8} / g^{0.2} \]  

where \( A_0 \) is the catchment area, defined as the surface area of distributor plate per orifice, which defines an initial bubble size. \( A_0 \) was determined by fitting the data. The simulation results for the average bubble size compare favourably with the Darton equation, except for deviation at the very bottom and the very top of the bed. The deviation at the top can be explained by the fact that the bubbles begin to shrink when they are very close to the bed surface, as the bubble gas can pass through the thin layer of particles that separates the bubble from the freeboard. The bars are not error bars. Instead, they indicate the standard deviation around the average, and are a measure of the width of the bubble size distribution at a given height. The quality of the fit is acceptable and within the error of the correlation. The equivalent bubble diameter is defined as the diameter of a sphere of the same volume as the bubble.

Figure 3-4 shows the comparison between the simulated average bubble rise velocities for the cases of the small and wide beds without secondary injection and the simplified Hilligardt and Werther equation [19] (as presented by Kunii and Levenspiel [3]):

\[ U_b = 1.6\left[(U_0 - U_{mf}) + 1.13d_b^{0.5}\right]d_b^{1.35} + 0.711\sqrt{gd_b} \]  

In Figure 3-4, only the rise velocities of the bubbles found in the middle half of the bed are presented, in order to only look at bubbles that have fully formed and are not yet erupting at the bed surface. As can be seen from the figure, the simulated average bubble rise velocity data are not in very good agreement with the Hilligardt and Werther equation, with deviations as large as 50%. The decrease in rise velocity apparent for bubbles larger than 1.5 cm is due to shrinkage of large bubbles whose roof approaches the bed surface. Even
though the top 25% of the bed is not considered, these bubbles are so large relative to the system size that their centres are actually in the middle portion of the bed, and are thus included in the data shown in the figure. As mentioned earlier, these bubbles shrink because there is only a thin layer of particles between the bubble and the freeboard, so gas escapes even prior to bubble eruption. Therefore, the decrease in rise velocity shown at large bubble diameters is a result of the bubble centers not moving as fast because the bubbles suddenly lost much of their gas over the course of a time-step. This effect is attributed to the small system size. An example of this shrinking behaviour is shown in Figure 3-5.

Poor agreement with the Hilligardt and Werther equation for bubbles similar in size to the ones found in these simulations was also observed in a previous study [20]. This disagreement was attributed partly to the fact that the Hilligardt and Werther equation was only based on bubbles greater than 4 cm in diameter, which is even larger than the system size in our simulations. In Figure 3-4 the bars represent one standard deviation about the mean. However, since the bubble rise velocities are grouped by similar bubble sizes, the standard deviation is no longer representative of the bubble size distribution at a given height. In this case, the standard deviation indicates that the location of the bubble along the height of the reactor may be important. The Hilligardt and Werther equation assumes that bubbles of a given size will rise with a given velocity, which does not depend on height. The deviations exhibited by the simulated data are within the error of this empirical relation.
Modeling the Mechanisms behind the Effects of Secondary Gas Injection

Figure 3-4: Average simulated bubble rise velocity compared to the simplified Hilligardt & Werther Equation: (a) small bed, (b) wide bed. The bars represent ±1 standard deviation.

Because the system sizes studied here are very small, it is conceivable that bubble properties may be significantly influenced. This notwithstanding, our goal here is to compare the results of the model with secondary gas injection to the results without secondary gas injection. Since the same model is used in both cases, both sets of results will contain the same limitations and potential deviations; therefore, the qualitative comparison of the two is still expected to be valid, assuming that the model is not unrealistic. We stress that, given the small bed sizes accessible to current computer calculation power, it is very difficult to directly validate any discrete particle model for fluidized beds. However, the results compare favourably with the Darton equation and are at least of the same order of magnitude as the Hilligardt and Werther expression, which are two indications that the model is predicting reasonable behaviour and is useful for our purpose.

Figure 3-5: Large bubbles near the top of the bed shrink before erupting: (a) rising bubble; (b) shrinking bubble; (c) erupting bubble.
3.6. Results and Discussion

The purposes of this study are to gain insight into the mechanisms involved in the reduction of the bubble size and bubble fraction observed experimentally, and to determine the effect on the dense phase hydrodynamics when secondary gas is present. The system sizes here are very small, and only one or two injection points are being modeled, thus it is important to determine whether the simulations exhibit similar behaviour to the experiments. These effects will be treated separately, below. It should be noted that the tall bed simulations exhibited strong slugging behaviour because the height/diameter ratio was too large. An illustration of this behaviour is given in Figure 3-6. Because the tall beds (simulations 13 and 14) are not in the bubbling regime, they have very different characteristics, and these simulations were not considered any further.

Figure 3-6: Example of slugging behaviour in the tall bed simulations, $Q_0/Q_{mf} = 2$, $Q_s = 0$.

Bubble Size and Location

The bubble size results for the small and wide beds are shown in Figure 3-7. Increasing the secondary flow in the small bed does not show any reduction in bubble size. In the lower portion of the bed, the bubble size is even larger than in the base case. In the wide bed, however, there is a clear reduction in bubble size. Since the injection points, in this case, are off-centre, it is sensible that two injection points will have a greater effect than a single injection point because the region of influence of a single injection point is probably less than the width of the column. As a result, large bubbles can form outside the region of influence of the single injection point, which would not occur in the two-injection point case because the total region of influence reaches across the entire column width. The region of influence
can be clearly seen in Figure 3-8. This result suggests that such simulations can be valuable tools to optimize the distance between injection points in order to minimize bubble size. From the wide bed bubble size results, Figure 3-7b, it appears that there is a difference between the single injection point simulations. The simulation with a lower injection velocity (simulation 7) has a smaller average bubble size than the higher injection velocity simulation (simulation 6), though it also has a slightly (5%) smaller total flow rate. Interestingly, there is virtually no difference between these two cases when two injection points are present (simulations 8 and 9), but the injection velocities are half of those in the single injection point simulations because the same flows are split over two injection points. This result gives an indication that, either the injection velocity may be important for isolated injection points but is negligible when multiple injection points are present, or there is a critical injection velocity below which a change in velocity has no effect. A more detailed study is needed to elucidate this point.

It can be seen from the bubble positions in the wide bed without secondary injection (Figure 3-8a) that most of the bubbles travel through the middle of the bed. With one injection point there is an area above it free of bubbles (Figure 3-8b). There are fewer bubbles, of which a larger portion seems to move along the walls. With two injection points (Figure 3-8c) there are no bubbles above them, and the remaining bubbles tend to appear closer to the walls.

In the small bed (simulations 1-4), most of the bubbles are already traveling along the walls even in the absence of secondary injection. This may serve to explain why no difference in bubble size can be seen with secondary injection in this small system, since either the bubbles are effectively bypassing the region of influence of the injection point or the bubbles
at the wall are already smaller. The bubble positions for the small beds are shown in Figure 3-9. The results in the small bed simulations indicate that the small system size is dominating the hydrodynamics. In the wide bed, however, the system size is still limiting but it no longer dominates the hydrodynamics, and the effects of secondary gas injection can clearly be seen.

Figure 3-8: Centre positions of all simulated bubbles in wide beds for all gas time-steps; (a) no secondary injection (simulation 5); (b) one injection point, $Q_s/Q_m = 0.2024$ (simulation 7); (c) two injection points, $Q_s/Q_m = 0.2024$ divided over both injection points (simulation 9). The squares denote the injection point positions.

Figure 3-9: Centre positions for all bubbles in small beds: (a) no secondary injection (simulation 1); (b) one injection point, $Q_s/Q_m = 0.125$ (simulation 2); (c) one injection point, $Q_s/Q_m = 0.1875$ (simulation 3). The squares denote the injection positions.
Another important experimental result is the reduction in bubble fraction. Figure 3-10 shows bubble fractions calculated from the small and wide bed simulations. It is not surprising that the average bubble fraction in the small bed (simulations 1-4) does not change much with secondary gas injection (with the exception of the unexpected value for the highest secondary velocity, simulation 4), since the average bubble size is hardly changing. There is, however, a marked decrease in bubble fraction in all of the simulations with secondary injection in the wide bed, even though the total gas flow is slightly higher than the base case for two of the simulations (6 and 8). In fact, simulations 8 and 9 with two injection points show nearly homogeneous fluidization behaviour. The single injection point simulation with the lower injection velocity (simulation 7) has a lower bubble fraction than the other single injection point case (simulation 6). The difference between these bubble fractions might be due to the slightly lower total flow rate of simulation 7, but this explanation seems unlikely given that the difference between the flow rates is very small (5%), whereas the difference between the velocities is much more significant. Just as in the bubble size results, the cases with two injection points are nearly identical, indicating that, either injection velocity does not play an important role when multiple injection points are present, or the injection velocities used in these multiple injection point simulations are less than a critical value below which a change in velocity has no effect.

**Figure 3-10:** Average bubble fraction as a function of $Q_s$ in (a) the small bed (simulations 1-4) and (b) the wide bed.

To better understand the effect of secondary gas injection on the bubble fraction, other simulations in the wide domain were performed with varying secondary gas flow rates (simulations 10-12). These simulations were performed in two ways. The first group had a
constant total gas flow (simulations 5, 10, and 11), while the second group had a constant primary gas flow and an increasing secondary gas flow (simulations 10 and 12). These two groups together give us a more complete picture of the distribution of the secondary gas between the bubble and dense phases. The bubble fraction results as a function of height for the group with constant total flow are shown in Figure 3-11a, and the results of the constant primary flow simulations are given in Figure 3-11b. The simulations with constant total flow indicate that the bubble fraction decreases with an increasing amount of secondary gas. This is logical in the area below the injection point (at 2 cm), where the gas flow is less when secondary gas injection is present. However, the bubble fraction remains low even above the injection point where the total flow in all cases is the same. In the simulations with constant primary flow, the bubble fraction below the injection point is exactly the same because the flow rates are the same in this region. However, when secondary gas is added, the bubble fraction does not increase relative to the base case above the injection point despite the increase in the total flow. These results indicate that the secondary gas does not contribute to the total bubble volume, which can help to explain the reduction observed in the average bubble size. This confirms previous experimental findings [1].

_Dense Phase Porosity_

The results of both simulations and experiments show that the bubbles are smaller on average in the presence of secondary injection. Therefore, the bubble fraction should increase because smaller bubbles move more slowly and stay in the bed for a longer time. However, the results indicate that the bubble fraction decreases with higher secondary flow rates (Figure 3-11a). Even when the primary gas flow is kept constant and the secondary gas flow is increased the results indicate that the bubble fraction does not increase, despite the higher total gas flow (Figure 3-11b). This indicates that the secondary gas does not go into the bubble phase.

In order to gain further insight into how the bubble fraction is being reduced, and whether or not the dense phase flow is increasing, the local porosities have been time-averaged and the contours over the central vertical plane, parallel to the front of the bed, are shown in Figure 3-12 for three of the simulations in the wide bed: the base case (simulation 5); one injection point with \( U_s = 4 \text{ m/s} \) (simulation 7); and two injection points each with \( U_s = 2 \text{ m/s} \) (simulation 9). In these plots, the areas over which bubbles prefer to travel are characterized by higher porosities, since, on average, those areas will have fewer particles due to the presence of bubbles. In the base case, bubbles prefer to travel through the middle as can be seen by the higher porosities in the middle portion of the bed. In the case with a single injection point, the bubbles prefer to travel up the left wall or in the right half of the system.
In the case with two injection points, bubbles only travel up the walls. These results are consistent with Figure 3-8. The portions of the beds below the injection points are denser than the base case. There are two possible reasons for this. Firstly, the primary gas flow rate is lower than in the base case, therefore the bed is not as expanded, and there are fewer and smaller bubbles. Secondly, it is possible that the injection points act as blockages in the system that particles find difficult to move around. It has been shown that the physical structure of the fractal injector, without flow, can cause a reduction in the bubble diameter of approximately 5% because the internals help to induce bubble break-up [2]. In this case, however, it is probably more a function of the small system size that limits the ability of the fluidized particles to flow around the obstruction; thus they move upwards due to the drag force exerted by the gas flow but then jam together when they cannot move around the injection point fast enough.

The portions of the beds above the injection points also appear to be denser on average than the base case because far fewer bubbles flow through this region. The bed height is also lower when secondary gas is present, but this can be explained by the reduction in the bubble fraction. The question is why there is less gas present as bubbles in the region above the injectors. One hypothesis is that the injection points induce a lower porosity region that the bubbles will avoid because the resistance to flow is much higher. Thus, the bubbles are forced outwards towards the walls. This concept is consistent with the results, but is difficult to justify in a physical sense because it would seem more likely that the secondary gas would
force particles further apart rather than compact them. A second, seemingly contradictory, hypothesis is that more of the gas is in the dense phase and is unavailable to form bubbles. The denser regions seen in the overall porosity profiles above the injection point in the simulations with secondary gas are then a result of the reduction in the bubble fraction. This latter hypothesis is also consistent with the results and seems more physically plausible.

Figure 3-12: Time-averaged porosity contours of the wide bed simulations: (a) base case (simulation 5); (b) one injection point, \( U_s = 4 \) m/s (simulation 7); (c) two injection points, each with \( U_s = 2 \) m/s (simulation 9).

To gain further insight into this problem, the average porosity of only the dense phase was calculated. This was accomplished by setting a maximum threshold porosity of 0.5. Grid cells that have porosities above this value are assumed to be part of a bubble or cloud region surrounding a bubble at that moment in time, and are neglected. This value was chosen because the porosity at minimum fluidization is typically on the order of 0.4 for Geldart B particles, and we do not expect the dense phase porosity to increase by more than 25%. Each grid cell was averaged in time; only grid cells that met this porosity criterion more than 25% of the time were used; this tended to exclude only one or two grid cells adjacent to the injector point. The time-averaged porosities were then also averaged across the cross-sectional area for every height in the bed. This method gives us the average dense phase porosity as a function of height in the bed. The results based on simulations 5, 10, and 11 for different secondary gas velocities at the same total flow rate in the wide bed are shown in Figure 3-13a. Below the injection point, the average dense phase porosity for both cases with secondary gas injection is lower than the base case below the injection point. This coincides with the decrease in the total porosity seen in this area in Figure 3-12, and is because the superficial gas velocity is less than in the base case in that region. This result indicates that there is more expansion of the dense phase at higher flow rates. There is no
difference between the cases in the region around the injection point; this is probably because the injection point is a local blockage in the flow. Very interestingly, the dense phase porosity increases with secondary gas injection above the injection point. This is an important insight because it means that there are fewer and smaller bubbles above the injection point because more of the gas is in the dense phase, so that there is less gas available for the bubble phase. In the simulations where the primary flow is kept constant and the secondary flow, and therefore the total flow, is increased (simulations 12 and 13, shown in Figure 3-13b), the dense phase porosity increases above the injection point with secondary gas flow present. This result, coupled with the decrease in bubble fraction, means that the secondary gas stays in the dense phase, at least for the gas velocities studied.

These results support the second hypothesis discussed earlier, whereby the decreases in the total average porosity and bed height are due to an increase in the dense phase porosity and a decrease in the volume of the bubble phase. The evidence indicates that the secondary gas stays in the dense phase, resulting in better gas-solid contact. This effect is likely due to the secondary gas breaking up clusters of particles and giving particles more energy, such that bubbles become smaller and the dense phase expands. The focus of this work was on the gas distribution, however more insight into how the dense phase porosity increases may be obtained from studying the distribution of energy in the system or by looking at particle mixing and local granular temperature [21]. It is interesting to note that secondary injection appears to make the porosity more homogeneous.

![Figure 3-13](image)

**Figure 3-13:** Average dense phase porosity as a function of height for varying secondary gas velocities in the wide bed with (a) constant total flow, and (b) constant primary flow. The first dashed line indicates the location of the injection point and the second indicates the settled bed height.
Results from this study further show that the hydrodynamics of the simulated beds appear to be in the slow bubble regime [3], i.e., the bubble rise velocity is slower (Figure 3-4) than the dense phase gas velocity estimated by dividing the minimum fluidization velocity by the dense phase porosity. This regime typically occurs with larger particles; the gas in the dense phase shortcuts through the bubbles and decreases the gas-solid contact. The decrease in the bubble fraction caused by secondary injection reduces this bypassing and forces the gas to stay in the dense phase longer, which improves the gas-solid contact. These benefits are not limited to the slow bubble regime, however. The increase in the flow through the dense phase and the reduced bubble fraction will also improve the gas-solid contact in the fast bubble regime typically observed with small particles.

Further simulations should be carried out using larger system domains, or perhaps periodic boundary conditions, to reduce the effect of the walls on the fluidization behaviour. This issue appears to be dominant in the small bed simulations, while they cannot be ruled out of the wide bed simulations either. Given that the simulated beds are also extremely shallow, it is possible that the bubbles are not fully developed. The presence of distributed secondary injection points is also expected to hinder the bubbles from fully developing. Preventing the development of the bubbles should help to reduce their size. To study this particular property properly, much larger systems would have to be simulated, which is impossible at present. Nevertheless, the wide bed simulations gave qualitative agreement with experimental data on bubble size, suggesting that the small system dimensions do not dominate the results.

### 3.7. Conclusions

Discrete particle model simulations have been carried out for small bubbling fluidized beds containing one or two secondary gas injection points, in order to gain insight into the distribution of the gas between the phases and the mechanisms behind the reduction in bubble size that is observed in experiments with a fractal injector. The tall bed simulations had to be excluded from further analysis because they exhibited strong slugging behaviour instead of free bubbling. A 3 cm wide bed showed virtually no effect from secondary injection, but a plot of the bubble trajectories showed that the system size is dominating the hydrodynamics, as the vast majority of the bubbles travel up the walls even in the absence of secondary injection. The injection point, in this case, had little influence because bubbles effectively bypass it. The simulations with the 4.5 cm wide bed showed behaviour similar to the experiments. The average bubble size is significantly reduced with one injection point, and even further reduced with two. Even the simulations with total gas flows slightly higher than the base case of $2\times Q_{mf}$ showed a reduction in bubble size with secondary injection
compared to the base case. The bubble fraction was also significantly reduced, with the cases with two injection points showing nearly homogeneous fluidization behaviour. Even in cases with constant primary flow and increasing secondary flow, the bubble fraction remained unchanged despite the increase in the total flow. The secondary gas, as a result, does not contribute to the bubble phase. The simulation results show that secondary injection induces a higher dense phase porosity. This increased gas flow through the dense phase means that less gas is available for the bubbles, which results in a decreased bubble size. Both of these results imply that the gas-solid contact is improving. It is hypothesized that the secondary gas breaks up particle clusters and gives them more energy, which causes an expansion in the dense phase and reduces the bubble size. Further studies are needed to verify this claim, however. The domain sizes studied here exhibited strong wall effects, particularly in the smallest simulation domain where the hydrodynamics were dominated by wall effects. However, the wider bed exhibited the expected behaviour based on qualitative comparison with experiments, indicating that, while the wall effects may still be present, they are no longer dominant. A methodology that enables us to simulate much larger systems within a reasonable time is needed to further advance our understanding of fluidized beds with a fractal injector.

3.8. Acknowledgements

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3.9. Notation

\( \Delta t_p \)  Particle time-step, [s]
\( A_0 \)  Catchment area used in Darton equation, [m\(^2\)]
\( d_b \)  Bubble diameter, [m]
\( d_{rel} \)  Relative elemental diameter, [m]
\( d_r \)  Reactor diameter, [m]
\( E \)  Collision elasticity, [Pa]
\( g \)  Acceleration due to gravity, [m/s\(^2\)]
\( h \)  Height in bed, [m]
\( K \)  Number of particle time-steps per collision, [-]
\( m_{rel} \)  Relative elemental mass, [kg]
\( Q_0 \)  Total volumetric flow rate, [m\(^3\)/s]
\( Q_p \)  Primary volumetric flow rate, [m\(^3\)/s]
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\( Q_s \) Secondary volumetric flow rate, \([m^3/s]\)
\( t_c \) Collision time, \([s]\)
\( U_0 \) Total gas velocity, \([m/s]\)
\( U_b \) Bubble rise velocity, \([m/s]\)
\( U_{\text{ref}} \) Minimum fluidization velocity, \([m/s]\)
\( U_p \) Primary gas velocity, \([m/s]\)
\( u_{\text{rel}} \) Relative particle velocity, \([m/s]\)
\( U_s \) Secondary gas velocity, \([m/s]\)

3.10. References


Gas Residence Time and Mixing

The work presented in this chapter studies how distributed secondary injection affects the residence time and macroscopic mixing of the gas in a bubbling fluidized bed. These properties are important because they have an influence on the level of conversion that can be achieved.

Residence time distribution experiments were conducted in a quasi 2-D fluidized bed to determine how secondary gas distribution affects the average residence time of the gas and the macroscopic mixing of the gas, which is characterized by the variance (width) of the distribution. Based on a simplistic model, the average residence time is not expected to change, but the results of these experiments indicate that there is a decrease. This drop in residence time is greater when larger amounts of secondary gas are injected, but even at the highest secondary gas velocities, is relatively small. In light of the results of the previous chapter where the dense phase porosity is increasing, a possible explanation for the decrease in the residence time is that the velocity of the gas in the dense phase is increasing.

The macroscopic mixing (axial back-mixing) of the gas was determined to decrease with increasing secondary injection. This result means that the overall gas behaviour is more plug flow-like with secondary gas injection. This result is significant because this behaviour will help to maintain a high concentration gradient in the reactor, which is the driving force for positive order chemical reactions.

Although the average residence time decreases slightly, the improved gas-solid contact resulting from the decrease in bubble size and increase in dense phase porosity is more important for heterogeneous reactions. These effects are expected to be significantly larger than the effect of the reduced residence time.

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4.1. **Abstract**

Experiments were carried out to determine the effects of secondary gas injection on the gas residence time and macromixing characteristics in a bubbling fluidized bed. Primary gas is introduced via a bottom distributor plate, while secondary gas is introduced via a fractal injector submerged in the bed. Results indicate that the average residence time decreases only slightly. Calculated overall reactor Péclet numbers indicate that the gas experiences less back-mixing with secondary gas injection. The bubble size was observed to decrease by up to 70%, indicating improved gas-solid contact. Taking this improved contact and plug flow behaviour into account, the conversion in a fluidized bed with secondary gas injection is expected to increase significantly, particularly for mass-transfer limited reactions.

4.2. **Introduction**

For several applications of fluidized beds it can be useful to manipulate the structure, and thereby introduce additional degrees of freedom, in order to intensify the process [1]. The secondary injection of gas directly inside the fluidized bed by using a fractal injector (right-hand side of Figure 4-2) can significantly reduce the bubble size and decrease the rate of bubble coalescence [2,3]. This decrease in bubble size should increase the rate of gas exchange between the bubbles and the surrounding solids suspension, thus increasing conversion for a mass-transfer limited reaction. Previous experiments indicate that the total volume of gas present in bubbles is reduced as well, implying that there must be more gas in the dense phase, which results in a better gas-solid contact [2,3]. Injection of gas into a fluidized bed at locations throughout the reactor, instead of through the windbox alone, can also be used to effectively improve reaction selectivity and to maintain high reactant feed rates while still avoiding possible explosion limits [4,5]. All of these effects contribute to the intensification of fluidized bed processes.

The addition of gas higher in the bed affects the micro- and macro-mixing behaviour in the fluidized bed. Around each injection point of the fractal injector (see Figure 4-2) there is increased micromixing due to the additional flow, which can improve the local gas-solid contact [6]. On the macro-scale, the whole flow pattern in the bed may be altered due to the distribution of the gas injection. This is important because a decrease in back-mixing will increase the concentration gradient of a reactant, which is the driving force for a chemical reaction (with positive order kinetics), resulting in a higher conversion. Although the gas-solid contact time is needed to predict conversions in heterogeneously catalyzed systems [7,8], the gas residence time distribution (RTD) is still useful to determine the gas holdup and the macromixing characteristics of the fluidized bed [9,10]. The purpose of the current study
is to determine what effects secondary gas injection via a fractal injector has on the gas holdup (i.e. residence time) and the macromixing characteristics of a bubbling fluidized bed. The approach taken here is to measure the residence time distributions in such a system using pulse-response experiments with an inert tracer at different primary to secondary gas flow ratios and at different total gas flow rates. The RTD’s are then used to determine the average residence time and to calculate the Péclet numbers, which are a measure of the amount of macromixing (axial dispersion) in the system.

4.3. Background

What effects do we expect to find with secondary gas injection on the residence time and mixing in the system? First, consider the effect of secondary gas injection on the average residence time, $\tau$, of the gas. Specifically consider the comparison of two identical fluidized beds with the same total flow rate, but one that has a portion of the total flow introduced higher in the bed. At first thought, $\tau$ might be expected to decrease because gas is being injected higher in the reactor. However, the fact that the gas at the bottom of the reactor travels more slowly (as compared to the bed without secondary injection) cancels out the reduced average residence time of the fresh gas that is injected further up. This can be shown through a simple derivation adapted from Coppens [6]:

For a theoretical tank with one input and one output, the average residence time is defined as the volume of the tank divided by the total volumetric flow rate (assuming no volume change due to reaction),

$$\tau = \frac{V}{Q}$$  \hspace{1cm} (4.1)
With one secondary injection height, the reactor is split into two volumes, $V_1 + V_2 = V$, with a fraction $\rho$ of the total flow going towards the windbox, and a fraction $(1 - \rho)$ being injected as secondary gas. Therefore, in this simple model of secondary injection, the volumetric flow rate into $V_1$ is $\rho Q$, and the flow rate into $V_2$ is $\rho Q + (1 - \rho) Q = Q$. Since the primary gas must go through both volumes, the average residence time of the primary gas is calculated as the sum of the residence times for each tank:

$$\tau_{\text{primary}} = \frac{V_1}{\rho Q} + \frac{V_2}{Q}$$  \hspace{1cm} (4.2)

Similarly, the average residence time of the secondary gas is:

$$\tau_{\text{secondary}} = \frac{V_2}{Q}$$  \hspace{1cm} (4.3)

To obtain the overall average residence time we must use a weighted average of $\tau_{\text{primary}}$ and $\tau_{\text{secondary}}$ according to the fractions of the total gas that go through the primary and secondary flows. Thus, the total average residence time is:

$$\tau_{\text{total}} = \rho \cdot \tau_{\text{primary}} + (1 - \rho) \cdot \tau_{\text{secondary}} = \frac{V_1 + V_2}{Q} = \frac{V}{Q}$$  \hspace{1cm} (4.4)

This tanks-in-series model shows that the average residence time should not change at all. Strictly speaking, the above derivation is only valid for systems that behave ideally with uniform, additive flow. It does not account for possible deviations, such as bypassing (or stagnation) where some fluid elements travel at significantly different velocities than others (e.g. bubbles typically travel faster than the gas in the dense phase), and it assumes that there is no back-flow of gas from $V_2$ to $V_1$. Previous research [2,3] has shown that secondary gas injection reduces the size of the bubbles. As a result, the rise velocity of the bubbles decreases and the rate of gas bypassing drops. Thus, it is reasonable to expect that the average residence time should not change.

Interestingly, Al-Sherehy et al. [4] found that the addition of secondary gas as a jet (at velocities high enough for the jet to span the diameter of the column) with constant primary flow had only a very small negative effect on the residence time of the gas, even though their total gas flow was increasing with jet velocity in their experiments. In the current experiments, the secondary gas is distributed across the width of the reactor due to the uniform (albeit discrete) placement of the injection points on the fractal injector, and we maintain our total flow rate constant. Therefore, little or no negative effect on the residence time of the gas is expected.

Now consider how the macromixing of the gas in a fluidized bed with secondary injection could be affected. Since the bubbles are smaller (and thus travel with a slower velocity) and they have a lower rate of coalescence, the amount of mixing in the bed is expected to decrease. This decrease is because the bubbles themselves are a major driving force for the
Gas (and solids) mixing. Vigorously bubbling beds will have much more dispersion than beds where the bubble behaviour is more controlled. Another effect is the nature of the secondary injection device. In this work a fractal injector with four levels of injection points is used. This way to inject gas can promote gas staging without the use of baffles [6]. Gas staging is beneficial because it causes the bed to be broken up into smaller mixing cells, and, as the number of cells increases, the overall flow behaviour approaches that of plug flow. Controlling the bubble behaviour and inducing gas staging are two reasons why we can expect secondary gas injection to shift the behaviour of the gas closer to the ideal of plug flow.

4.4. Residence Time Theory

Gas residence times are frequently determined by using tracers that follow the flow. A complicating factor with secondary gas injection is that there are multiple flows. To determine the overall RTD of the gas, the residence times of both the primary and the secondary gas must be combined. Several researchers have developed a theory for residence times of systems with multiple inputs and outputs [11,12,13,14,15]. The theory of Buffham and Kropholler [11,12] appears to be the most generally applicable. Their general equation for systems with multiple inputs and outputs is:

$$f(t) = \frac{1}{Q} \sum_i \sum_j Q_j f_{ij}(t)$$  \hspace{1cm} (4.5)

where \(f(t)\) is the combined tracer response as a function of time, \(Q\) is the total flow rate, \(Q_j\) is the flow rate at outlet \(j\), and \(f_{ij}(t)\) is the tracer response at outlet \(j\) due to an ideal pulse of tracer at inlet \(i\). For a system with only one output, equation (4.5) reduces to:

$$f(t) = \sum_i f_i(t)$$  \hspace{1cm} (4.6)

where \(f_i(t)\) is the response at the outlet due to an ideal pulse of tracer at inlet \(i\). However, the development of these equations assumed that the concentration of the tracer in all entering streams was the same. As will be explained in the Experimental section, in the current experiments a constant volume of tracer is injected, while the flow rates (and thus the concentration of tracer) of all feed streams, \(Q_i(t)\), vary and do not usually equal each other. Thus, equation (4.6) needs to be modified to remove the effect of different tracer concentrations. This is done by normalizing the area under each \(f_i\) curve to unity and multiplying the result by the probability that any given tracer element originated from input \(i\), i.e. the fraction of the total flow that originated from \(i\), such that:

$$\frac{f(t)}{\sum f_i(t)} = \frac{1}{Q} \sum_i Q_i \left( \frac{f_i(t)}{\sum f_i(t)} \right)$$  \hspace{1cm} (4.7)

In terms of the residence time distributions for each inlet, \(E_i(t)\), this equation becomes:
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\[ E(t) = \frac{1}{Q} \sum Q_i E_i(t) \]  \hspace{1cm} (4.8)

Technically, the residence times of the gas from each input should be measured, of which there are 17 – the windbox plus the 16 injection nozzles in this particular fractal injector. Such an experiment would be very difficult to perform because all of the fractal injector nozzles are connected to the same feed source. This is, in fact, one of the advantages of the fractal structure! Fortunately, the flow rates and tracer concentrations through each injector nozzle are the same, which implies that the measurement of the combined tracer response of the entire injector yields the same result as if the response from each nozzle had been measured separately and later combined using equation (4.8). This effectively reduces the system to two inputs – the windbox (primary flow) and the fractal injector (secondary flow).

To calculate the RTD’s of the gas that enters through each of these inputs, we inject tracer into either the primary or the secondary flow and measure the tracer concentration, \( C(t) \), at the surface of the bed. The RTD is then calculated using:

\[ E_i(t) = \frac{C_i(t)}{\int_0^\infty C_i(t) \, dt} \]  \hspace{1cm} (4.9)

where the subscript \( i = p \) denotes the primary gas, and \( i = s \) denotes the secondary gas.

Using equation (4.8) to combine the primary and secondary gas, the overall RTD of the gas in the fluidized bed is determined. The average gas residence time, \( \tau \), is calculated from \( E(t) \) through:

\[ \tau = \int_0^\infty t \cdot E(t) \, dt \]  \hspace{1cm} (4.10)

By determining the residence time distributions of the gas for different secondary and total flow rates, the effect of secondary injection on \( \tau \) is elucidated.

Another useful parameter is the variance, \( \sigma^2 \). The variance is a measure of the spread of the data around the mean, which is a characteristic of the macromixing phenomena occurring within the bed. The variance can be calculated from:

\[ \sigma^2 = \int_0^\infty (t - \tau)^2 \cdot E(t) \, dt \]  \hspace{1cm} (4.11)

However, when studying the mixing characteristics of the system it is best to have a tracer injection that is independent of how and where the gas is injected. For example, since the tracer that is injected through the fractal injector will exit the nozzles simultaneously at 16 different locations (4 different heights), the tracer is already dispersed. To calculate the variance based on the entire RTD of the gas would give an incorrect view of the mixing characteristics of the system. It is better to have the tracer injection at a single location. This is the equivalent of only using the RTD of the primary gas to study the mixing behaviour,
since the tracer is only introduced at the bottom of the bed and is influenced by both input flows before exiting the bed.

From the mean residence time and the variance, the overall reactor Péclet number, $Pe_r$, is calculated: this is the ratio of the rate of transport by convection to the rate of transport by diffusion or dispersion. Therefore, high $Pe_r$ numbers are associated with plug flow-like behaviour, while very low $Pe_r$ are associated with well-mixed behaviour. According to the dispersion model [16] with closed-closed boundary conditions (i.e., no dispersion across the system boundaries), $Pe_r$ can be calculated from:

$$\sigma^2 = \frac{2}{Pe_r} - \frac{2}{Pe_r^2} \left(1 - e^{-Pe_r}\right)$$

(4.12)

Closed-closed boundary conditions are a reasonable assumption because gas is not expected to back-diffuse across the porous distributor plate due to the associated pressure drop, while the recapture of gas from the freeboard should be minimal because the particle concentration there is very low. Knowing the values of $Pe_r$ at varying flow conditions helps to understand the effect of secondary injection on the macromixing characteristics of the system. If $Pe_r$ is seen to increase with increasing secondary injection then it can be concluded that secondary injection is pushing the gas flow more towards plug flow behaviour.

### 4.5. Experimental

Stimulus-response studies of a helium tracer pulse were carried out in a 20 cm wide×1.5 cm deep quasi-2D column with glass beads having a density of 2462 kg/m$^3$ and an average particle size of 355 μm. The particle size distribution was relatively narrow with over 75 vol.% of the particles being between 300 and 400 μm in diameter. The fixed bed height of the solids was 40 cm. A 16-nozzle fractal injector was placed in the bed, centered laterally, and positioned such that the bottom row of nozzles was at a height of 6 cm above the distributor plate, while the top row was at 14 cm above the distributor plate. The minimum fluidization velocity was determined experimentally to be 11.4 cm/s, which translates into a minimum fluidization flow rate ($Q_{mf}$) of 20.5 L/min. Total flow rates, $Q_b$, were varied from 1.5 to 4.0 times $Q_{mf}$. The primary gas flow ($Q_p$) also varied from 1.5 to 4.0 times $Q_{mf}$; the minimum $Q_b = 1.5 \times Q_{mf}$ was chosen to ensure that the entire bed was always well fluidized. The secondary gas flow ($Q_s = Q_b - Q_p$) was varied from 0 to 2.5 times $Q_{mf}$.

The helium tracer could be injected either into the primary or into the secondary gas. The helium concentration was measured near the surface of the bed as a function of time with a Valco Instruments Company micro-volume thermal conductivity detector (TCD).
The entire system was located within a temperature-controlled cabinet. Both primary and secondary airflows were humidified to prevent the build-up of static charge in the column, preventing agglomeration of the particles or freezing of areas of the bed. This was accomplished by passing the gas streams through heated columns packed with 5 mm glass beads and with water feeds controlled by peristaltic pumps. The water pumps were controlled relative to the set points of the mass flow controllers controlling the airflows (and not to a dew point meter) in order to minimize the number of outputs required on the data acquisition system. The relative humidity for both flows was kept constant at 50% for all flow rates, although changes in the humidity of the incoming plant air may have affected the total humidity slightly.

Helium Tracer Injection

Helium was used as the tracer because of its inert properties and large thermal conductivity relative to that of the fluidizing air, which makes it very easy to detect with a TCD. A helium injection system was designed and built specifically for these experiments (shown in Figure 4-2). There are three parallel lines, two air lines for the primary and secondary gas flow, while the third is a constant-volume sample loop and purge line for the helium tracer. The tracer line is only linked to one air line, but a set of 3-way valves permits the two incoming airflows to be interchanged, allowing tracer injection into either stream. To keep the flow rates constant, the tracer line and the associated air line both have the same internal volume. Since the tracer line contains a loop to hold the tracer ‘slug’, a similar loop was installed in the air line. All of the valves can be controlled remotely for automation purposes. This system is fully automatic and controlled by LabView™ software. The data acquisition system starts sampling at the exact moment the valves are switched to inject the helium slug into the air stream.

Figure 4-2: Simplified schematic of the tracer pulse injection system; the flow is always kept constant. With the use of the three-way valves, it is possible to inject the tracer into either the primary or the secondary gas. A representation of the fractal injector is located within the column on the right-hand side.
A disadvantage of this system is that the valve changes cause pressure waves. If uncontrolled, these pressure waves can influence the fluidization behaviour for a short period of time (< 1 s). These waves are exacerbated if the pressures in the lines that the valve is switching between are unequal. In order to minimize the waves, the pressures in the individual lines were controlled and buffers were installed on the lines leading to the bed (not shown in the schematic). There is a trade-off with the use of buffers, however, because increasing the volume of the buffer to better dampen out the pressure wave also causes greater dispersion of the tracer slug before it arrives at the column. Due to the length of the lines leading to the column and the fact that the windbox is also a good mixing cell, the buffers (one on each line) were kept as small as possible. With these techniques the pressure fluctuations induced by the valves were limited to only a few millibars. The dispersion of the helium tracer is, however, still significant. If the amount of dispersion were the same at all experimental conditions, then the data would be affected in the same way, and comparisons could still be drawn. The dispersion, however, is highly dependent on the flow rate and whether it is injected through the windbox or the fractal injector. As a result, the tracer responses measured at different conditions will have undergone different dispersion processes and will no longer be consistent with one another. To solve this issue, a deconvolution method developed by Mills and Dudukovic [17] was used. This technique allows the estimation of what the tracer response at the outlet of the reactor would have been had the tracer been introduced into the bed as an ideal pulse. To do this, the concentration of the tracer entering the bed (the input signal) had to be measured in addition to the concentration of the tracer leaving the bed (the output signal). The transfer function of the bed could then be calculated from these two signals. Further details about the method are provided in the Appendix.

Measurements of the Input and Output Signals and Error Analysis

The primary input signals were measured directly above the distributor plate without particles in the bed to prevent the force exerted by the particles from shifting the probe. The secondary input signals were measured at the outlet of an injector nozzle, also without particles present. Each input signal was measured 50 times and found to be highly reproducible.

The output signals for both cases (i.e., tracer injection through the windbox or through the fractal injector) were measured at approximately 2 cm above the surface of the bed at precisely the same lateral location. It was found previously both in our laboratory as well as by Al-Sherehy and co-workers [4], that the secondary gas mixes very quickly, and was thus
well distributed across the cross-section of the reactor, which implies that one sampling position is representative of the overall surface, at least at reasonably low gas velocities. At higher gas velocities (greater than those studied here), non-uniformities can occur because the large bubbles tend to migrate towards the middle of the bed. Thus a probe position at the wall could miss the tracer in the bubble.

A large portion of the tracer gas is carried to the surface of the bed in bubbles, and as these bubbles erupt they eject little pockets of tracer gas, which is detected by the TCD. The residence times are quite short; therefore relatively few bubbles are detected. The bubbles also behave chaotically, which means that the bubbles will erupt at different locations and at different time intervals. As a result, the signal can vary considerably from one sample to the next because the number and size of the bubbles is unlikely to have been the same during subsequent measurements (Figure 4-3). Therefore, to obtain the general behaviour of the system, 200 samples were measured, and the average was used as a representative average output signal in all further calculations. A typical averaged output signal is shown in Figure 4-A1, in the Appendix. In all cases the sampling time was 20 seconds.

![Figure 4-3: Three typical examples of individual output tracer response signals, before averaging. The curves have been offset on the ordinate for clarity. The effect of bubble eruption at the surface of the bed is clearly seen.](image-url)

A special note on error analysis is required here because each of the 200 samples is measuring a different set of bubble events. Calculating a standard deviation or a 95% confidence interval on the average signal of the 200 samples is non-trivial, because the
distribution of errors between an individual sample and the mean is not necessarily Gaussian, since these are not measurements of the same event. In order to estimate the error, the samples were randomly grouped in subsets and their means calculated. The overall error was estimated by subtracting the overall mean from the grouped-set mean, and then the normality of the error was tested using the Lilliefors test statistic (a goodness-of-fit to a normal distribution test based on the Kolmogorov-Smirnov test). In this way a minimum of 10 samples per group was determined to be required in order for the error to be Gaussian and thus representative of the true error surrounding the overall average signal. Looking at Figure 4-3, this makes physical sense: one individual signal is representative of only those few bubbles that have passed in 2-3 seconds, while a grouped subset emerges from dozens of bubbles, a statistically better measure for the fluidized bed behaviour. Therefore, the 200 samples were randomly assigned to 20 groups. The standard deviation of the group means was used to estimate the true error associated with the overall average signal. The error was estimated through subsequent calculations using standard propagation techniques. One notable exception, however, is the deconvolution calculation. Strictly speaking, the normality of the error distribution is not necessarily preserved through non-linear transformations, such as Fourier transforms. In this case, a simplification representing the worst-case scenario of the error estimate was chosen by assuming that the errors are additive. The 95% confidence intervals surrounding the RTD results, presented later, are the result of this error analysis.

Due to the number of samples needed and the number of flow rates studied, a full data set (the set containing the data of all flow rates studied) took approximately one week to obtain. Therefore, factors such as barometric pressure and outside air humidity possibly varied over the course of a data set, as well as between data sets. Three full data sets were measured to have an idea of this variability.

*Bubble Size Measurements*

As reported earlier, secondary injection with a fractal injector significantly reduces the size of the bubbles in a bubbling fluidized bed. It is useful to conduct more bubble size measurements here for the purpose of completeness and to help characterize the effects of secondary injection on the residence time distribution. The experimental procedure will be briefly described here. More extensive details can be found in van der Schaaf et al. [18] and Kleijn van Willigen et al. [19]. It has been shown that pressure fluctuations in a fluidized bed are made up of fast wave global processes (perceived everywhere in the bed simultaneously), such as bubble formation and coalescence, and slow wave local processes (perceived only in small regions), which are associated with the rising bubbles. The pressure fluctuation signal sampled at relatively high frequencies (>200 Hz) can be decomposed into its coherent part.
Gas Residence Time and Mixing

(representing the global waves) and incoherent part (representing the local waves) using spectral analysis. This decomposition is done by comparing the time series obtained at any given height in the bed to the time series obtained in the windbox (or just above the distributor plate).

The variance of the incoherent part of the pressure fluctuation signal, \( \sigma^2_{\text{IOP}} \), is directly related to the bubble size. In quasi-2D beds, that means the frontal area of the bubble. A calibration constant needs to be calculated from associated video analysis experiments in order to obtain the absolute bubble size from the pressure fluctuations. Here, however, it is sufficient to only look at the relative bubble sizes, i.e., the ratio of the bubble sizes that occur with secondary injection to the bubble sizes that occur without secondary injection at the same total flow rate. For each experiment, ten minutes of data were collected, providing enough information for good statistics. The pressure fluctuations were measured with Kistler piezoelectric pressure transducers, model 7261. The pressure probes were made of copper tubing with an inner diameter of 4 mm and approximately ten centimeters long – well within the guidelines presented by van Ommen et al. [20] for the optimal probe size for dynamic pressure measurements. The signals were amplified and high-pass filtered at 0.16 Hz to prevent signal drift [19] using Kistler type 5011 amplifiers and simultaneously sampled with an LMS-Difa SCADAS III data acquisition system.

The bubble size results presented here were obtained with the fractal injector submerged in the bed for all experimental conditions, including those with no secondary gas. Previous results have shown that the injector itself (without secondary flow) can reduce bubble size on the order of 10% [3]. The results reported here demonstrate further bubble reductions with respect to this already (slightly) reduced bubble size.

The estimation of errors in the bubble size results is somewhat simpler than for the residence time experiments. The whole signal (ten minutes) was cut into two-minute segments, long enough to be representative of the entire signal. The 95% confidence interval was then calculated over these segments, and this is the error reported in the bubble size results presented later.

4.6. Results and Discussion

Bubble Size Measurements

As discussed earlier, the variance of the incoherent part of the pressure fluctuations are a good measure of the bubble size (defined here as the frontal area of the bubble in a quasi-2D
Gas Residence Time and Mixing

Figure 4-4 shows the bubble size as a function of the secondary flow rate for different total flow rates at two different heights in the bed, 19 and 30 cm above the distributor. It is clear that secondary injection via a fractal injector significantly reduces the size of the bubbles at all total flow rates. The bubbles become smaller as the amount of secondary gas is increased. Remarkably, the range of the effect is very long: we could have expected to return to the normal case soon after rising above the area containing the fractal injector (the maximum height of the injector is 14 cm). This is not the case, however, with significant bubble size reductions at 30 cm and even higher in the bed. This delayed bubble growth and agglomeration can be attributed to the good uniformity of the gas flow distributed by the fractal injector. The gas is well distributed across the area of the bed, which helps to prevent bubble coalescence and minimize the gulf streaming of bubbles through the middle of the bed, while breaking up existing bubbles.

![Figure 4-4: A measure for bubble size ($\sigma^2_{IOP}$) as a function of the secondary flow rate at different total flow rates at (top) 30 cm and (bottom) 19 cm above the distributor plate. The effect of the secondary injection is evident far above the fractal injector (the top of the injector is at 14 cm above the distributor plate).](image)

Figure 4-5 shows the bubble size obtained with secondary injection as a fraction of the bubble size obtained at the same total flow rate without secondary injection at the two different heights studied. The maximum bubble size reductions of 50% (at 30 cm) and 70% (at 19 cm) were achieved at the highest secondary flow rates. Earlier results [2, 3] have
shown that the total volume of bubbles decreases, while the amount of gas in the emulsion phase increases. The combined effect of these results is that the use of secondary injection significantly improves the gas-solid contact. It is interesting to note that the curves at a sufficiently high total flow rate collapse onto a single line. In other words, a given secondary flow breaks bubbles up to an extent that is independent of the primary flow. This may be useful in the prediction of bubble size reductions at other flow rates.

![Graph showing bubble size reduction with secondary gas flow rate](image)

**Figure 4-5:** Bubble size (characterized by \( \sigma_{IOP}^2 \)) normalized by the bubble size in the absence of secondary injection as a function of the secondary gas flow rate.

**Average Gas Residence Time**

Figure 4-6 shows the average residence times of three averaged data sets, measured at three different dates as discussed in the Experimental section, as a function of the secondary flow rate for different total flow rates. The results indicate that there is a slight decrease in the residence time with increasing secondary flow rate. These results are not expected on the basis of the simple model discussed in the introduction. One hypothesis for this decrease is that, since the dense phase porosity is increasing [2, 3], the particles are more mobile and can more easily flow around rising bubbles. Such a decrease in bubble flow resistance would result in a higher bubble velocity, even though the decrease in the bubble size would have the opposite effect. In addition, the gas velocity in the dense phase itself may also increase.
because of the greater gas flow through it. More work is needed to determine the exact reasons for the slight decrease in average residence time. Whatever the true explanation is, it is almost certainly coupled to a change in the hydrodynamics of the system.

Interestingly, a few of the curves appear to be significantly different from their “replicates”, measured on different days, despite the fact that most physical parameters were controlled, e.g., cabinet temperature and humidity of the flow, and the averaging over no less than 200 measurements. Figure 4-7 shows the comparison between the three sets at a total flow rate of $2.5 \times Q_{mf}$. There must be some other factor changing between, and even during, experiments. This change could be due to something as simple as a change in the humidity of the incoming air from the compressor or as abstract as a change in the chaotic state of the fluidized bed [21]. It is not certain what causes the differences in the replicates. As a result it was chosen not to average the results, but to present each data set separately.

Figure 4-6: Average residence times for three averaged data sets (a, b, and c) as a function of the secondary flow rate. The error bars represent the 95% confidence intervals. There is a slight decrease in the average residence times.
Figure 4-7: An example of the difference between the three data sets. The total flow rate is $2.5 \times Q_{mf}$. There can be large differences between the data taken at different times.

Figure 4-8 shows the ratio of the average residence times to the base average residence time (the case without secondary flow at the same total flow rate) for each replicate as a function of the secondary flow rate. We would expect all of these curves to lie along the horizontal at a value of 1. As already shown above, there is a slight decrease in $\tau$ with increasing secondary gas flow. The maximum decrease in residence time is approximately 15%, while most of the data shows less than 10% decrease. This decrease is small and should have little impact on the conversion of a chemical reaction, particularly one that is mass transfer limited. Note that the residence times are very short as well. Thus, reliably detecting small changes on these short time scales is difficult. It would be useful to study the effect of secondary injection in a fluidized bed with longer residence times to better resolve the differences.

The positive effect of the improved gas-solid contact resulting from the reduced bubble size should overcome the small decrease in residence time. As a result, secondary gas injection via a fractal injector is expected to improve reactor performance.
Figure 4-8: The ratio of the average residence times with secondary gas injection to the average time obtained without secondary injection, at the same total flow rate. Results are presented for different total flow rates and as a function of the secondary gas flow rate for each of the three data sets (a, b, and c). There is a maximum decrease of ~15%, but most reductions are below 10%.

**Macromixing Characteristics**

Figure 4-9 shows the calculated reactor Péclet number, $Pe$, as a function of the secondary flow rate for the various total flow rates. The reactor Péclet number gives insight into how the overall macromixing characteristics of the system are changing when secondary gas is introduced through a fractal injector. It is apparent that with increasing secondary flow, $Pe$ increases, which indicates that the amount of back-mixing is decreasing. This is a good indication that the fractal injector induces air staging, meaning that the overall hydrodynamics is being broken into smaller cells. These smaller cells cause a reduction in the upstream dispersion of the gas. At the higher secondary flow rates this trend levels off, and in some cases, starts to decrease again. This result suggests that more secondary injection points may be desired to better distribute that gas at these higher secondary flow rates, as the bubbles will tend to break up the induced stages. It is important to note that, within the range of flows studied, the Péclet number never drops below the case without secondary injection. As a result, reduced axial dispersion is assured with secondary injection via a fractal injector.
Figure 4-9: The reactor Péclet number as a function of the secondary gas flow rate for different total flow rates for each data set (a, b, and c). The plug flow behaviour increases significantly before leveling off, and in some cases, decreases again.

4.7. Conclusions

An experimental study into the effects of secondary gas injection in a bubbling fluidized bed indicates that there is a decrease in the average residence time, but that this decrease is small. Importantly, the bubble size is being greatly reduced, which results in improved gas-solid contact. For heterogeneously catalyzed chemical reactions, this enhanced contact is of greater importance than a slight reduction in the average residence time. Secondary gas injection has also been shown to decrease the overall back-mixing of gas in a fluidized bed. The reduced axial dispersion and better gas-solid contact should improve the conversion and selectivity of a chemical reaction in a fluidized bed with secondary gas injection, although conversion experiments are required to quantify this improvement.

4.8. Acknowledgements

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4.9. Notation

- $C$: Second-order difference matrix, a smoothing function that limits the vertical distance between consecutive data points.
- $C(t)$: Tracer concentration distribution.
- $E(t)$: Residence time distribution.
- $F$: Fourier transform.
- $f(t)$: Combined tracer response of the system for all inputs and outputs of the system.
- $F^{-1}$: Inverse Fourier transform.
- $f_i(t)$: Tracer response at the only outlet as a result of an ideal pulse at inlet $i$.
- $f_{ij}(t)$: Tracer response at outlet $j$ as a result of an ideal pulse at inlet $i$.
- $p$: Fraction of total gas flow that is primary gas flow, [-].
- $P_e$: Reactor Péclet number, [-].
- $Q$: Volumetric flow rate, [m$^3$/s].
- $Q_{of}$: Minimum volumetric flow rate required for fluidization, [m$^3$/s].
- $Q_p$: Volumetric flow rate of the primary gas, [m$^3$/s].
- $Q_s$: Volumetric flow rate of the secondary gas, [m$^3$/s].
- $V$: Volume, [m$^3$].
- $x$: Input signal for the deconvolution, the signal measured at the exit of a gas inlet.
- $y$: Output signal for the deconvolution, the signal measured at the top of the bed.
- $z$: Deconvolved signal, i.e., the desired tracer response.

Greek and Symbols

- $*$: Denotes the complex conjugate.
- $\sigma^2$: Variance, [s$^2$].
- $\sigma^2_{IOP}$: Variance of the incoherent part of the pressure fluctuation signal, which is directly related to the frontal area of a bubble in a quasi-2D fluidized bed, [A.U.].
- $\tau$: Average residence time, [s].

4.10. Appendix - Deconvolution

Mills & Dudukovic [17] reported on a particular application of deconvolution, which allows one to determine the transfer function that was applied to a set of known data to obtain another set of known data. Applied to the system studied in this paper, the transfer function determines how a fluidized bed alters the entering dispersed helium slug to obtain the helium measurement at the top of the bed. In other words, deconvolution deduces what the helium concentration at the top of the bed would have been had the tracer been injected as an ideal...
pulse. To do this, measurements are needed of the helium concentration entering the bed (the input signal), in addition to the tracer concentration at the top of the bed (the output signal). These signals are denoted here as $x$ and $y$, respectively. To perform the deconvolution these signals are taken into the frequency domain; the transformed output is divided by the transformed input; and the result is transformed back into the time domain, as in:

$$z = F^{-1} \left( \frac{F(y)}{F(x)} \right)$$

(4.13)

where $z$ is the desired signal, $F$ is the Fourier transform, and $F^{-1}$ its inverse. This assumes that the signals are fully dependent in a deterministic way. The fluidized bed acts as a transfer function that transforms one signal into another. A complicating factor is that measurements contain a stochastic component or "noise". During the deconvolution operations, this noise could be amplified to such an extent that it completely masks the signal being sought (Figure 4-A1). Mills and Dudukovic present a smoothing technique based on second-order differences that removes this noise:

$$z_{\text{smoothed}} = F^{-1} \left( \frac{F(y)}{F(x)} \right) \left( 1 + \frac{F(C) \cdot F(C)^*}{F(x) \cdot F(x)^*} \right)$$

(4.14)

where $C$ is the second-order difference coefficient matrix, $\gamma$ is a scalar quantity, and $^*$ denotes the complex conjugate. The reader is referred to Mills and Dudukovic [17] for a derivation. One drawback of this technique is that the required magnitude of the smoothing, $\gamma$, has to be guessed. If $\gamma$ is too small, then the signal will still be too noisy, if $\gamma$ is too large, then the curve will be over-smoothed with the result that the distribution broadens, which has an impact on the interpretation of the results, such as overestimating the amount of mixing occurring. In this work, this issue is resolved by testing a range of $\gamma$ values and selecting those that give a relatively noise-free result. To ensure that the signal was not over-smoothed, the resulting smoothed signal is re-convolved with the original input signal to obtain a new output signal, using:

$$y_{\text{new}} = x \otimes z_{\text{smoothed}} = F^{-1} \left( F(x) \cdot F(z_{\text{smoothed}}) \right)$$

(4.15)

This new output signal is compared with the original output signal and if the peak has not broadened with respect to the original one, then that particular value of $\gamma$ is deemed sufficient for that set of data. Care should be taken here. If different values of $\gamma$ are used for different experiments, then the results will have different amounts of smoothing and thus possibly different amounts of noise still present in the signal. This remaining noise may cause artificial differences in average residence times. Since the experimental apparatus and operation conditions are identical (with the exception of gas flow rates) the value of $\gamma$ is not
expected to change, although there could be a different $\gamma$ depending on whether the tracer is injected through the windbox or the fractal injector, since there are more significant differences in the flow path of the tracer. Therefore, one single $\gamma$-value of $1 \times 10^{13}$ was applied to all experiments.

![Graphs showing smoothing results for different $\gamma$ values.](image)

**Figure 4-A1:** Smoothing is critical in order to obtain the desired signal after deconvolution. Shown here are the results for four different $\gamma$ values, indicated in the upper right hand corner of each plot.

### 4.11. References

The previous chapters have shown that the mass transfer and gas-solid contact in a bubbling fluidized bed are being significantly improved with the use of distributed secondary gas injection via a fractal injector in a 2-D column. These results indirectly indicate that the conversion should increase, at least for the case of a mass transfer-limited reaction. This chapter extends these studies to a more realistic 3-D column using the 2.6-dimensional fractal injector shown in the introduction, and presents the results of a direct study of the influence of secondary injection on the conversion and selectivity in a fluidized bed reactor.

The results indicate that all of the previous trends seen in the 2-D bed still hold in the 3-D system. In this case, collapse tests are used to determine the bubble fraction instead of video analysis, which is no longer possible in a 3-D bed. Although collapse tests of Geldart B particles were inconclusive, experiments using Geldart A particles showed a massive decrease in the bubble fraction. Further hydrodynamic experiments with Geldart A particles (bubble size, mixing, etc.) showed that, even though Geldart A particles exhibit a maximum bubble size, secondary injection is still effective in reducing the size and improving the gas-solid contact. Furthermore, a model previously developed is further refined and shown to adequately describe a new set of conversion experiments. The model does not take into account an increase in the dense phase flow and, as a result, can only describe the experimental data when an increase in interaction between the bubble and dense phases is assumed via increased micromixing around the injection points. This model is applied to the production of maleic anhydride, a much more complex reaction, and the production and selectivity of maleic anhydride are found to increase, even without optimization of the feed concentrations.

The results of this chapter give direct evidence that distributed secondary gas injection via a fractal injection increases the performance of a bubbling fluidized bed reactor. This study also shows that the fractal injector has great potential for reactions of industrial interest. A few aspects of applying this technology in industry are discussed.
This chapter has been accepted for publication as:

5.1. Abstract

Distributed secondary gas injection via a fractal injector was studied in a lab-scale 3-D fluidized bed to determine its effect on bubble size, bubble fraction, residence time, mixing, and conversion. The experimental results indicate improved reactor performance and are consistent with earlier work in 2-D beds. A model was developed based on simple two-phase theory that describes the effect of distributed secondary injection on the performance of ozone decomposition in a bubbling fluidized bed. The model was used to predict the performance of a reactor for the production of maleic anhydride from n-butane, which includes consecutive and side reactions. The results showed that the production and selectivity of maleic anhydride were significantly improved. It can be concluded that distributed secondary gas injection improves the mass transfer and gas-solid contact, which results in increased reactor performance. It likely achieves these improvements by enhanced gas flow through the dense phase, and more micromixing around the injection points, which causes greater interaction between the phases. Some aspects of applying this technology in industry are discussed.

5.2. Introduction

Interphase mass transfer in bubbling fluidized bed reactors is often poor because most of the reactant gas is contained in bubbles that are nearly devoid of catalyst particles. This poor gas-solid contact suppresses the conversion and forces the use of recycle streams or larger reactors to obtain the desired production rates. In addition, the bubble hydrodynamics are chaotic and scale-dependent, which complicates the scale-up of bubbling fluidized beds. Both challenges can be overcome by structuring the hydrodynamics of the bed in such a way as to reduce the bubble size and encourage more predictable, scale-independent behaviour.

Previous studies on distributed secondary gas injection, whereby a portion of the total gas flow is introduced into the column via a fractal injector, Figure 5-1, have shown promising results. In a study in a quasi 2-D column using 550 μm glass beads, it was found that the bubble diameter was reduced by more than 50%, bubble coalescence was significantly hindered, and the bubble fraction in the bed was lowered [1]. These results suggest that the flow through the dense phase is higher to account for the decrease in the total bubble volume. This implies improved external mass transfer because of the reduced bubble size, but also increased gas-solid contact by the higher gas flow through the dense phase. In addition, residence time distribution (RTD) experiments in a 2-D column revealed that the overall gas back-mixing decreases with distributed gas injection, although the average gas residence time also slightly decreases [2]. The improved plug-flow behaviour and the large
decrease in bubble size are expected to more than compensate for this small decrease in residence time, particularly since it is expected that the gas-solid contact time is increasing, which is more important for heterogeneously catalyzed reactions [3,4].

The use of a fractal injector partially addresses the problem of reactor scale-up as it is trivial to scale up (self-similar) fractal structures by adding additional generations of the repeating geometric unit. If the distributed gas injection imposes a structure on the hydrodynamics then it is more likely that this structure will persist after proper scaling of the fractal injector, facilitating the scale-up process of the reactor. Scale-up experiments, however, are required to support this assertion. This issue is not discussed here.

The previous work focused on the hydrodynamics of a 2-D non-reactive system. The purpose of the current study is threefold: first, to extend the previous work to more realistic 3-D systems to determine if the previous conclusions still hold; second, to quantify and explain the effect of distributed secondary gas injection on the performance of a bubbling fluidized bed reactor, and in particular to determine the repartition of secondary gas between the dilute and dense phases; and finally, to develop a reactor model that adequately describes the effect of distributed secondary gas injection on the conversion and selectivity in a fluidized bed reactor to gain further insight into the gas distribution. In addition to residence time distribution experiments and bubble size measurements in a 3-D column, collapse tests were performed to characterize the effect of secondary injection on the bubble fraction, since this cannot be done in 3-D systems via video analysis, as was done in 2-D systems [1].

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**Figure 5-1:** (a) Schematic of a fractal injector inside a fluidized bed; (b) photograph of a fractal injector prototype with a fractal dimension of 2.6 for use in 3D columns.
test also has the advantage of allowing the determination of the dense phase voidage [5]. The effect of distributed secondary gas injection on conversion is determined using ozone decomposition as a test reaction using the same bed material in the same 3-D bed as in the other experiments described here. Using the same conditions enables us to maintain a consistent set of experimental parameters to allow for a complete description of the system. A model, developed previously [6], is further simplified and refined using the latest experimental results of the ozone decomposition test reaction. It is used to predict the conversion and selectivity of the partial oxidation of n-butane to form maleic anhydride, which has consecutive and side reactions, and is an industrially useful reaction.

5.3. Experimental

Experimental Setup

All results were obtained using the same column, particles, and bed mass, except where noted, in order to achieve a consistent description of the effects of distributed secondary gas injection. The column used was a 10 cm I.D. Perspex column, 70 cm tall. The column contained measurement ports every 5 cm axially. The distributor used was a sintered stainless steel porous plate. The fractal injector used is 2.6-dimensional (i.e., non-volume filling) and has 72 injection points distributed over 4 heights (Figure 5-1b). The heights of the injection points were 6, 12, 18, and 24 cm above the distributor. All experiments used a bed mass of 1.8 kg, which gave a settled bed height of 30 cm. Sieved Sasol Puralox alumina, with a \(d_{50}\) (diameter at which 50 mass% of the solids have a smaller diameter) of 318 \(\mu m\), was used as the bed material. The particle size distribution was approximately Gaussian with a standard deviation of 49 \(\mu m\). The particle density was 1290 kg/m\(^3\), and the loose bulk density was 793 kg/m\(^3\). The minimum fluidization velocity was determined to be 2.9 cm/s. Static effects can have an influence on the fluidization behaviour. Therefore, the relative humidity of the fluidizing gas was controlled at 20% (±2%) to minimize static effects, except in the conversion experiments, where water content has a very strong negative influence on the reaction kinetics. The sensitivity of the reaction kinetics to the moisture content implies that the humidity should be extremely stable to obtain reproducible results, and low to avoid kinetic limitations. For these experiments, dry air, with a relative humidity of 1% (±0.3%), was used. For consistency, the bubble size was also determined at these dry conditions. The column was contained in a climate-controlled cabinet, where the temperature of the surroundings and of the gas was 30°C, except for during the conversion experiments; the temperature for these experiments was 55°C to enhance the reaction rate. This difference in temperature between the various experiments is relatively small, and is not expected to result in significant changes in the hydrodynamics of the fluidized bed. All experiments, even
without secondary gas, were performed with the fractal injector physically present inside the bed to ensure that any differences seen between the experiments are related to the distribution of the gas inside the reactor and not due to the internals themselves. All experiments within a particular experiment type were randomized as much as possible to prevent possible time-related drifts from producing artificial trends in the data.

**Bubble Size Measurements**

The bubble size in a fluidized bed can be determined from spectral analysis of pressure fluctuations using the method proposed by Van der Schaaf et al. [7] and validated by Kleijn van Willigen et al. [8]. The basic principle is that pressure fluctuations measured at sufficiently high frequency (200 Hz, in this case) capture both the fast pressure waves generated by phenomena such as bubble eruption that are felt simultaneously throughout the bed, and slow phenomena such as bubble passage that are only felt locally. These two components in the pressure fluctuation signal can be separated from each other by spectral decomposition. The standard deviation of the local component, called the incoherent output power ($\sigma_{IOP}$), is directly and linearly related to the bubble diameter at the height of the sensor. Typically, a calibration factor (usually obtained from video analysis or optical probes) is required to determine an absolute bubble size with this technique, but, for our present purposes, only the relative change in bubble size with respect to the case without secondary injection is required, so that calibration was not needed. For more information regarding this technique, the reader is directed to the references listed above. Kistler type 7261 piezoelectric pressure transducers and Kistler type 5011 amplifiers were used to measure the pressure fluctuations at two locations – the reference sensor located in the windbox, and the other one at 30 cm above the distributor. The signals were sampled at 200 Hz and a high-pass filter at 0.16 Hz was used to remove sensor drift. The pressure transducers were connected to sample ports in the side of the bed at those locations by 10 cm long $\times$ 4 mm inner diameter metal tubes, well within the probe size recommendations proposed by van Ommen et al. [9]. A fine wire mesh (45 $\mu$m) was glued over the tube ends to prevent particles from blocking the sensors. These measurements were taken simultaneously with the conversion experiments described later. Six minutes of pressure fluctuation data were taken for each experiment.

**Collapse Tests**

Collapse tests give information about the bubble volume and amount of gas in the dense phase, which can be used to calculate the bubble fraction, $\epsilon_b$, and the dense phase porosity, $\theta_d$. A collapse test is conducted by suddenly shutting off the flow to the fluidized bed while
simultaneously measuring the bed height with time. The bed collapse can be described in three regions. Firstly, the gas in the bubbles escapes as it typically has a much higher velocity than the gas in the dense phase. This is recorded as a very sharp decrease in bed height. Secondly, the gas in the dense phase escapes at a slower and constant rate, resulting in a linear and more gradual decrease in bed height. Finally, the bed settles, or consolidates. These stages are denoted as I, II, and III in Figure 5-2. The line defining the dense phase collapse can be extrapolated backwards to give the fluidized bed height as if bubbles were not present. This height, along with the bubbling bed height, is used to calculate the desired parameters [10]. An inherent assumption in this analysis is that the gas in the dense phase continues to flow at the same rate in the bubble escape region, or, in other words, that the flow of bubbles does not influence the dense phase gas velocity.

Figure 5-2: Typical collapse curve of a bubbling bed of fine particles, where $H_{bub}$ is the total bubbling bed height, $H_{ex}$ is the height of the expanded dense phase, $H_{settled}$ is the settled bed height, $t_{bub}$ is the bubble escape time, $t_c$ is the bed collapse time, and $t_{end}$ is the total time including the consolidation stage. Figure adapted from Park et al. [12].

To prevent windbox gas from leaking across the distributor after the flow is shut off, which affects the collapse rate of the bed [5], the two-valve method was used [11,12], whereby the windbox is evacuated via another valve at the same moment that the flow is shut off. It has been shown that if the pressure drop over the distributor is sufficiently high then gas from the bed will not flow back into the newly depressurized windbox [12]. This arrangement simplifies the interpretation of the experimental data. In addition, since there are two gas streams entering the bed, one via the windbox, the other via the fractal injector, both flows must be stopped simultaneously. This was accomplished by using similar electronic valves, which have the same response time, on each gas line. These valves were computer-controlled using a common signal as a trigger. This ensured that the gas flows were cut off at precisely the same moment. It should be noted that the single-valve method was used on the fractal injector, but the internal volume of the injector is so small that any gas leakage into the bed is negligible.

Collapse tests are usually done with Geldart group A or C powders because they have slow, and easily measured, rates of de-aeration. Geldart group B powders are typically not used because the de-aeration rate is very fast and it is assumed that the dense phase expands
very little. Thus, if this were true, one would expect the bed to drop almost immediately to the packed bed state. We would like a simple way to determine the bubble fraction and dense phase voidage with the group B particles in the 3-D bed. This is usually not possible without the use of advanced radiation or capacitance techniques. The dense phase in a Geldart B particle bed does expand slightly, however, and we attempt here to capture this expansion with collapse tests using a high-speed video camera at 800 fps. Experiments using a Geldart group A powder (63-75 μm diameter, particle density of 1400 kg/m$^3$, loose bulk density of 770 kg/m$^3$, \(U_{mf}\) of 0.24 cm/s) were also carried out using the high speed video camera at 200 fps.

During the experiments, the relative humidity had to be increased to 50% to reduce the number of particles sticking to the wall. Even though, at the lower relative humidity of 20%, only relatively few would do so, their presence makes it more difficult to determine the bed height from video analysis.

*Residence Time Distribution Experiments*

The RTD experiments in the current study were conducted in the same 3-D column as previously mentioned. The experimental setup and data analysis were exactly the same as were extensively reported in an earlier study [2], with the exception of the 3-D column and particles. The basic concept was to inject helium tracer into the fluidized bed through either the primary or the secondary gas. The concentration of the helium was measured just above the bed surface using a thermal conductivity detector. Since the injected helium was a non-ideal pulse because the windbox acted as a mixing cell, the normalized measured outlet concentration was not the RTD. The desired RTD was the transfer function that linked the inlet distribution with that of the outlet. To calculate this transfer function, the deconvolution method proposed by Mills & Dudukovic [13] was used. Once the RTD’s for both the primary and secondary gas were obtained, they were combined into one overall RTD for the gas in the fluidized bed using the theory proposed by Buffham and Kropholler [14]. Standard residence time theory was used to calculate the average residence time and the variance of the distribution. The variance is the width of the residence time distribution and is a measure for the macroscopic mixing (axial dispersion) in the system. A small value of the variance means that the gas flow is approaching plug flow behaviour, whereas a large value means that the gas flow is well-mixed.
Conversion Experiments

To determine the influence of distributed secondary gas injection on the performance of a bubbling fluidized bed reactor conversion experiments were carried out using ozone decomposition as a test reaction. Ozone decomposition in a fluidized bed has no industrial value, but it is a good test reaction because ozone is easy to generate and detect at very low concentrations. Using low concentrations implies that the reactor will operate isothermally and that volume change due to reaction is negligible. Another advantage of this reaction is that it can be carried out at low temperatures, which allows the use of the same equipment used in the hydrodynamic studies.

Ozone was generated by an OAS Coolflow O$_3$ generator using a mixture of 20 vol% oxygen and 80 vol% argon as the feed. The use of this mixture instead of air greatly improved the stability of the generator as well as the stability of the catalytic activity of the alumina particles. It is surmised that nitrogen forms nitrogen oxides when it passes through a corona discharge [15]. This NO$_x$ not only scavenges the oxygen radicals and suppress the ozone production, but also poisons the catalytic sites on the alumina catalyst. The flow through the ozone generator was kept constant at 4 L/min, by means of a mass flow controller and was mixed with air after the generator to produce the desired total flow rate. A static mixer was used to ensure concentration uniformity in the gas. The total flow rates studied were 4 and 5 times the minimum fluidizing flow rate (54.7 and 68.3 L/min, respectively). The amount of argon present only accounted for 5-7 vol% of the feed. Thus, the feed gas was considered to have the properties of normal air. The ozone concentrations were analyzed with an INUSA 2000 O$_3$ analyzer with a range of 0-100 ppm, and an accuracy of 0.1 ppm,. The ozone concentration in the feed was typically between 45 and 70 ppm, depending on the total flow rate. The temperature of the feed gas and the cabinet in which the column was located were heated to 55°C. The relative humidity was controlled to 1% (±0.3%). The gas was split into primary and secondary gas flows by means of two low pressure drop mass flow controllers. A pressure controller upstream of these flow controllers kept the system pressure constant. A constant system pressure helped to improve the ozone generator stability, which is particularly important when the concentrations are in the ppm range. The feed concentrations were determined by drawing a sample stream off of the feed line (after the flow controllers) by a vacuum pump and another mass flow controller (to keep the sample flow rate constant). The vacuum pump and flow controller were both located after the analyzer so the ozone comes into contact with as little bare metal as possible. The product gas sampling point was located in the freeboard of the fluidized bed. The sample was first drawn through a particle filter made of polymeric (i.e., non-metallic) material to prevent small particles from entering the ozone analyzer. The sample flow rate, either feed or product,
through the ozone analyzer was constant at 2 L/min. All the tubing that had ozone-enriched
gas flowing through it was made of Teflon™. A manual 3-way valve was used to switch
between feed sampling and product sampling. The alumina was found to be very catalytically
stable with no deactivation observed during these experiments. The reactor was fluidized at
the desired flow conditions with ozone-enriched gas. A one-hour period was required to
stabilize the ozone generator. Following that period, measurements were taken by first
measuring the feed for 2 minutes, followed by changing the valve, waiting 2 minutes, and
measuring the product for 2 minutes. After that, the valve was changed back, and the feed
was measured again for a further 2 minutes. The flow conditions were then modified to the
next desired experiment and allowed to stabilize for several minutes. Experiments with
secondary gas were always preceded and followed by an experiment at the same total flow
rate without secondary gas. This allowed the comparison of conversion data taken at nearly
the same times to remove any possible time-dependent effects such as solids build-up in the
particle filter or limited catalyst deactivation.

5.4. Results and Discussion

Bubble Size

One of the goals of this study is to determine the distribution of the secondary gas in the
dilute and dense phases of the reactor. With this in mind, it is useful to look at a previous
study that led to comprehensive bubble size data in a 2-D column with a settled bed height of
40 cm of 550 μm glass beads [1]. The top of the 2-D fractal injector was at a height of 14
cm. The original study presented the data in terms of the bubble size with respect to
increasing total flow rate for various secondary gas velocities (reproduced here in Figure 5-3).
These data show that the bubble size decreases with increasing secondary gas injection at a
constant total flow rate. This is an important result by itself, but it does not give us an
indication of the flow distribution in the reactor. However, the same data can be rearranged
and presented in a different way. Figure 5-4 shows the bubble size data as a function of
increasing flow for constant primary flow rates. The solid lines show the data with increasing
secondary flow, i.e., where the primary flow rate is constant and equal to the initial primary
flow rate, \( Q_p = Q_p^0 \), and the secondary flow rate is increasing. Thus the total flow rate in the
cases with secondary flow is \( Q_0 = Q_p^0 + Q_s \). The dotted lines show the cases with only
primary flow, i.e., \( Q_0 = Q_p^0 + \Delta Q_p \) where \( \Delta Q_p \) is the increment in the primary flow rate. The
solid lines are very flat, i.e., the bubble size does not increase much beyond the size caused
by the primary flow, when measured at 19 cm above the distributor (5 cm above the fractal
injector). This implies that at least a portion of the gas being added via the fractal injector is
not making bubbles larger. This insight means that either the secondary gas is making new
smaller bubbles or is not going into the bubble phase at all. The data at 30 cm above the distributor is not quite as flat, but are still much lower than the cases without secondary flow. A possible explanation for this result is that the small bubbles generated by the secondary gas are starting to coalesce or that the extra gas that the influence of the injector stabilized within the dense phase is being ejected into the bubble phase as the dense phase reverts to its equilibrium condition. In either case, the secondary gas is not immediately contributing to bubble growth. Note that the data in both plots in Figure 5-4 are the bubble sizes at heights significantly above the fractal injector and the gas velocities at the injection points cannot be attributed to breaking up the bubbles at these particular locations. Therefore, a fundamental change in the hydrodynamics must be occurring.

Figure 5-3: Bubble size data previously reported for a 2-D column using glass beads (adapted from Kleijn van Willigen, et al.). $\sigma_{IOP}$, which is proportional to the bubble diameter, is shown as a function of $Q_0$ for various $Q_s$ (the data originally published were for $\sigma^2_{IOP}$, which is proportional to the area of a 2-D bubble) measured at (a) 30 cm and (b) 19 cm above the distributor plate. The top of the fractal injector is located at a height of 14 cm. The bars represent the 95% confidence intervals.

Figure 5-5 shows the new measurements of the relative bubble diameter in the 3-D bed for total flow rates of 4 and $5 \times Q_{mf}$ as a function of increasing secondary flow. Both curves show a decrease in the bubble diameter by as much as 30%. That means that the bubble volume is decreasing by nearly two-thirds, and the surface to volume ratio, so critical for mass
transfer, is increasing by almost 43%. The curve at $5 \times Q_{mf}$ does not decrease as smoothly as that at $4 \times Q_{mf}$ and the confidence intervals on the data are much larger. We surmise that at this high flow rate the bubble size distribution is much wider. As a result, the spread in the bubble size data is greater and there is more uncertainty. Taking longer data sets may reduce the size of the confidence interval and improve the smoothness of the curve. There is insufficient data to make a comparison such as that described above for the 2-D data, but this data is solid evidence that at least the qualitative trends between the 2-D and 3-D systems are similar, and that the bubble size reduction is not simply a 2-D phenomenon.

Figure 5-4: Data from Figure 5-3 rearranged to show $\sigma_{IOP}$ as a function of $Q_0/Q_p$. The curves with similarly shaped symbols are at the same $Q_0$. The data with solid symbols were obtained with $Q_s$ and the data with hollow symbols were obtained with only $Q_p$; measured at (a) 30 cm and (b) 19 cm above the distributor plate. The bars represent the 95% confidence intervals.
Figure 5-5: Relative bubble diameter versus secondary gas flow in the 3D column. (a) $Q_d = 4 \times Q_{mf}$ (b) $Q_d = 5 \times Q_{mf}$. Measured at 29 cm above the distributor plate. The top of the injector is located at 24 cm. The bars represent the 95% confidence intervals.

**Collapse Tests**

Collapse tests were carried out to determine the amount of gas in the bubbles and the amount of gas in the dense phase. We tested the 318 μm group B alumina particles in the experiment using a high-speed camera (800 fps) to monitor the bed height during its collapse. As expected, the bed collapse occurs very quickly, within 0.5 s. We found that the bed displayed ‘typical’ collapse behaviour only if there were no bubbles near the bed surface when the valves were shut off. This limitation arises because the bubbles in Geldart B powders are large and their eruptions have a serious influence on the measurement of the instantaneous bed height, particularly in the small setup being used. The result is that the obtained collapse curves are not reproducible, which makes interpretation very difficult. The four curves in Figure 5-6, obtained at a total flow rate of $4 \times Q_{mf}$ with no secondary gas, show this poor reproducibility. The solid black line shows the behaviour typical of group A powders but on a much smaller time scale, even though group B particles were used. However, we cannot be certain that this behaviour was not fortuitous. The biggest obstacle to interpret these results is that both the dense phase collapse and bubble escape occur simultaneously; there is no distinction between stage I and stage II. The variation between the collapse curves shown in Figure 5-6 can be attributed to differences in the instantaneous bubble hold-up. If the size and location of the bubbles are known in time, then by removing the effect of
Figure 5-6: Collapse curves of group B particles; $Q_d=Q_p=4\times Q_{mf}$ no $Q_s$

their volume on the instantaneous bed height would probably cause the resulting collapse curves to be much more similar. A mathematical technique looking at the convolution of the bubble effects, similar to the problem of distinguishing overlapping concentration peaks in chromatography applications, could be developed to study this possibility, but it would be an indirect method of determining the collapse properties and would likely require extensive validation. Simpler interpretation of collapse tests with Geldart B particles could be possible if many experiments were averaged together to obtain the mean behaviour. An analysis of the bubble eruption frequency at the bed surface would give insight into how many experiments would be necessary. A more practical solution may be to use a larger diameter column, as the bubble diameter to bed diameter ratio will be smaller, and individual bubble eruptions would not span the entire diameter, making the measured bed height fluctuations less severe. One obvious aspect, however, is that the number of experiments required will increase with gas velocity as the bubbling becomes more vigorous. The significant overlap in time scales of the two phenomena could remain an issue. Another observation in the group B collapse tests is that the bed height is lower with than without secondary gas, at the same total flow rate (not shown). This is further discussed below.
In light of the difficulties interpreting the Geldart B collapse results, we chose to test a Geldart A powder in the collapse experiments to gain insight into the effect of distributed secondary gas injection on the bubble fraction and the dense phase voidage. Alumina powder was sieved, and the particles retained between the 63 µm and 75 µm meshes were used as the bed material. The alumina is of the same type, and was manufactured by the same company, as the Geldart B material, but was from a different batch for smaller particle sizes. There is a significant difference in the fluidization properties of these two powders but we believe it is reasonable to expect that the effects that we are studying will be qualitatively similar in both cases, although possibly weaker with group B particles. We conducted experiments at two flow conditions, a base case with all gas as primary flow at $4 \times Q_{mf}$ and a case where the flow was evenly split between the primary and secondary streams ($Q_s=2 \times Q_{mf}$, $Q_p=2 \times Q_{mf}$). Five replicates at each flow condition were measured and found to be very reproducible. The averaged results are shown in Figure 5-7.

![Figure 5-7: Collapse curves of 63-75 µm group A particles with and without $Q_s$, $Q_0=4 \times Q_{mf}$](image)

The three stages of collapse are clearly visible, and the interpretation is straightforward [5]. The bubble fraction and dense phase porosities are presented in Table 2. The bubble fraction results show a similar trend to that observed in the earlier video analysis of the 2-D experiments [1], the bubble fraction decreases when secondary injection is used. In this
Table 2: Collapse test results using 63-75 µm alumina particles at a total flow rate of 4×Q_{mf}

<table>
<thead>
<tr>
<th>Property</th>
<th>Q_{s}=0 (1)</th>
<th>Q_{s}=2×Q_{mf} (2)</th>
<th>Ratio (2)/(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bubble fraction (m^3_{bubble}/m^3_{bed})</td>
<td>0.0587</td>
<td>0.0238</td>
<td>0.405</td>
</tr>
<tr>
<td>Dense phase porosity</td>
<td>0.498</td>
<td>0.491</td>
<td>0.986</td>
</tr>
<tr>
<td>Bubble escape velocity (m/s)</td>
<td>0.0136</td>
<td>0.00742</td>
<td>0.545</td>
</tr>
<tr>
<td>Dense phase gas velocity (m/s)</td>
<td>0.00590</td>
<td>0.00550</td>
<td>0.932</td>
</tr>
</tbody>
</table>

In a bed of Geldart B particles we do not necessarily expect the same decrease in bubble fraction using secondary injection as we see with the A powder, particularly since the dense phase does not expand as much. However, the qualitative trend should be similar. The most important results from this experiment show that secondary gas injection significantly reduces the bubble fraction, and a higher proportion of the gas in the reactor is contained within the dense phase, although possibly for a shorter length of time due to the distributed secondary gas injection. These results are consistent with discrete particle model simulations with a single injection point in a bed of Geldart B particles, which indicate that the bubble fraction in the bed decreases significantly and the dense phase porosity increases above the injection point [17].
Residence Time Distributions

Residence time distribution (RTD) experiments were carried out to determine the effect of distributed secondary injection on the average gas residence time and the macroscopic mixing behaviour in the fluidized bed. The residence time cannot be used to predict conversions in heterogeneous reactions. This requires the contact time distribution [4], but it will give some insight into how the gas is distributed inside the reactor. Based on a simplistic model, presented in an earlier study [2], the average residence time is not expected to change even though a portion of the gas is being injected higher in the bed when a fractal injector is used. This expectation can be explained by the fact that, although gas introduced into the bed via the injector may have a shorter average residence time, the gas injected through the bottom of the bed stays in the bed longer, and the overall average remains unchanged. The residence time distribution, however, will be different. The inherent assumptions in this model are that the reactor volume is constant regardless of the value of $Q_s$ and the flow behaviour is ideal, i.e., that there is no gas bypassing. Previous experimental results from a 2-D setup, presented in the same study, showed that there is, in fact, a slight decrease in the average residence time. This result could imply that the secondary gas moves immediately into bubbles, which leave the bed very quickly. This would, however, also imply that the distribution would become broader, but, according to previous 2-D results, the opposite is true. This explanation would also contradict the collapse results. Another possibility is that the gas in the bottom of the reactor does not stay in the bed as long as expected because it bypasses through the bubbles. Although there is less primary gas, and the bubbles are smaller and travel slower, there is still some gas bypassing through bubbles, and gas travels faster in the bubbles than in the dense phase. A further possibility is that some other unknown parameter is changing, such as the reactor volume.

Residence time distributions were determined in the 3-D column for both the Geldart B particles at various flow conditions, and for the Geldart A particles at the conditions studied in the collapse tests. The average residence times and the relative change in average residence times for the various flow conditions with the Geldart B particles are shown in Figure 5-8. The average residence time tends to decrease with increasing secondary gas flow. The decrease appears larger than with the results reported earlier for the 2-D column, but this can be explained by the fact that the maximum height of the injector with respect to the bed height in the 3-D reactor is much higher than it was for the 2-D system: 6 cm below the settled bed height in the 3-D case as compared to 26 cm below the settled bed height in the 2-D case. Therefore, the gas entering the bed through the highest injector row in the 3-D column has a very short residence time. There is a maximum decrease in the average
residence time of approximately 20%, which is significant. It is important to note, however, that the contact time is more important in a heterogeneous reaction.

In the Geldart A system the average residence time also decreased, from 41.6 s to 38.5 s, at the same flow conditions as those used in the collapse tests of these particles. The decrease in residence time can be partly explained by the drop in bed height. In the case of the Geldart A particles, the decrease in bed height was 4.6%, while the decrease in the residence time was 9.3%. The average residence time is defined as the volume of gas in the reactor divided by the volumetric flow rate. Assuming that the average bed porosity is ~50%, which is reasonable given the results shown in Table 2, then a decrease of bed volume of 4.6% will account for a decrease in the gas volume of 9.2% (the amount of solids is constant). Therefore, the decrease in the average residence time of the gas is almost entirely due to the decrease in the bed volume, which, in turn, is mostly due to the decrease in bubble volume.

With Geldart B particles, the decrease in bed volume will also help to explain the reduction in average residence time of the gas. In this case, however, it is not clear whether this decrease is large enough to account for the entire reduction. Better measurements of the bed height with group B particles and secondary injection are required. Any portion of the reduced residence time not attributable to the decrease in bed volume may be caused by non-ideal flow and gas bypassing in the reactor. A contributing factor may be that a portion of the primary gas does not stay in the bottom of the bed as long as expected because of bypassing in the bubbles that form in this region. However, this effect should decrease with increasing secondary gas and decreasing primary gas, which is opposite to what is observed. Another possible explanation is that the gas in the dense phase above the injector travels at a higher velocity because there is more gas in this phase. Also the bubble rise velocity above the injector may be higher than expected for a given size because of reduced resistance to flow through the higher porosity dense phase.

It is interesting to note that the decrease in average residence time witnessed with the group A particles is not as great as that of the group B particles at the same multiple of their respective values of $U_{mf}$ for primary and secondary gas. This may be an indication that the increase in flow through the dense phase, where the velocity is lower, induced by secondary injection (as indicated by the decrease in bubble fraction) may be higher for group A powders than for group B.

The variance of the residence time distribution is a measure of the axial dispersion of the gas in the reactor. A special note is required on the interpretation of the variance in systems with secondary gas injection. The axial dispersion of the gas is being artificially increased because
of the gas injection at different axial positions, even if the mixing characteristics remain unchanged. Thus, if the variance becomes larger with secondary gas injection, it does not necessarily mean that there is more gas back-mixing, and this is complicated by the fact that the amount of gas flow is not constant throughout the reactor. However, if the variance becomes smaller with secondary gas injection, then the gas back-mixing is being significantly reduced, as the effect to promote plug flow behaviour is larger than the artificial dispersion.

To take the artificial dispersion properly into account, residence time distribution experiments would have to be carried out by injecting tracer through only one level of the fractal injector at a time to properly determine the dispersion from each level. This is not possible with the current fractal injector, since all injection points are connected to each other, although future work could use individually fed injection points to study this issue. The artificial dispersion makes quantitative analysis of the gas back-mixing difficult, however the qualitative analysis as described above is still valid.

![Figure 5-8](image.png)

**Figure 5-8:** (a) Average residence time as a function of increasing secondary gas flow; (b) the relative change in the average residence time as a function of the secondary gas flow, for Geldart B particles

The variances of the distributions, which are a measure for the macromixing properties of the bed, are presented in Figure 5-9 for the Geldart B particle system. In most cases the width of the distribution decreases, indicating that the back-mixing of the gas is being reduced,
despite the artificial dispersion induced by the fractal injector, as discussed earlier. Interestingly, the lines reach minima at flow conditions where the primary gas flow is $2 \times Q_{mf}$. This general trend was also seen in the 2-D results, where the back-mixing decreased with increasing secondary gas until a minimum in back-mixing was reached, then increased again with further increases in $Q_s$. This sudden increase may point to changing hydrodynamics in the bottom of the bed when the primary gas flow is close to $Q_{mf}$. The results obtained with the Geldart A particles also show a decrease in back-mixing. The variances were 1148 s$^2$ and 1000 s$^2$ for the cases without and with secondary gas, respectively. Thus, the decrease in both average residence time and back-mixing are standard characteristics for both 2-D and 3-D systems. It is thought that increasing the number of injection points on the fractal injector (by adding another generation) will reduce the velocity of the gas injection and lead to a smaller decrease in average residence time (lower gas velocity and less bypass through jetting) and behaviour closer to plug flow. However, to truly understand how distributed secondary gas injection affects the gas-solid contact, reaction time experiments would need to be performed. Nauman and Collinge [4] and Orcutt et al. [3] describe how this can be done. The continuous decrease of the average residence time with increasing secondary injection suggests that there is an optimal secondary flow to maximize reactor performance.

![Graph showing variance of the residence time distribution as a function of increasing secondary gas flow](image)

**Figure 5-9:** Variance of the residence time distribution as a function of increasing secondary gas flow
Conversion Experiments

Ozone decomposition experiments were conducted with the Geldart B alumina particles at total flow rates of 4 and $5Q_{mf}$. The conversion is typically on the order of 70%. The relative conversion, defined as the ratio of the conversion obtained with secondary gas to the conversion of the base case without secondary gas, is shown as a function of increasing $Q_s$ in Figure 5-10. As expected from the decrease in bubble size and bubble fraction, the conversion increases at both total flow conditions studied. The conversion increases with increasing $Q_s$ to a maximum, after which it slightly decreases. The conversion never drops below that of the base case for the flow conditions studied. The relative increase is small, with a maximum on the order of 2.5%, but this is because the bubble size, even without secondary injection, is quite small – the settled bed height is only 30 cm – and, as a result, the mass transfer is not strongly limiting the reaction. The effect of intraparticle mass transfer was estimated using the Weisz-Prater criterion, and was found to be negligible; the small particle diameter is the dominant term. Therefore, it can be assumed that the mass transfer from the dense phase to the catalyst surface is also negligible.

Figure 5-10: Relative conversion of ozone as a function of increasing secondary gas flow in a 3-D bed. (a) $Q_s=4Q_{mf}$ (b) $Q_s=5Q_{mf}$. The bars represent the 95% confidence interval.
The drop-off of the relative conversion at the higher secondary flow rates is not thought to be a result of the reduction in the average residence time because it is, in fact, the contact time that influences the conversion. The experimental results suggest that the gas-solid contact is increasing. The decrease in residence time does not necessarily limit the contact time, especially when reactant adsorption on the catalyst surface is taken into account. A possible explanation for the slight drop-off in the conversion data is that the velocity of the gas flowing through the dense phase at the higher secondary flow rates is increased to the point that, although more gas comes into contact with the solids, it does so for less time. However, this argument suggests that the reaction is then kinetically limited and we would then expect to see a plateau in the conversion trend, not a decrease. A second explanation is that the injection velocity of the gas at the higher secondary flow rates is such that the injected gas behaves as if it is channelling through the bed. This argument is consistent with the residence time data; the residence time decreases as more gas takes shortcuts through the bed. The bubble size would continue to decrease at these high velocities because the gas stays in preferred channels and cannot coalesce, and the initial bubble size is smaller. The gas velocity is low enough that significant jetting does not occur, but the gas may still have enough momentum to flow very quickly through the portion of the bed where it is injected, mimicking a sort of bypassing. It would be interesting to study the same system with a fractal injector that has more injection points. The gas-solid contact may be further improved, and the drop-off of the relative conversion at high secondary flows may disappear, because of the decreased injection velocity. The large variability in the data at $5 \times Q_{mf}$ which was also seen in the bubble size data, suggests that longer data sets should be measured to improve the statistics.

The increase in conversion confirms that distributed secondary gas injection increases the gas-solid contact. This effect will be much more significant at larger reactor scales where the bubbles can grow much larger and the mass transfer from the bubbles to the dense phase is much more limiting.

5.5. Reactor Modeling

Two reactor models were developed and their predictions compared to the experimental conversion data to determine whether they could correctly predict the trends, and to gain further insight into how the secondary gas is distributed within the reactor. The models presented here are based on Grace’s two-phase bubbling bed model [18] and Kunii and Levenspiel’s intermediate particle model [19], and are essentially simplifications and refinements of a model developed previously [6].
The models consider only two phases, the bubble phase and the dense phase. In the basic model, the flow through the dense phase is considered negligible compared to the flow through the bubbles, and, therefore, the convective flow term in the mass balance of a reactant species over the dense phase is ignored. The gas that enters the reactor flows through the bubble phase. This gas reacts with the small fraction of particles present in this phase, diffuses to the dense phase, or continues to flow upwards through the bubble phase. We will call this Model 1. The assumption of negligible dense phase flow is questionable at the relatively low flow conditions studied here ($Q = 4 \times Q_{mf}$). However, the predictions are still useful, especially as a basis for comparison, and in combination with the results from other models discussed below, to give us insight into the distribution of the gas within the fluidized bed with secondary injection.

Model 1 can be extended to include convective flow through the dense phase at $Q_{mf}$ to account for the fact that the flow through the dense phase, which is assumed to be at minimum fluidizing conditions, is not negligible compared to the total flow in the current study. Using this modification, the resulting model is very similar to Kunii and Levenspiel’s intermediate particle model [19]. We will call this Model 2.

The mass transfer coefficient, describing the transport of species between the phases for both models, is given by the semi-empirical correlation of Sit & Grace [20], which accounts for gas throughflow through the bubbles (based on Murray’s hydrodynamic analysis of bubbles [21], which states, in part, that the velocity of the throughflow of gas through the bubble is $U_{mf}$ greater than the bubble velocity itself), diffusion, and the enhancement observed between interacting bubbles. The Darton correlation [22] is used to predict the bubble size as a function of height in the reactor. To account for the bubble size reduction that is observed with the use of a fractal injector, the bubble diameter predicted by this correlation is multiplied by the relative bubble size determined from experiments at the same flow conditions. The basis for these models are thoroughly described elsewhere [18,19], so we simply summarize the equations here.

For Model 1, the mass balances of a reactant in the bubble and dense phases, in the case where dense phase flow is neglected, are:

$$\eta U \frac{dC_{A,b}}{dh} = -K_{bd} a_b \phi_b \left( C_{A,b} - C_{A,d} \right) + \phi_b \sigma A_b$$

$$0 = K_{bd} a_d \phi_d \left( C_{A,b} - C_{A,d} \right) + \phi_d \sigma A_d$$

where $\eta$ is the fraction of gas in the bubble phase at any height, and is defined in the Orcutt et al. model as [3]:
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\[
\eta = \frac{(U - U_{mf})}{U} \tag{5.3}
\]

However, since there is no dense phase flow in the model used here, \(\eta\) is assumed to be unity [18].

For Model 2, the mass balances on the phases, which include flow through the dense phase at \(U_{mf}\) are:

\[
\varepsilon_b U_b \frac{dC_{A,b}}{dh} = -K_{ab}a_b\varepsilon_b (C_{A,b} - C_{A,d}) + \phi_d r_{A,b} \tag{5.4}
\]

\[
(1 - \varepsilon_b) U_{mf} \frac{dC_{A,d}}{dh} = K_{ab}a_b\varepsilon_b (C_{A,b} - C_{A,d}) + \phi_d r_{A,d} \tag{5.5}
\]

where the volume fraction of the bed in the bubble phase is \(\varepsilon_b\) and is given by:

\[
\varepsilon_b = \frac{U - U_{mf}}{U_b} \tag{5.6}
\]

Note that \(\varepsilon_b\) is not the same as \(\eta\) in equation (5.1); here we use the relations defined by Kunii and Levenspiel instead [19]. In equations (5.4) and (5.5), \(a_b\) is the surface to volume ratio of a bubble, i.e., \(6/d_b\), assuming spherical bubbles. Note that the reaction rate terms, \(r_{A,b}\), are negative for the consumption of species A or positive for the production of species A. The interphase mass transfer coefficient, \(K_{bd}\), is given by [20]:

\[
K_{bd} = \frac{U_{mf}}{3} + \frac{4D_{c,mf} U_b}{\pi d_b} \tag{5.7}
\]

where the bubble rise velocity, \(U_b\), is given by:

\[
U_b = U - U_{mf} + 0.711 \sqrt{g \cdot d_b} \tag{5.8}
\]

The parameters \(\phi_b\) and \(\phi_d\) are the volume fractions of the bed associated with the particles in the bubble and dense phases respectively. They are given by:

\[
\phi_b = (0.003) \varepsilon_b \tag{5.9}
\]

\[
\phi_d = (1 - \varepsilon_{mf}) (1 - \varepsilon_b) \tag{5.10}
\]

where the dense phase is assumed to be at minimum fluidizing conditions, and the value 0.003 is the volume fraction of particles in the bubble phase and is an assumed value; its typical range is between 0.001 and 0.01 [19].

The velocity \(U_{b}^*\), which appears in equation (5.4), is the velocity of the gas in the bubble phase and is greater than the velocity of the bubble itself to take into account the throughflow of gas. It is estimated, using Murray’s analysis, by:

\[
U_{b}^* = U_b + U_{mf} \tag{5.11}
\]

The bubble diameter, \(d_{b}\), is calculated using the Darton relation [22] adjusted for the bubble size reduction:
The term $\psi$ is the experimental relative bubble size shown in Figure 5-5, or:

$$
\psi = \frac{d_{b,\text{exp}}}{d_{b,0,\text{exp}}}
$$

The parameter $A_0$ is the 'catchment' area that characterizes the distributor plate, and can be interpreted as the area of plate per orifice. It essentially defines an initial bubble size. Darton found that a reasonable $A_0$ value for a porous plate distributor, based on published experimental data, is 56 mm², and this value is used in the current work.

The ozone decomposition reaction is well known to be (close to) first order in the ozone concentration. Therefore, the reaction terms in the mass balances above become $-k_{C^3,i}$ in the $i^{th}$ phase (either bubble or dense), with it being negative to represent the consumption of ozone. Although the bubble fraction was observed to decrease in the experiments, we chose to let the model predict the bubble fraction based on equation (5.6) because the 3-D experiments did not give information on the bubble fraction as a function of height and we do not have quantitative information of the bubble fraction for group B particles. Since the bubble fraction is dependent on the local superficial gas velocity, it will take the gradient in the flow along the height of the reactor into account, although it is a conservative estimate given that secondary injection lowers it.

Secondary injection is included in these 1-D models by assuming that the gas is injected uniformly over the entire cross-section at a given height. This is schematically shown in Figure 5-11.
The secondary gas is included in the models by updating the flow rate at each injection level and by modifying the concentration of the reactant in each phase at these levels. The latter is accomplished three different ways:

1. In the case of no dense phase flow (Model 1), the dense phase concentration is left unmodified. All of the secondary gas is assumed to go directly into the bubble phase, and the new concentration in the bubble phase is a volume-weighted average of the existing concentration and the concentration in the fresh feed.

2. With dense phase flow (Model 2a), the secondary gas is still assumed to enter only the bubble phase, and the new concentrations are calculated as in 1.

3. With dense phase flow (Model 2b), a portion of the secondary gas flow is assumed to instantaneously mix with the gas in the dense phase. The dense phase remains at $U_{mf}$ conditions and all excess gas (at the new concentration) goes immediately into the bubble phase, where this is used to update the bubble phase concentration. This situation can be interpreted as the fraction of time that an injection point is located within the dense phase as opposed to being inside a passing bubble, or as increased micromixing at the injection points, improving the gas-solid contact.

Model 1 only uses assumption 1 listed above, while Model 2 can use either assumptions 2 or 3 above. These will be denoted by Model 2a and Model 2b, respectively.

The value of the reaction rate constant, $k$, was not known for the catalyst used in the experiments. Therefore, the value of $k$ used was the value that made the models (without secondary flow included) match the absolute conversion observed for the experiment at $4 \times Q_{mf}$ without secondary flow. This essentially makes $k$ a fitting parameter. As a result, only the trends in the relative conversions will be informative. For Model 1 $k$ was determined to be $2.0 \, \text{m}^3_{\text{gas}}/(\text{m}^3_{\text{catalyst}} \cdot \text{s})$. For Models 2a and 2b, $k$ had a value of $1.4 \, \text{m}^3_{\text{gas}}/(\text{m}^3_{\text{catalyst}} \cdot \text{s})$. Note that the predicted conversions are higher with dense phase flow, as is expected. This is reflected by the lower value of $k$ required in Model 2 to obtain the same conversion. The value of $k$ was held constant for a given model regardless of the amount of secondary gas injection.

Model for the Production of Maleic Anhydride

Instead of only modeling reactions with first-order kinetics, we should also consider more complex reaction mechanisms. Doing so will allow us to study the effect of secondary injection on selectivity in addition to conversion. Here we model the production of maleic anhydride from the partial oxidation of n-butane, which includes consecutive and side reactions. It is also a relevant reaction for the chemical industry. The kinetics of the reaction over a vanadium-phosphorus mixed oxide catalyst and at a temperature of 300°C, described
by Centi et al. [23], were used in the modeling. There are three reactions: the partial oxidation of n-butane to form maleic anhydride, the complete oxidation of n-butane to water and carbon dioxide, and the further oxidation of maleic anhydride to water and carbon dioxide:

\[
\begin{align*}
C_4H_{10} + 3.5O_2 & \rightarrow C_2H_4 (CO)_2 O + 4H_2O \\
\frac{1}{4} C_4H_{10} + 6.5\frac{1}{4} O_2 & \rightarrow CO_2 + \frac{5}{4}H_2O \\
C_2H_4 (CO)_2 O + 3O_2 & \rightarrow 4CO_2 + H_2O
\end{align*}
\]  

(5.14)\hspace{1cm} (5.15)\hspace{1cm} (5.16)

Some carbon monoxide is also formed, but for simplicity only carbon dioxide production is considered. Obviously, the desire is to maximize the first reaction, while minimizing the other two. It was found that the reaction rate of equation (5.14) depends only on the n-butane and oxygen concentrations in the form:

\[
r_1 = \frac{k_1 K_{eq} C_1 C_2^{\alpha}}{1 + K_{eq} C_1}
\]

(5.17)

where \(K_{eq}\) is the adsorption equilibrium constant of n-butane, and is equal to 2.616 m\(^3\)/mol, and the exponent \(\alpha\) is equal to 0.23. The formation of carbon dioxide from the complete oxidation of n-butane was found to depend only on the oxygen concentration, following a power law:

\[
r_2 = k_2 C_2^{\beta}
\]

(5.18)

where the exponent \(\beta\) is also equal to 0.23. The further oxidation of maleic anhydride depended on the concentrations of n-butane, oxygen, and maleic anhydride, and the reaction rate could be described by:

\[
r_3 = k_3 C_{\text{ma}} \frac{C_2^{\gamma}}{C_4^{\delta}}
\]

(5.19)

where the exponents \(\gamma\) and \(\delta\) are equal to 0.63 and 1.15, respectively. The model requires a mass balance equation for each species in the kinetics and for each phase, thus six equations in total (not shown here). The reaction rate terms for the individual species are:

\[
r_{C_4} = -r_1 - \frac{1}{4} r_2
\]

(5.20)

\[
r_{O_2} = -3.5r_1 - 6.5\frac{1}{4} r_2 - 3r_3
\]

(5.21)

\[
r_{\text{ma}} = r_1 - r_3
\]

(5.22)

Maleic anhydride production was modeled using the flow conditions and reactor size described in the current experimental work. Since all of the hydrodynamic data is for the Geldart B alumina particles, we will use the same properties in the model for the production of maleic anhydride. The kinetics are known at a temperature of 300°C, therefore the model reactor will also be at this temperature. The feed gas consists of 1.38-mol% n-butane, an oxygen/n-butane ratio of 15 and the remainder of the gas nitrogen. Given the low concentration of n-butane, the gas can be assumed to have the properties of air at 300°C.
This is much higher than the temperature in the experimental studies discussed here. It is assumed that the elevated temperature and subsequent changes in gas properties do not affect the bubble size reduction, however the gas density and viscosity were updated and a new value of $U_{mf}$ was estimated to be 2.23 cm/s. The kinetic rate constants were found to have the following values at 300°C [23]:

$$k_1 = 3.357 \times 10^{-7} \times 1000(1-\alpha) \cdot \text{mol}^{(1-\alpha)} \cdot \text{m}^{3\alpha} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$$

$$k_2 = 2.001 \times 10^{-7} \times 1000(1-\beta) \cdot \text{mol}^{(1-\beta)} \cdot \text{m}^{3\beta} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$$

$$k_3 = 4.400 \times 10^{-8} \times 1000(\delta-\gamma) \cdot \text{mol}^{(\delta-\gamma)} \cdot \text{m}^{2(\delta-\gamma)} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$$

Note that the factors of 1000 convert from the units originally reported to those used here. The molecular diffusion coefficients for the three species in air at 300°C were estimated using the method proposed by Chen and Othmer [24], which is simple and accurate [25].

5.6. Model Results

Ozone Decomposition

Figure 5-12 shows the relative conversions calculated using Models 1, 2a and 2b, along with the experimental data. In the case of Model 2b, it was assumed that either half (50%) or all (100%) of the secondary gas mixes instantaneously with the dense phase before flowing into the bubble phase.

Model 1, in which the dense phase gas is neglected, clearly underestimates the trend seen experimentally. The predicted conversion decreases with increasing secondary flow despite the inclusion of the bubble size reduction in the model. This lack of agreement is probably due to the predicted mass transfer characteristics not being enhanced sufficiently despite the reduction in bubble size.

The trend in the conversion predicted by Model 2a exhibits even greater disagreement with the experimental data. The trend does not change even if the same value of $k$ is used as in Model 1. This behaviour occurs because the gas in the dense phase is flowing instead of the phase being stagnant, and has a high initial concentration of reactant. In Model 1, any reactant gas that transfers from the bubble phase to the dense phase is considered converted because it is not leaving the reactor, since the flow rate through the dense phase is zero. This is not the case, however, with Model 2a, where there is still unconverted reactant leaving the dense phase. The rate of mass transfer from the bubble to the dense phase is lower in Model 2a because the concentration gradient, which is the driving force, is not as large as it is in Model 1, where there is no reactant initially in the dense phase.
The results for Model 2b are much more characteristic of the experimental data. The situation with all of the secondary gas mixing with the dense phase before flowing into the bubble phase over-predicts the data, but it does show a reasonable trend. The conversion initially increases until a maximum is reached, then decreases again, but not below the base case. When 50% of the secondary gas is assumed to mix with the dense phase gas, the predicted trend is close to the experimental data. If the first interpretation of assumption 3 is true, then this value of 50% indicates that the injection point spends the other 50% of its time inside bubbles. The actual bubble fraction is much lower than this, however, and is typically on the order of 20%. Therefore, this interpretation cannot be valid. As a result, the other interpretation that assumption 3 is representative of improved micromixing, which encourages better gas-solid contact, is more likely.

The trends calculated by Model 2b at 50% slightly over-predict the conversion at low values of \( Q_s \) and under-predict it at high values. The over-estimation is thought to be due to the assumption that a constant proportion of the secondary gas mixes with the dense phase, thus increasing the amount of reactant in the dense phase (but not the flow), regardless of the amount of secondary flow. The model may improve its predictions by varying this amount with \( Q_n \) but without experimental evidence to quantify the amount of micromixing, this factor would quickly become a fitting parameter with little physical meaning. The under-prediction of the conversion at high values of \( Q_s \) is thought to be due to over-estimation of the bubble fraction. Recall that the bubble fraction is calculated by equation (5.6) and is not corrected for the decrease seen experimentally. Further experimental measurements of the bubble fraction with secondary injection would be required to refine its prediction.

The model results presented here are further evidence that distributed secondary gas injection via a fractal injector encourages interaction between the phases and improves the gas-solid contact. This is in agreement with the results of discrete particle model simulations with a single injection point, which show that gas-solid contact improves with secondary gas [17]. The secondary gas does not contribute to bubble growth, but instead stays in the dense phase.
The Production of Maleic Anhydride

Model 2b with 50% of the secondary gas flow mixing with the dense phase was chosen to predict the performance of a reactor with distributed secondary gas injection in the production of maleic anhydride. The concentrations of all feed streams were the same; no attempt has been made to improve selectivity by changing the composition of the secondary gas, although this would be a very important option in any optimization study. Figure 5-13 shows the concentration profiles for each reactant along the height of the reactor, as well as the bubble size predicted by the Darton relation, for (a) the situation without secondary flow, and (b) the situation with secondary flow at 2.5×Q_{mf}. It is apparent that the difference between the concentrations of a reactant in the bubble and dense phases is much smaller with secondary injection than without, and that the concentrations decrease (for n-butane and oxygen) or increase (for maleic anhydride) faster, although the latter is more...
difficult to see. Also, the initial conversions are greater, but this is because the flow rate near the distributor is lower, increasing the residence time of that fraction of the gas.

The relative conversion and selectivity results are shown in Figure 5-14 as a function of increasing secondary gas flow. The conversion of both n-butane and oxygen increases with secondary injection. The production of maleic anhydride also increases, but levels off slightly at the higher secondary gas flow rates. The selectivity to maleic anhydride increases very slightly up to a maximum, then decreases again, but never to values lower than in the situation without secondary gas injection. The increase in conversion is due to the enhanced gas-solid contact that the secondary injection generates. The increase in selectivity, although small, is important because it means that more maleic anhydride is being produced per mole of n-butane – maximizing the production of the desired product while minimizing the material required. The relative increases may seem small, but it should be noted that the reaction is modeled in a small reactor, only 35 cm tall, and the mass transfer is not severely limited by the relatively small bubble sizes. The effect of distributed secondary gas injection is expected to be greater at larger scales because the bubbles will be much larger and represent a significant mass-transfer resistance in the reactor. Also, an increase in production of maleic
anhydride of 4% may not seem like much, but when a reactor is producing kilotonnes per year, this 4% represents a very significant amount.

To demonstrate the effect of secondary injection in a larger reactor, we modeled the production of maleic anhydride in a reactor 3 times the height of the first at the same flow conditions. The spacing between the injection levels was kept the same as in the small reactor model, but 3 times as many levels were used. The results are shown in Figure 5-15. They show a much greater increase in conversion and selectivity with secondary injection than in the small reactor model, most likely because the bubbles are able to grow much larger in the base case. The larger bubbles result in more significant mass transfer limitations. The fact that the selectivity increases by almost 9% and the production of maleic anhydride improves by almost 15% demonstrates that secondary injection can have a significant positive impact on reactor performance. Note that no optimization of the concentrations of the injected gas has been done. Reducing the oxygen ratio in the feed or injecting higher concentrations of n-butane in the secondary gas may further improve the selectivity. Another possibility would be to use the secondary injection to introduce oxygen, thereby dosing the oxygen into the reactor at heights where the oxygen in the reactor has already been depleted, thereby limiting the complete oxidation of n-butane.
5.7. Aspects of Industrial Application

The experimental and modeling results reported here were obtained in laboratory-scale equipment, where the bubble size is small and limited by the dimensions of the reactor. The bubbles will not be limited in most industrial applications, and the mass transfer and gas-solid contact will be much worse as a result. Although the increase in conversion in the lab-scale reactor is modest, we expect the effect of distributed secondary injection to be much greater at larger scales, where the reactions are severely limited by the poor mass transfer. In addition, most of the conversion in industrial reactors occurs in the bottom portion of the bed, where the bubbles are small. The bubbles can be kept small throughout the reactor using a fractal injector; the conversion, as well as the catalyst efficiency, will be higher throughout the reactor as a result.

A further advantage of using a fractal injector is that it allows the selective introduction of chemical species into the bed when the reaction involves more than one reactant. For instance, it can be used to stage the oxygen injection in an oxidation process to allow higher throughputs, while operating outside the flammability limits. This benefit can also be used to
optimally dose a reactant to improve the selectivity towards a desired product by limiting the extent of consecutive reactions, or by forcing chemical equilibria in the desired direction.

Erosion is a significant issue in industrial fluidized beds with internals. In erosion studies (e.g., [26,27]) erosion was found to be primarily caused by particle impact; abrasion also occurred but the erosion it causes was much less significant. The primary mechanism for the impact wear was the mass of particles in the wakes of the bubbles colliding with the internals. Wear also tended to be greater in the middle of the bed where the bulk bubble flow occurs, and it also increased with bubble velocity (i.e., larger bubbles). When tube bundles were present, the amount of wear was found to decrease significantly because neighbouring tubes tend to cause a decrease in the particle impact velocity. The erosion of a fractal injector will be significantly less than what would be expected of normal internals given the above criteria because secondary injection significantly changes the hydrodynamics of the bed. Firstly, the bubbles are much smaller with secondary injection. This implies that both the rise velocity and the mass of the particles in the wake will be substantially lower and the rate of wear less. In terms of failure of an internal, local wear is much more important than average wear. Secondary gas injection causes a more uniform distribution of the bubbles and prevents them from massing in the middle of the column, which causes higher local rates of erosion. This effect will lead to more uniform wear and result in a longer lifetime of the internals. The nature of the fractal injector also means that a substantial number of tubes will be present, which may also lead to a reduction in the wear rate similar to the effect of a tube bundle. All of these hydrodynamic effects imply that the wear of the fractal injector will be much lower than in normal fluidized beds. It should also be noted that the presence of secondary injection will also decrease the wear rate of other internals that may also be present in the bed, such as heat exchanger tubes, for exactly the same reasons.

Another concern in industrial applications is maintaining the high rate of heat transfer achieved by the strong solids mixing inside the bed. Bubbles actually improve the rate of solids mixing and therefore contribute to the heat transfer. It is important to realize that secondary injection does not eliminate the bubbles, thus they will still contribute to the heat transfer. Also, the bubbles may be smaller, but there are more of them, although the total bubble volume is decreasing. The uniformity of the gas distribution will prevent, or at least delay, the formation of large particle circulations where the particles flow up the middle of the column in the wake of the bubbles and then flow down at the walls. The particles at the wall, in this case, are densely packed and the particles move less with respect to one another. Instead, localized particle mixing zones will be created, causing the local heat transfer rates to be more uniform throughout the bed. The increased particle mixing may actually improve the overall rate of heat transfer because the freer motion of the particles around heat transfer
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tubes and walls will allow more particles to make contact with the cooling tubes and maintain a high temperature gradient. Further studies would be needed to confirm this hypothesis, however. An additional benefit of the fractal injector is that it can be used as a heat exchanger. The heat being generated by the reaction can conduct through the walls of the injector to the gas flowing through the fractal injector, thereby preheating the reactants before they are injected into the bed. The magnitude of this effect will depend on the length of time the gas spends in the fractal injector and the thermal conductivity of the material from which the injector is constructed.

In terms of manufacturing a fractal injector, it should be quite simple even though the structure appears very complex. The fractal injector consists of a very simple repeating geometric unit, such as the ‘H’ mentioned above. The simplicity of the repeating unit means that the injector will be easy to produce. Most of the parts will be similar, which will decrease costs because of economies of scale. The final injector can be pieced together from these common parts, much like a set of industrial Lego™. The optimal structure for the fractal injector will likely depend on the desired reaction and system configuration, but once that structure is determined the difficulty of manufacturing it should not change.

5.8. Conclusions

Experiments in a 3-D lab scale bubbling fluidized bed with distributed secondary gas injection have shown that all of the measured phenomena, such as bubble size, average residence time, and back-mixing of the gas, show the same trends with increasing secondary gas flow as had already been observed in 2-D beds. The decrease in bubble diameter is as large as 30%, which means that the bubble volume is being drastically reduced. Collapse tests show that, not only is the bubble diameter getting smaller, the bubble fraction is being greatly reduced – counter to what is normally expected if the bubble volume were to stay the same but with a decreased bubble size (and, hence, rise velocity). These two results imply that the mass-transfer and gas-solid contacting are being improved with a fluidized bed with a fractal injector. The results of these experiments also seem to indicate that the flow of gas through the dense phase is increasing, but more experiments are needed to verify this claim. It is worth mentioning that discrete particle simulations of small fluidized beds with a single injection point also show a decrease in the bubble fraction and an increase in the dense phase porosity [17].

Residence time experiments indicate that there is a decrease in the average residence time, although there is also a decrease in gas back-mixing. The decrease in residence time may help to explain the conversion results, where the conversion is seen to increase with higher
secondary flow to a maximum after which it decreases slightly, although never below the base case. It is thought that, at the higher values of secondary flow, the negative effect of later introduction of reactant gas starts to counter-balance the positive benefit of the improved gas-solid contact, although the conversion never drops below the base case within the experimental conditions studied. The point at which the maximum occurs will depend on the kinetics of the reaction, where reactions with very slow kinetics will see a decrease in conversion at lower secondary flow rates, but reactions with fast kinetics will still exhibit an increase in conversion at higher $Q_s$. Distributed secondary gas injection is focused towards increasing mass transfer and gas-solid contact, so application in systems that were not limited by mass-transfer was never intended, although this technique may also have a benefit in systems where selectivity is a problem, as the example of maleic anhydride synthesis demonstrated.

Simple models based on a combination of Grace's two-phase bubbling bed model and Kunii and Levenspiel's intermediate particle model were developed. The model that included flow through the dense phase as well as instantaneous mixing of the secondary gas with the dense phase proved to reasonably describe the trend in the experimental ozone decomposition data. It was concluded that the increase in reactor performance with secondary injection is likely due to increased micromixing around secondary injection points, which causes a greater interaction between the phases and an improved gas-solid contact.

The reactor model was further extended to model the production of maleic anhydride from n-butane. It was found that secondary gas injection not only improves the production rate of maleic anhydride but also increases its selectivity, implying that more product is being made per mole of reactant. It was concluded that, although the increases are small, the mass transfer is most likely not limiting in the very small-scale reactors studied here, where the bubble size is only on the order of a few centimetres. Application at larger scales will see greater benefit as the bubbles become much larger and more limiting for mass transfer. Some aspects of applying this technology in an industrial setting were discussed.

5.9. Acknowledgements

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### 5.10. Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_0$</td>
<td>Area of distributor plate per orifice, [m²]</td>
</tr>
<tr>
<td>$a_b$</td>
<td>Bubble surface to volume ratio, [m⁻¹]</td>
</tr>
<tr>
<td>$C_{A,0,i}$</td>
<td>Initial concentration of reactant in phase $i$, [mol/m³ gas in phase $i$]</td>
</tr>
<tr>
<td>$C_{A,i}$</td>
<td>Concentration of reactant in phase $i$, [mol/m³ gas in phase $i$]</td>
</tr>
<tr>
<td>$D$</td>
<td>Molecular diffusion coefficient, [m²/s]</td>
</tr>
<tr>
<td>$d_b$</td>
<td>Bubble diameter, [m]</td>
</tr>
<tr>
<td>$d_{b,0,exp}$</td>
<td>Bubble diameter measured in experiment without any secondary gas, [m]</td>
</tr>
<tr>
<td>$d_{b,exp}$</td>
<td>Bubble diameter measured in experiment, [m]</td>
</tr>
<tr>
<td>$d_{b,min}$</td>
<td>Minimum bubble diameter allowed, [m]</td>
</tr>
<tr>
<td>$g$</td>
<td>Acceleration due to gravity, 9.8 [m/s²]</td>
</tr>
<tr>
<td>$h$</td>
<td>Current height in the bed, [m]</td>
</tr>
<tr>
<td>$k$</td>
<td>First-order reaction rate constant, [m³ gas/(m³ solid · s)]</td>
</tr>
<tr>
<td>$K_{bd}$</td>
<td>Mass transfer coefficient between bubble and dense phases, [m/s]</td>
</tr>
<tr>
<td>$Q_0$</td>
<td>Total volumetric flow rate, [m³/s]</td>
</tr>
<tr>
<td>$Q_{mf}$</td>
<td>Minimum fluidization volumetric flow rate, [m³/s]</td>
</tr>
<tr>
<td>$Q_p$</td>
<td>Primary volumetric flow rate that enters the bed via the windbox, [m³/s]</td>
</tr>
<tr>
<td>$Q_s$</td>
<td>Secondary volumetric flow rate that enters via the fractal injector, [m³/s]</td>
</tr>
<tr>
<td>$r_A$</td>
<td>Reaction rate of species A, [mol/m³ solid·s]</td>
</tr>
<tr>
<td>$U$</td>
<td>Superficial gas velocity in the reactor at a given height, [m/s]</td>
</tr>
<tr>
<td>$U_0$</td>
<td>Total superficial gas velocity in the reactor, [m/s]</td>
</tr>
<tr>
<td>$U_b$</td>
<td>Bubble rise velocity in a bubbling fluidized bed, [m/s]</td>
</tr>
<tr>
<td>$U_b^*$</td>
<td>Rise velocity of gas inside a bubble, [m/s]</td>
</tr>
<tr>
<td>$U_{mf}$</td>
<td>Minimum fluidization velocity, [m/s]</td>
</tr>
<tr>
<td>$X$</td>
<td>Conversion of the reactant with secondary gas injection, [-]</td>
</tr>
<tr>
<td>$X_0$</td>
<td>Conversion of the reactant without secondary gas injection, [-]</td>
</tr>
</tbody>
</table>

### Subscripts

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_4$</td>
<td>n-butane</td>
</tr>
<tr>
<td>$i$</td>
<td>Hydrodynamic phase, either (b)ubble or (d)ense phase</td>
</tr>
<tr>
<td>MA</td>
<td>maleic anhydride</td>
</tr>
<tr>
<td>$O_2$</td>
<td>oxygen</td>
</tr>
</tbody>
</table>
Reactor Performance: Conversion and Selectivity

Greek

\( \varepsilon_b \) Volume fraction of the bed in bubbles as defined by Kunii and Levenspiel, \([\text{m}^3_{\text{bubble}} / \text{m}^3_{\text{bed}}]\)

\( \eta \) Volume fraction of the bed in bubbles as defined by Orcutt et al., \([\text{m}^3_{\text{bubble}} / \text{m}^3_{\text{bed}}]\)

\( \theta_d \) Dense phase porosity, \([\text{m}^3_{\text{gas}} / \text{m}^3_{\text{dense phase}}]\)

\( \phi_i \) Volume fraction of the bed associated with the particles in the \( i \)th phase, [-]

\( \sigma_{\text{IOP}} \) Incoherent output power, a measure of bubble size, \([\text{Pa}^2]\)

\( \sigma^2 \) Variance (width) of the residence time distribution, \([s^2]\)

\( \tau \) Average residence time, [s]

\( \tau_{\text{w.o.}} \) Average residence time without secondary gas injection, [s]

\( \psi \) Bubble diameter reduction factor, [-]

5.11. References


6. Conclusions and Outlook

6.1. Conclusions

The use of distributed secondary gas injection via a fractal injector has been shown to overcome significant limitations in a bubbling fluidized bed reactor. This technique improves the gas-solid contact and mass transfer, and makes the bubble behaviour more controllable. These factors improve both the conversion and scalability of bubbling fluidized beds and may make this reactor type attractive for more applications.

The results of this work have been presented in terms of the influence of distributed secondary gas injection on four key areas: the effects on the hydrodynamics, the mechanisms responsible for these effects, the residence time and mixing of the gas, and the reactor performance.

It has been shown that secondary gas injection significantly reduces the bubble size in both 2-D and 3-D systems at the same total flow rate. This effect is not solely due to the lower gas velocity in the lower portions of the bed; results with a constant primary flow and increasing secondary flow show that much of the secondary gas does not contribute to bubble growth. The number of bubbles increases with secondary injection, which indicates that coalescence is being hindered. Results from the simulations indicate that these bubbles will typically travel along preferred paths, which also limits the likelihood of coalescence by keeping them away from each other. This effect helps to keep the bubbles small and makes the bubble pattern more predictable. Even with these extra bubbles, however, the total gas volume in bubbles decreases with secondary injection. This decrease in the bubble fraction implies that more gas must be traveling through the dense phase.

Computational fluid dynamic simulations of small beds with a single injection point show the secondary gas also tends to stay in the dense phase. These effects are seen from the results that few bubbles are present above the injection point and the dense phase porosity is increasing. This increase in dense phase porosity means that there is less gas available to go into the bubble phase and therefore the bubble fraction drops, despite the fact that more small bubbles should result in an increased bubble fraction. It is hypothesized that secondary
injection causes break-up of particle clusters, which decreases the bubble size and gives more energy to the particles. This results in an expansion of the dense phase beyond its stable equilibrium condition. This may also explain why the effect of secondary gas injection is seen even far above the height of the fractal injector. The dense phase does not destabilize immediately; it takes time for it to revert back to its equilibrium state, typically by ejecting small bubbles.

Distributed secondary gas injection also has a significant influence on the overall gas flow in the system, as measured by the gas residence time and mixing characteristics. The average residence time of the gas decreases, but the amount by which it does so depends on the configuration and placement of the fractal injector. This result is contrary to what is expected based on a simplistic model, but the improved gas-solid contact resulting from the effects of secondary gas injection on the bubble and dense phases is much more significant than the relatively modest decrease in residence time. The drop in residence time with Geldart A particles is much less than with the Geldart B at the same multiple of the respective $U_{mf}$. This is an indication that the expansion of the dense phase caused by secondary injection may be greater for group A particles than for group B. The macromixing behaviour of the gas is also being significantly reduced by the introduction of gas through the fractal injector. This is despite the artificial axial dispersion induced by the gas injected into the reactor at different heights. This reduced axial dispersion will have a positive influence on the conversion of any reaction with positive-order kinetics. It is proposed that by adding additional generations to the fractal injector, particularly at the higher flow rates, the resulting lower injection velocities and more homogeneous distribution of the secondary gas may lessen the decrease in the average residence time and improve the plug flow behaviour.

Conversion experiments using ozone decomposition as a test reaction demonstrate that the increased gas-solid contact results in an increased reactor performance. The conversion was significantly enhanced by secondary gas injection; however, a maximum in the trend with increasing secondary injection was present. A model based on simple two-phase theory (that ignores the increase in the dense phase porosity because of a lack of quantitative data) adequately predicts the trend in conversion only when there is enhanced interaction between the two phases by increasing the local micromixing around the injection points. This interaction increases the concentration of the reactant in the dense phase, but does not increase the gas flow. When applied to a more complex reaction with the presence of consecutive and side reactions, such as the production of maleic anhydride from n-butane, the model predicts that the conversion of n-butane, the production of maleic anhydride, and the selectivity towards maleic anhydride are enhanced. These results give further evidence
that using a fractal injector to distribute a portion of the feed gas into a bubbling fluidized bed reactor is a very promising technique to improve the performance of this reactor type.

6.2. Outlook

Although the results of this study are very positive, there remain many challenges and uncertainties that need to be addressed before this technique can be applied in an industrial fluidized bed application. Among these challenges are the optimization of the fractal injector for a given reaction, the scale-up of a fluidized bed with secondary injection, and the construction of the injector for large-scale application.

The present study lays the fundamental groundwork required for optimization studies to proceed, but the challenge lies in the actual optimization. The structures of the fractal injectors used in this study were only initial ideas as to what they be. The possibilities for different structures are literally endless. As such, a design methodology will have to be developed that will focus on – first and foremost – simplicity, in both design and construction. In all likelihood, the optimal structure will be different for different applications, especially for complex reactions where selectivity is an important issue. The use of computational fluid dynamics will make this process easier and cheaper and can be used now to study the hydrodynamics, and will, in the near future, also encompass reactions. Experiments will always be required, however, to validate the predictions from these models. The models will at least indicate good starting points for further experimental study. Simple models should not be overlooked, however. Two-phase models such as Grace’s bubbling bed model or Kunii and Levenspiel’s fine or intermediate particle models can already be used to optimize the injector in a single dimension – height. This type of optimization may already be useful for simple reactions.

The results of video analysis that show the rate of bubble coalescence being reduced with secondary gas injection bode well for the scalability of the system. This result means that the bubble behaviour is being, to some extent, controlled. However, scale-up has not been explicitly studied in this work. It is surmised that if distributed secondary injection imposes a dynamic structure on the hydrodynamic behaviour of the fluidized bed, then these structured hydrodynamics will persist if the spacing of the injection points is kept the same and the reactor and injector are scaled up. This hypothesis has not been tested, however. Also, the injector spacing used in this work is on the order of 5 cm; such a small spacing may not be practical in an industrial application because large numbers of tubes may hinder the solids circulation. Since the injector can have any fractal dimension less than 3, there is no limit, in theory, on the number of injection points that can be used because the structure will never
Conclusions and Outlook

fill the volume of the reactor. However, the volume of the injector should be kept as small as possible. Studies will need to be done, linked with the optimization challenge mentioned above, to determine if the effects seen in laboratory-scale reactors will persist in larger reactors. In this case, CFD may not be as useful if the systems get too large to simulate in a reasonable amount of time. The simple two-phase models will also be somewhat limited in their use because they cannot take the radial direction into account. Modeling in three dimensions will be increasingly important when studying the effect of the fractal injector at larger scales, where the current assumption that the secondary gas is uniformly distributed across the cross-section of the reactor may no longer be valid.

The technical aspect of building a large-scale fractal injector also has to be addressed. It is true that fractal structures tend to be stronger than non-fractal counterparts, but this will still be an issue in a reactor that operates under such harsh conditions of temperatures and wear. Wear will be less of a problem considering the arguments presented at the end of Chapter 5, and we can also consider that, with secondary injection, the flow rates can be lowered to obtain the same production rates as the situation without secondary injection. However, there will still be the technical challenges, like materials selection and installation of the injector in such a fashion that bed oscillations will not cause it to sway or damage it. This may be a significant engineering challenge considering that industrial sized fluidized bed reactors are often several meters in diameters and many meters tall.

Although there are significant challenges still ahead before this technology can be applied at a large industrial scale for bulk products, they can be overcome. The outcome of the present work gives strong evidence that distributed gas injection via a fractal injector has major benefits for the performance of a bubbling fluidized bed reactor.
Appendix: On Distributor Plates and Injector Tips

Distributor Plates

Distributor plates are critical in achieving uniform gas flow from the air plenum (windbox) into the bed of particles. There are many designs in use in industrial-scale fluidized beds, ranging from perforated plates (a metal plate with holes punched out of it) to bubble caps (similar in appearance to a typical distillation tray) and many variations. In lab-scale experiments, perforated plates and sintered metal porous plates are often used. These designs are simple and easy to implement. Porous plates have a very high pressure drop, which helps to ensure flow uniformity. They are impractical for industrial use, however, because of the associated high compressor costs and relative fragility. Porous plates are used for the distributor plates in the various columns used in this work.

Porous plates need to be installed with care. The plates should only be handled at the edges or by wearing clean gloves because oil and dirt from the user's hands can block the small pores. The plates should be visually inspected for damage before installation. Once installed, the flow uniformity should be checked, since it is possible that there may be manufacturing irregularities, such as varying thickness or blocked pores. This is typically done by pouring a small amount of de-ionized water on the plate while air is blown through from the bottom, simulating a bubble column. This allows for direct visual determination of the uniformity. The water is then drained, while the air is allowed to flow until the plate is dry again.

In our experience, stainless steel porous plates offer very good performance and reproducibility. The bronze plates, however, are more troublesome, and several plates usually have to be made for the column before one is found to be adequate. This is because the material is much softer and more prone to deformation and damage to the pores.

In both the 2-D and 3-D columns, GKN SIKA R3-AX stainless steel porous plates were used as the distributors. These plates are 3 mm thick and have a nominal pore size of ~3 μm.

Fractal Injector Tips

The tips of the injection points can play an important role in the uniformity of the flow through the fractal injector, particularly when the velocity, and hence the pressure drop across the injector, is relatively low compared to the difference in the static pressure in the reactor column. In the 2-D injector this was not an issue because there was always a
relatively high velocity through the relatively few tips (16 tips in the 2-D injector compared to the 72 tips in the 3-D injector). This high flow created a sufficiently large pressure drop to ensure a uniform distribution of the flow. Small pieces of 45 μm mesh were glued over the injection points to prevent the particles from blocking the tips. These meshes were always checked and, if necessary, cleaned between experiments.

Using mesh to cover the injection tips was not sufficient for the 3-D injector because the flow through each tip was relatively low. Therefore, to ensure even distribution of the flow, small porous metal disks were attached to the tips to generate a higher pressure drop. These disks were also extremely effective in preventing particle from blocking the tips. These disks were made of GKN SIKA R15-AX porous stainless steel. They were 3 mm thick with a nominal pore size of ~20 μm.
List of Publications


http://services.bepress.com/eci/fluidization_xii/98.


Acknowledgements

I would first like to thank my professor and promotor, Prof. dr. ir. Marc-Olivier Coppens for giving me the opportunity to come to Europe, and to the Netherlands, to work on this really interesting topic. I have always been interested in the ‘green’ side of chemical engineering, such as sustainable energy and technologies. Working in the Nature-Inspired Chemical Engineering group, where the idea is to learn from nature to improve man-made processes, matched my own outlook very well. I want to thank him, as well as dr. ir. Ruud van Ommen and ir. John Nijenhuis, for guiding me and for (maybe more than) occasionally providing the ‘stok achter het deur’ to keep me moving.

To John and Ruud, thank you for making the ‘Proeffabriek’ a wonderful place to work! The atmosphere was always excellent (I would even say ‘gezellig!’) – for both work and play. You manage to keep the mood relaxed, informal, and playful, which makes the work more pleasurable!

To all of the support staff – Mieke Jacobs, Caroline Monna, Els Arkesteijn, to name a few – thank you for keeping everything running smoothly, even through the re-organization. It seems to me as if everything was in a constant state of flux for the entire time I have been here, yet you all took it in stride and kept the wheels turning.

I want to thank all of the workshop staff; you are all truly professionals in the best sense of the word! To Ruud Monna and Nico Alberts, in particular – your excellent work on the fractal injectors has proven to me again and again that there are no such things as problems, only challenges that can be overcome – with a smile! I’d also like to take this opportunity to congratulate Ruud, who has recently retired after 43 years of service to the university. That is an amazing accomplishment that is increasingly rare in today’s world! That kind of experience will be very difficult to replace in the workshop, but that’s just another challenge – right, guys? Ruud, have a great time sailing around Friesland!

Along the way, I guided a few students – and they guided me as well! Claire Tange, Rianne Grinwis, David Vervloet, Vincent Twigt, Aylin Ulusoy, and Hamed Karimi Bahri – thank you all for your hard work, for being able to put up with me, and for your good humour! You all made significant contributions to this work. I learned a lot from you, and I hope that vice versa is also true. It was a pleasure!
In the last four years, I have learned a lot of the Dutch language – but apparently not enough to write the summary in Dutch without giving some people headaches! I want to thank Renske Beetstra for her invaluable help with the Dutch translation.

To my fellow PCMT’ers and NICE’ers (some of which are also Proeffabriekers): Stefan & Irina, Antonia, Veronica, Wang Jia, Wang Gang, Raghu, David N., Alexei, Vijay, Prasant, Vincent van H., and the inestimable Kourosh – it was a pleasure to work with you all! I seem to remember a few group Christmas parties with Irina organizing just about everything. I remember going to the Lichtjesavond in Delft (twice), getting nearly soaking wet the second time and sitting in a Greek restaurant for 3 hours to have a snack! I remember a particular barbecue in the Delftsehout, hearing Veronica no matter the distance between you and her, which was very convenient when people kept getting lost in the park. And what about the Polish dance bar at Scheveningen? Six of us went with one Polish friend, and we had to keep explaining that “we’re with her!” as absolutely everyone else (maybe not so surprisingly) was Polish! And, ah yes, the long discussions (usually someone complaining about something) in the coffee room by Prof. Frens’ office. Let’s not forget that Stefan & Irina make some of the best homemade cheese around!

To my fellow Proeffabriekers: John, Ruud, Flip, Malte, Eivind, Soren, Vincent B. van N., Ali, Mike, David V., Roderik, Alex, Jeroen, Aylin, Hamed, Claire, Rianne, Kalyani, the incomparable Birol, Ronald, Renske, Andres, Bart, Patrick, Koos, Marnix, Sijbe, Michael – thank you all for making working in the Proeffabriek so enjoyable. We had a great time at work and play! I have a lot of fond memories of this gang. I remember us solving all of the world’s problems over coffee (at least theoretically). The barbecues (and lots of ‘em!), rain or shine. Ice cream-IJS! (and lots of it!). I always enjoyed having those really thought-provoking conversations with Malte, and also occasionally David and Birol, over a pint. And speaking of pints...going to the pub to watch the match! What about Flip & Gwen’s 70’s themed wedding? We all got dressed up with big hair and even bigger sideburns! I also remember Stefan & Irina’s vizslas running around the proeffabriek very excitedly... Do you remember Kourosh and Vijay’s famous ‘discussions’? I think I might miss the bicycle bell on the stairs – and the antics John does to get our attention when we ignore the bell! A not-so-fond memory? Me having some unintentional ‘fun’ with electricity and a short-circuit.

To a few close friends in particular – Flip & Gwen, Stefan & Irina, and John & Mirjam – thank you very much for your friendship and support. Among other things, you really helped me settle into a new country and a new life.
My fondest memory would have to be attending a Burgerscentrum company tour with Flip. Now, as we all know, Flip is a nice guy, but that’s not what I’m referring to here. Let me explain. In this particular instance the research institute had arranged a tour of Philips in Eindhoven. Characteristic of us, we arrived just on time. As we walked into the lecture room where the tour was to begin, I happened to notice a particular blonde female, who was giggling away quite happily with her dark-haired friend – they were also here to take the tour. After staring at the back of her head for the rest of the day (she sat in the front row, I was at the back), I finally managed to actually see her face at the borrel (drinks) at the end of the day. After chatting with her briefly, I got her name. The rest is, how you say... history. To Tamara, thank you for being a ray of sunshine in my life. Everything seems so much brighter after we met! Thank you for your support, your patience, and your sense of humour, mixed in with a little bit of silliness that so often matches my own! You keep me grounded, yet you dare me to dream.

A special thank you to my parents, Ann and Errold, and to my brother, Ian. Where would I be without you? My parents always encouraged me to try my best, and to just get out there and try new things. Don’t sweat the little stuff. Make sure the big things are taken care of; the little things will work themselves out. They taught me independence, and they instilled in me the desire to travel. Both of these, I found out, would later lead to increasing my self-confidence and, eventually, lead me to the Netherlands. My brother was always there for me, giving me advice as only a big brother can. Everything from helping me with calculus at one point, many moons ago, to picking out wet-weather clothing (very useful, I must say) and to being an inspiration to me.

In short, thank you all!
About the Author

Dana Christensen was born on the 9th of June, 1976, in Ottawa, Canada. After completing high school in 1995, where he had some very fun and exciting chemistry classes, he decided to study chemical engineering at the University of Waterloo. He gained valuable work experience via a number of co-operative education work terms in many different industries ranging from breweries to gold mines to government departments and research. He was a member of the University of Waterloo Alternative Fuels Team in 1999-2000 and had a great experience working on the 2000 Ethanol Vehicle Challenge (EVC) in which the student team had to modify a gasoline-powered pick-up truck to run on ethanol instead. The team was very successful, finishing 2nd overall out of 15 teams from across North America. Upon completion of his undergraduate degree (Honours, Co-operative Education), he immediately enrolled in the Master of Applied Science program at the same university under the supervision of Dr. Eric Croiset, Prof. Pete Silveston, and Prof. Bob Hudgins. His thesis work was to study the production of hydrogen from ethanol – essentially continuing and expanding the work he did for the EVC. Upon completion of his MASc in 2003, he decided to continue in research, and desiring a change of scenery, he moved to the Netherlands to join the Nature-Inspired Chemical Engineering group of Prof. Marc-Olivier Coppens. After four years, numerous articles and presentations, several fractal injector prototypes, and many new experiences, he joined Altran Technologies Nederland as a consultant in the Sustainable Energy group in October 2007.