CHAPTER 1

INTRODUCTION

Packed bed reactors that process gas and liquid reagants are extensively utilised in industry, most notably in the petrochemical industry for hydroprocessing (Satterfield, 1975; Gianetto and Specchia, 1992). Other typical examples of the industrial applications of these reactors include the production of fine chemicals via a catalysed gas-liquid reaction step and the catalytic oxidation of wastewater.

For the succesful commercialisation of a specific reaction process, it is necessary to develop and/or select a suitable catalyst, to design and develop a viable reactor with appropriate surrounding unit operations and finally to operate the resulting plant well enough to meet production specifications. Historically, these steps would be performed completely seperately: For example, a catalysis group develops or identifies a suitable catalyst with primary focus on the chemistry of the reaction. A preliminary design of a commercial process for this reaction is then verified with pilot studies, after which commercialisation can be initiated. Finally, the process is operated on a commercial plant. In all these steps, different aspects of the final process are emphasised so that it is quite possible that catalyst design teams may have little or no knowledge of reactor scale effects such as heat and mass transfer or flow characteristics, and that pilot scale studies are interpreted with little regard to the effect of scale. However, reactor operation and optimisation are often performed without proper knowledge of the underlying catalysis process. It is clear that such an approach, though successful to some extent, probably would not lead to optimal processes.

It is for this reason that a more integrated approach is advocated, where both the chemistry (catalysis) and engineering (reactor design and operation) are of importance throughout the development of the process (Dudukovic et al., 2002; Larachi, 2005). To achieve such integration, a good understanding of both particle-scale (e.g. catalysis and particle efficiency) and reactor-scale behaviour (e.g. hydrodynamics and transfer pro-

cesses) is important.

In packed bed gas-liquid reactors, it is well known that flow configuration and characteristics have an important effect on the behaviour of a reactor. These reactors can be operated in gas-liquid cocurrent downflow, cocurrent upflow, or countercurrent flow. Due to flexibility in terms of throughput, gas-liquid downflow reactors, commonly known as trickle-bed reactors (TBRs), are often preferred when large process streams are involved (Sie and Krishna, 1998; Dudukovic et al., 2002). The hydrodynamic behaviour of these reactors and its effect on reactor performance are especially intricate, due to the possible existence of incomplete catalyst wetting, multiple flow morphologies and hydrodynamic hysteresis.

Though not only studies regarding the solid catalysis of gas-liquid reaction systems, but also studies regarding trickle-bed reactor hydrodynamics are abundant, the development of the relevant theories is mostly driven separately. For example, a large part of the literature data and theoretical developments regarding trickle-bed hydrodynamics is based on cold mock-ups (involving for example air and water without any reaction). Such studies are of great importance to the understanding of trickle-bed reactors, but can ultimately only speculate about that which is of final importance, i.e. the influence on reactor performance. By contrast, many pilot studies exist with a predominantly practical focus, for example to prove the concept of a new process. Reactor hydrodynamics is then only loosely touched upon.

Proper reactor studies will always be needed to verify and guide theoretical development (including cold data), and highlight which knowledge of hydrodynamics is of primary importance. However, it is very difficult and even unlikely to understand a reactor correctly without the knowledge resulting from studies that focus exclusively on reactor hydrodynamics and relevant theories, or studies that focus entirely on the catalytic process on particle scale. One will never reach the goal of integrated reactor development without integrated research.

This work follows an integrated approach to studying the role of liquid-solid contacting in a trickle-bed reactor. The study focuses on two aspects of liquid-solid contacting: partial wetting and liquid-solid mass transfer rates. Firstly, fractional wetting in a TBR is characterised on a bed and particle scale in a non-reactive air-water experimental study, making use of colorimetry. Results regarding particle-scale wetting topology form the basis for numerical modelling of reaction within monodispersed and eggshell catalysts under different reaction conditions (i.e. rate, kinetic expression, internal and external mass transfer resistances), which is in turn used in the verification of existing pellet efficiency models and the development of new ones. The knowledge obtained from the visualisation of wetting efficiency and subsequent particle efficiency modelling is then used for the interpretation of conversion data and the development of a novel method of wetting efficiency/liquid-solid mass transfer measurement in a large-scale high-pressure

pilot reactor. This reactor study is based on a reaction for which the rate is limited by the rate of liquid reagent supply to the catalyst.

It is clear that liquid-solid contacting is strongly affected by flow morphology and local liquid velocity profiles. Previous studies have established that these are subject to hydrodynamic multiplicity when operating in the partial wetting (trickle) flow regime: Flow patterns and behaviour are strong functions of the history of flow (Kan and Greenfield, 1978; Lutran et al., 1991). Multiplicity behaviour should therefore be included in the study of solid-liquid contacting. It is possible to operate along the boundaries of hydrodynamic multiplicity by utilising predefined pre-wetting procedures (Loudon et al., 2006; van der Merwe and Nicol, 2009). This strategy is followed for all the presented experimental studies in order to explore the boundaries of hydrodynamic multiplicity.

Wetting efficiency and liquid-solid mass transfer measurements, partially wetted pellet efficiency modelling and reactor conversion data interpretation are not new. Even the integration of hydrodynamic theory with reactor conversion data measurements is, though less abundant than studies that focus almost exclusively on either reactor perfomance or hydrodynamics, quite common. The literature review in the next chapter serves to identify and illustrate where contributions can be made to the study of liquid-solid contacting and its effect on reactor performance, and motivates the experimental and theoretical developments in the subsequent chapters. The literature study is a broad review of studies relevant to the overall contribution of this work. More specific literature is discussed in each chapter, if necessary.

CHAPTER 2

LITERATURE

Apart from the catalytic process itself, several mass transfer steps can influence the rate and/or selectivity of a solid catalysed gas-liquid reaction as illustrated in Figure 2.1. In packed bed gas-liquid reactors, it is well known that flow configuration and characteristics have an important effect on these transfer processes. Especially for trickle-bed reactors operating in the trickle flow regime, these processes can have an intricate interaction. Trickle flow is characterised by gravity-driven liquid flow over a packed bed with gas continuous flow. The liquid trickles down the packing, giving rise to (possibly) incomplete wetting, liquid velocity profiles and liquid maldistribution. This morphology of liquid flow directly influences the mass transfer steps depicted in Figure 2.1:

- The area available for liquid-solid mass transfer is directly affected by the fraction of external particle area contacted by the flowing liquid.

- The area available for gas-solid mass transfer is directly affected by the fraction of external particle area contacted by the flowing liquid. Gas-solid mass transfer is generally regarded as being fast enough not to be rate-determining.

- Liquid velocity and liquid velocity profiles will affect gas-liquid and liquid-solid mass transfer coefficients.

- The geometry and the extent of fractional wetting affect intraparticle diffusion (Yentekakis and Vayenas, 1987).

- Maldistribution of the liquid can cause parts of the catalyst bed to be almost completely dry or almost completely flooded. The former gives rise to bed-scale incomplete catalyst utilisation if the liquid reagent is non-volatile, or the formation of hot spots if reaction can occur in the gas-phase (Sedriks and Kenney, 1972). The
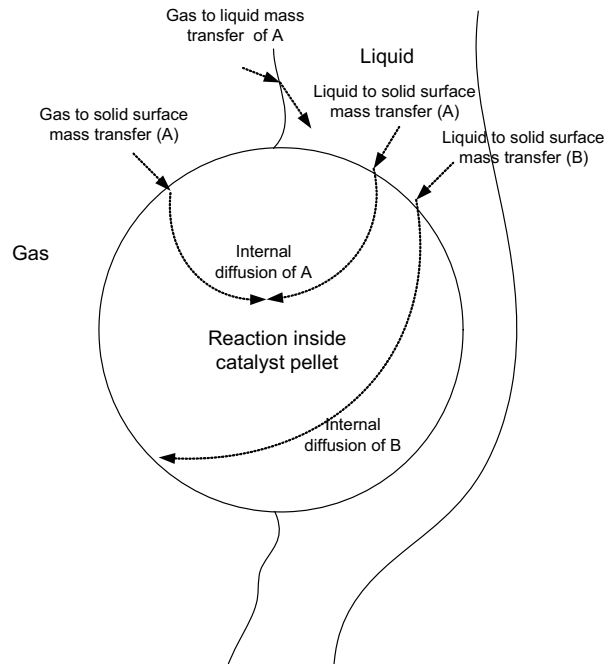
Figure 2.1: Mass transfer steps in a trickle-bed reactor.

latter can result in part of the bed becoming completely deprived of the gaseous reagent (Ravindra et al., 1997b).

In this thesis, the interaction between liquid flow morphology and the different mass transfer steps is collectively termed liquid-solid contacting. The primary focus is on liquid-solid mass transfer and internal diffusion as affected by liquid flow morphology. Since the study of partial wetting is integral to all work, the study focuses mainly on trickle flow, where partial wetting occurs and mass transfer effects are of major importance. Several other flow regimes are possible for gas-liquid downflow in trickle-bed reactors. Flow maps (Satterfield, 1975; Gianetto and Specchia, 1992; Sie and Krishna, 1998) and correlations (Fukushima and Kusaka, 1977; Larachi et al., 1999) can be used to determine the flow regime applicable to a specific reactor. In terms of pilot and industrial trickle-bed reactors, the trickle and pulsing flow regimes are the most important (Gianetto and Specchia, 1992). An excellent hydrodynamic description of pulse flow as a hybrid between trickle flow (at the high interaction boundary) and dispersed bubble flow is provided by Boelhouwer et al. (2002).

2.1 Liquid-solid contacting: A short historical overview

The simplest way of modelling a trickle-bed reactor is by assuming first-order kinetics, plug flow behaviour and no resistances to mass transfer of the reagents to the catalyst surface, so that the general design equation can be used:

$$-\ln(1 - X) = k_r \cdot \tau \qquad (2.1)$$
$$\tau = \frac{V_R}{Q_L}$$

where k_r is based on the active catalyst volume. This basis for k_r is not standard, but will be used throughout this chapter to link with the notation used in Chapter 4. Early work on trickle-bed reactors showed that such ideal behaviour cannot be assumed even if dispersion is not expected to play a role (Mears, 1971), and is summarised by Satterfield (1975). An interesting early study that gives evidence of hydrodynamic effects on reaction rates in trickle-bed reactors was performed by Henry and Gilbert (1973) who studied pilot reactor conversion data to find the following approximate proportionality:

$$-\ln(1 - X) \propto Z^{1/3} \tau^{2/3} d_p^{-2/3} \qquad (2.2)$$

This translates to an effective rate constant proportional to $v_{SL}^{1/3} d_p^{-2/3}$. According to a laminar film flow model developed by Satterfield et al. (1969), the liquid holdup in a trickle-bed reactor is proportional to $v_{SL}^{1/3} d_p^{-2/3}$. The authors therefore proposed that the efficiency of a trickle-bed reactor is directly determined by the liquid holdup. Though Satterfield (1975) disputed this proposal soon afterwards, the observations are clear evidence of hydrodynamic effects. Satterfield (1975) suggested that the observed proportionality may be a result of decreased particle size leading to higher catalyst efficiency factors; and/or increased velocities and bed lengths leading to less dispersion. Mears (1974) stated that the effect of incomplete catalyst wetting was observed, supported by the correlation of Puranik and Vogelpohl (1974) that states that wetting efficiency is proportional to $v_{SL}^{0.31}$.

By proposing a direct proportionality between reaction rates in a trickle-bed reactor and wetting efficiency, one of the following is indirectly suggested:

- Particles in a trickle-bed reactor are either completely dry or completely wetted; or

- catalyst efficiency for a partially wetted pellet is directly proportional to the fractional coverage of its surface with the flowing liquid; or

- external liquid-solid mass transfer is proportional to wetting efficiency and determines the rate of reaction.

Dudukovic (1977) argued that the effect of incomplete wetting should be considered on a particle scale, rather than a reactor scale and, based on the work of Aris (1957), arrived at the following expression:

$$-ln(1-X) = \eta \cdot k_r \cdot \tau \tag{2.3}$$

$$\eta = f \cdot \frac{\tanh\left(\frac{\phi_G}{f}\right)}{\phi_G} \tag{2.4}$$

More details of the derivation appear in Chapter 4. The original work also incorporated incomplete pore filling of the catalyst. This is not shown here, since complete pore fill-up is generally assumed, ever since the residence time distribution study of Schwartz et al. (1976)[1]. The effects of external liquid-solid mass transfer were not considered, due to the notion of Satterfield et al. (1969) that external liquid-solid mass transfer probably does not play a role in a trickle-bed reactor. This was later incorporated in the usual way that external mass transfer resistances are treated:

$$-ln(1-X) = \eta_0 \cdot k_r \cdot \tau$$

$$\eta_0 = \eta \cdot \frac{C_s}{C_{bulk}}$$

$$k_{LS}S_p.f(C_{bulk} - C_s) = \eta \cdot k_r V_R C_s$$

$$\therefore \eta_0 = \eta \frac{C_s}{C_{bulk}} = \eta \left(1 + \frac{\phi_G^2}{Bi'.f}\eta\right)^{-1} \tag{2.5}$$

All the work discussed so far was about reactions for which the reagent(s) in the liquid determine the overall rate of reaction inside a trickle-bed reactor and are non-volatile. Early evidence of wetting efficiency effects on reactions involving volatile or gaseous reagents was provided by Sedriks and Kenney (1972) for the hydrogenation of crotonaldehyde. Reactor conversions for the dry startup and pre-wetted startup of a trickle-bed reactor were compared. It was visually observed that the wetting efficiency for dry startup was considerably lower than when the bed was pre-wetted, but conversions were considerably higher for dry startup, especially at low liquid flow rates. As for the approach of Mears (1974), the effect of wetting efficiency was modelled as a bed-scale effect:

$$r = (1-f) \times r_d + f \times r_w \tag{2.6}$$

At atmospheric pressure, where the reaction was performed, both reagents were present

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[1]An exception is the case of highly exothermic reactions. These are not considered in this work, but for more information on this work, read for example Kirillov and Koptyug (2005).

in the gas phase. Due to the smaller resistances to external and internal mass transfer for dry pellets, $r_d \gg r_w$, resulting in higher reaction rates for lower wetting efficiencies. It is debateable whether this bed-scale decription is entirely correct, but a pellet scale model for a reaction that is limited by a volatile reagent on a partially wetted catalyst, derived by Ramachandran and Smith (1979) suggest more or less the same form. The only difference is that the particle is internally wetted, so that partial wetting only affects the overall particle effectiveness through enhanced external mass transfer over the dry pellet surface and not through enhanced internal diffusion. Nevertheless, the rate enhancement effect of partial wetting for volatile limiting reagents was observed several times, with the data of Mata and Smith (1981) giving a fine illustration of the combined effect of wetting efficiency and liquid-solid mass transfer for such a reaction. The pellet scale model of Ramachandran and Smith (1979) is discussed in more detail in Chapter 4, where it forms an integral part of the work. Apparently there are no suggestions in the literature for the simple treatment of reactions for which both the liquid and gas reagents play a role.

As for most hydrodynamic parameters in trickle-bed reactors, early estimations of wetting efficiency were based on packed column data, but not long after it was shown that wettig efficiency could be of importance in trickle-bed reactors, methods for the measurement of this hydrodynamic parameter were suggested (Schwartz et al., 1976; Colombo et al., 1976) and more and more data became available. This is discussed in section 2.2.1. Possibly due to the early general consensus that liquid-solid mass transfer is of lesser importance, liquid-solid mass transfer measurements remained mostly based on dissolution techniques for larger size, non-porous particles. The first reactor-derived data were published by Morita and Smith (1978) for the hydrogenation of α-methylstyrene to cumene. The importance of liquid-solid mass transfer had however been illustrated several times before for the oxidation of components in an aqueous solution (Klassen and Kirk, 1955; Hartman and Couglin, 1972; Goto et al., 1975). Based on mass transfer correlations and typical reaction rates, Sie and Krishna (1998) estimate that liquid-solid mass transfer can play an important role in hydrotreaters. Measurement of and correlations for liquid-solid mass transfer are discussed in section 2.2.2.

2.2 Measurement and correlations for solid-liquid contacting

2.2.1 Wetting efficiency

The first wetting efficiency correlation that was used in TBR studies/modelling is based on packed column data (Puranik and Vogelpohl, 1974). Most wetting efficiency data are derived from a tracer response measurement technique, based on the effect that

intraparticle diffusion has on a tracer response curve. The technique was first proposed by Colombo et al. (1976) and later streamlined by Mills and Dudukovic (1981). Based on a Thiele modulus argument related to the work of Dudukovic (1977), the wetting efficiency is taken as the square root of the apparent effective diffusivities measured for trickle- and single-phase liquid flow.

$$f = \sqrt{\frac{D_{TBR}}{D_{LF}}} \tag{2.7}$$

A more complete theoretical development of the effect of partial wetting on a tracer response curve was given by Ramachandran et al. (1986), but was never used for the measurement of wetting efficiency. The work was however used by Julcour-Lebigue et al. (2007), for a theoretical validation of the usual tracer technique. The major disadvantage of the tracer wetting efficiency measurement method is that it is model-based.

For the purpose of correlating wetting efficiency with liquid and gas properties and operating conditions, the tracer technique has always been the most important tool for data generation. Other important wetting efficiency measurement methods are the dissolution method (Specchia et al., 1978; Lakota and Levec, 1990; Gonzalez-Mendizabal et al., 1998), colorimetry and reaction methods. Pironti et al. (1999) proposed a wetting efficiency measurement method based on pressure drop, which was later shown to be inaccurate by Baussaron et al. (2007).

The dissolution method compares dissolution rates for trickle flow with dissolution rates in liquid-full operation at the same interstitial velocities. The disadvantage of this method is that liquid-full operation measurements are required over the whole flow range and that a good estimate is needed for liquid holdup (interstitial velocity). Also, it is not completely certain whether or not single-phase liquid flow and trickle flow has the same mass transfer characteristics at the same interstitial velocities. A second disadvantage is that non-porous or slightly porous soluble packing material is used, contrary to the porous catalysts encountered in trickle-bed reactors.

Colorimetry makes use of colourant in the liquid to colour particles in the bed where they were in contact with the liquid. The bed is dismantled, and the particles are then examined through optic methods such as photography and subsequent image processing. The major advantage of colorimetry is that it is direct and no model or assumptions are needed. Also, more information can be extracted about catalyst wetting other than the average wetting efficiency. The liquid flow pattern should however be stable so that the wetting efficiency is not overestimated. The major disadvantage is that the method is destructive and requires bed re-packing after each experimental run. Other aspects of and the possible pitfalls in the colorimetric evaluation of wetting efficiency is discussed in Chapter 3, which reports a colorimetric study to obtain the distribution of particle wetting. Until recently, very little colorimetric wetting efficiency data were available in the

literature, with the first data for trickle-bed reactors reported by Lazzaroni et al. (1988). Thereafter, Ravindra et al. (1997a) performed a colorimetric study to describe trickle-flow morphology rather than to measure wetting efficiencies. Recently, Baussaron et al. (2007) generated an extensive amount of colorimetric wetting efficiency data for several fluids, expanded by Julcour-Lebique et al. (2009) to propose a colorimetry-based wetting efficiency correlation.

In terms of direct applicability, wetting efficiency measurements from reactor studies are arguably the most important. After all, an important reason for the study of wetting efficiency or any hydrodynamic parameter is to understand the possible effects it has on reactor performance. The biggest disadvantage for reaction methods as a tool for parametric studies of wetting efficiency, is that most reaction studies are specific to a certain system with specific reagents and catalyst combined under specific operating conditions. Also, the existing reaction methods are based on some reactor model that require estimates for either external mass transfer or particle kinetics or both. Specific reaction-based wetting efficiency studies are discussed in more detail in section 2.3.

Figure 2.2 shows wetting efficiency correlations developed from data that were obtained with different measurement methods. Predicted wetting efficiencies are applicable to the reaction system that is employed in the study that is reported in Chapter 5. Also included is the prediction of the artificial neural network (ANN) of Larachi et al. (2001). It is based on almost all the known wetting efficiency data published before the correlation was developed, and can therefore be recommended for trickle-bed reactors where there are no experimental studies at the exact reactor conditions. However, empirical correlations can fail to extrapolate accurately, and it is often recommended that correlations that were developed from data generated at conditions close to the conditions of interest should be used (Dudukovic et al., 2002). To reduce sensitivity to extrapolation, Iliuta and Larachi (1999) developed a semi-theoretical model which integrates liquid holdup, pressure drop and wetting efficiency.

In Figure 2.2, only v_{SL} is shown as independent variable which determines wetting efficiency. Generally, the liquid flow rate increases wetting efficiency and incomplete wetting can be expected for liquid velocities less than $4 \, \mathrm{mm/s}$. Though important, v_{SL} is of course not the only parameter that affects wetting efficiency. The effect of gas flow rate and pressure is rather disputed in the literature. The most widely accepted theory is that increased gas mass velocity helps with spreading the liquid over the particles, thus increasing the wetting efficiency (Al-Dahhan and Dudukovic, 1995; Dudukovic et al., 2002), but some studies suggest the opposite (Burghardt et al., 1995; Herskowitz and Mosseri, 1983) whereas yet others did not find any noteworhty effects of the gas flow rate(Lazzaroni et al., 1988). Decreased particle size and porosity improve wetting due to cappilary forces (Lappalainen et al., 2008), but porosity variations can adversely affect the overall liquid distribution (Sie and Krishna, 1998). The contact angle between the liquid and the
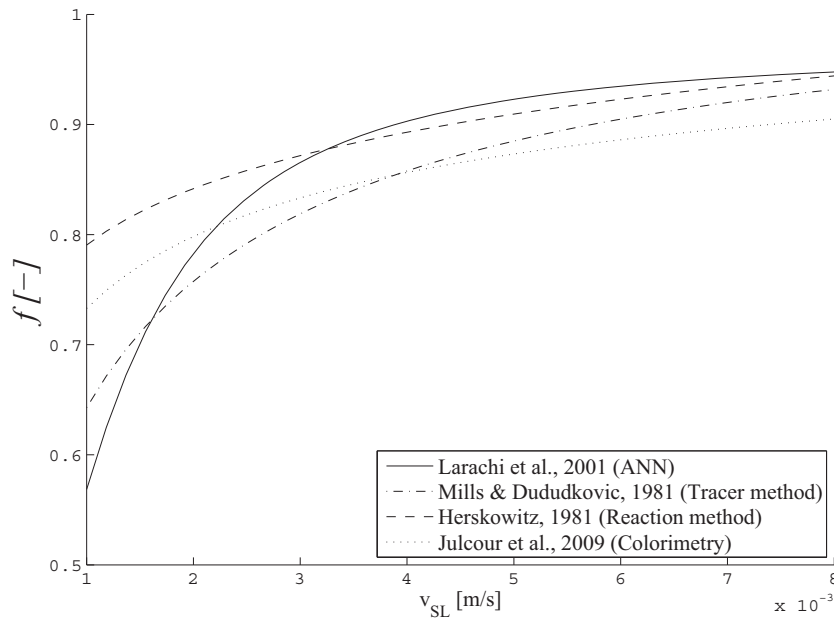
Figure 2.2: Literature correlations for wetting efficiency as measured with different methods.

solid affects spreading of the liquid, and also has a major effect on liquid distribution or multiplicity behaviour (van der Merwe and Nicol, 2009).

2.2.2 Mass transfer

The overwhelming majority of liquid-solid mass transfer measurements were obtained using either a dissolution or an electrochemical technique. The dissolution technique makes use of packing material which is coated with a soluble solid, and the amount of solute in the effluent can be used to determine the rate of liquid-solid mass transfer. The effluent concentrations should be far from equilibrium to ensure that the process is controlled the rate of liquid-solid mass transfer. The solute is usually sparingly soluble in the liquid to prevent excessive change in packing characteristics. Typical coating materials for the dissolution in water (which is generally used in this technique) are bezoic acid and naphthalene (Specchia et al., 1978; Lakota and Levec, 1990). In the electrochemical technique, an electrolyte solution is used as the process liquid, and undergoes an electrochemical reaction with a cathode in the bed. The cathode is usually a single pellet with the same geometry as the packing, and the method is therefore especially suited to the measurement of local mass transfer rates at a specific position in the bed. An example of this is the characterisation of liquid-rich and gas-rich pulses in the pulsing flow regime (Chou et al., 1979). Since it has to be an electrolyte, the choice of process liquids is limited (Latifi et al., 1988), which make it unsuitable for liquid-solid mass transfer measurement for typical trickle-bed reactor systems such as hydroprocessing reactors.

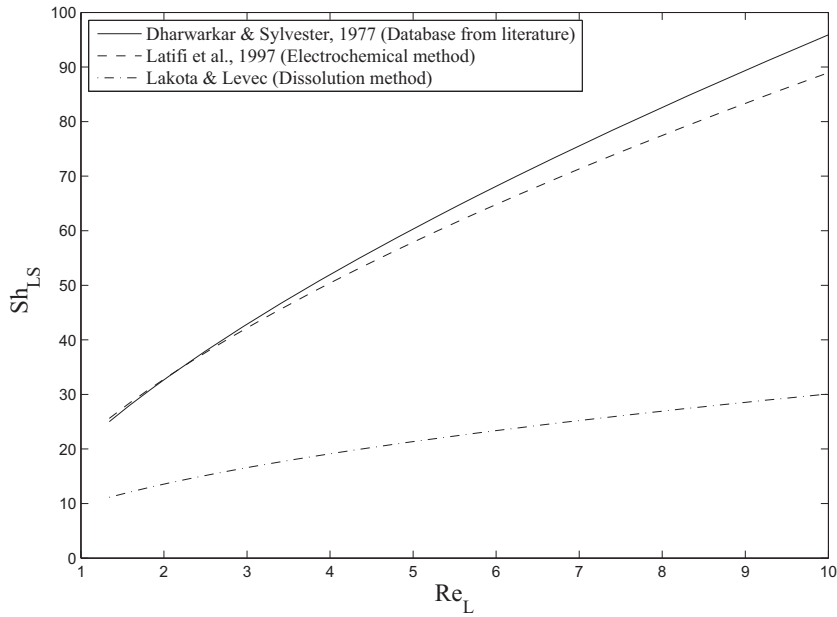Most trickle-bed reactor studies make use of a correlation based on one of the above

Figure 2.3: Literature correlations for liquid-solid mass transfer as measured with different methods.

techniques to estimate liquid-solid mass transfer, if necessary. Exceptions are those of Morita and Smith (1978) and Goto et al. (1975). The latter measured liquid-solid mass transfer with the dissolution technique, after which it was applied to the catalytic oxidation of formic acid in a trickle-bed reactor. Banchero et al. (2004) measured overall gas-to-particle mass transfer rates and concluded that currently, mass transfer resistances are overpredicted for high-pressure trickle-bed reactors[2]. There is a large deficiency of reactor-based measurements, especially under high pressures (Highfill and Al-Dahhan, 2001; Dudukovic et al., 2002). Most correlations of liquid-solid mass transfer are of the form

$$Sh = A \cdot Re_L^n Sc_L^{1/3} \tag{2.8}$$

Some liquid-solid mass transfer correlations for different measurement methods are shown in Figure 2.3. Again the figure is based on the reaction system in Chapter 5 ($Sc_L \approx 2000$).

Gas-liquid mass transfer is usually measured through the physical absorption or desorption of a gaseous component in the liquid or through chemical absorption using of a fast (uncatalysed) reaction between a gas and liquid component (Marquez et al., 1994). The overall resistance to gas-liquid mass transfer is constructed of a gas-side and a liquid-side mass transfer resistance (see Figure 2.1). The gas-side mass transfer coefficient is usually much faster and therefore less important than the liquid-side coefficient, but may have an effect when the gas density is high (Dudukovic et al., 2002). At atmospheric pressures,

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[2]The authors did not take into account any partial wetting enhancement effect, which may be an explanation. Still, operation was at typical near-complete wetting conditions.

where most experimental studies are performed, only the liquid-side mass transfer coefficients are usually measured. Based on literature correlations, overall gas-liquid mass transfer coefficients appear to be of the same order of magnitude as liquid-solid mass transfer, though possibly slightly lower[3]. Gas-solid mass transfer is generally considered to be instantaneous for all practical purposes.

2.2.3 Liquid flow morphology and multiplicity

Insights into liquid flow morphology are usually obtained by "visual" studies such as tomography (Lutran et al., 1991; Sederman and Gladden, 2001; van der Merwe et al., 2007) or colorimetry (Ravindra et al., 1997a). In the trickle-flow regime the liquid is suggested to be present in the form of film-type flow or rivulet-type flow (Zimmerman and Ng, 1986; Lutran et al., 1991). For poor inlet distribution, channelling of the liquid can also be expected (Ravindra et al., 1997a). The different flow structure types have been used to explain the phenomenon of hysteresis in trickle flow, where the hydrodynamic behaviour of the bed is a function of flow history (Kan and Greenfield, 1979; Christensen et al., 1986). A more theoretical account of the mechanism underlying hysteresis behaviour was given by van der Merwe and Nicol (2009) in terms of pore cappilary forces and liquid-solid contact angles. It has been shown that the boundaries of hydrodynamic multiplicity can be defined by the behaviour of the bed after it has been subjected to specific pre-wetting procedures (Loudon et al., 2006; van der Merwe and Nicol, 2009). The most important amongst these are Levec pre-wetting, which represents the lower boundary in pre-wetted beds for most hydrodynamic parameters, and Kan-liquid or Super pre-wetting representing the upper boundary. In the former case, the bed is pre-wetted and drained prior to operation whereas the Kan-liquid boundary is obtained by operating the bed in the pulsing regime before steady state operation. Super pre-wetting refers to a startup where the bed is flooded, but not drained before the liquid is introduced at the operational flow rate. It was shown that Kan-liquid and Super pre-wetted beds have similar behaviour (van der Merwe, 2008), and these pre-wetting methods are collectively referred to as "extensive pre-wetting" in the rest of this thesis. In most investigations, some form of pre-wetting is employed in order to be able to generate repeatable results. The precise pre-wetting procedure is often not reported.

Almost all morphological and hysteresis studies are performed for atmospheric air-water systems, though Kuzeljevic et al. (2008) recently quantified pressure-drop hysteresis for a high-pressure system and van der Merwe et al. (2008) investigated the hysteretic behaviour of a pilot trickle-bed reactor. Most hysteresis studies report pressure-drop and liquid holdup data. Little work on the multiplicity behaviour of wetting efficiency

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[3]Unlike liquid-solid mass transfer, gas-liquid mass transfer is depends strongly on the gas flow rate. A direct comparison is therefore not possible.

(van der Merwe and Nicol, 2009) and liquid-solid mass transfer (Sims et al., 1993) has been performed so far.

2.3   Reactor studies and liquid-solid contacting

Though countless trickle-bed reaction studies are avaiable in literature, only those that integrate knowledge of hydrodynamics with trickle-bed reactor results will be discussed here. Generally, two approaches are taken to the integration of reactor studies with trickle-flow hydrodynamics: Either, hydrodynamic theory is used to predict reactor performance such as conversion, which is then compared to experimental reaction data (predictive approach); or reaction data are used to make hydrodynamic measurements (diagnostic approach).

In the latter category, several studies were done to obtain estimations of wetting efficiency under trickle-flow conditions, sometimes coupled with measurements for liquid-solid or gas-liquid mass transfer coefficients. In most of the studies the limiting reagent was present in the gas and the liquid, or only in the gas. The effect of wetting efficiency and mass transfer resistances is then described according to the additive model stated in Equation (2.6), first used by Hartman and Couglin (1972) to find agreement between experimental data and a model based on literature estimation of gas-liquid and liquid-solid resistances.

Though most of these studies employ the additive model, they do so in different ways and are sometimes interpreted differently. As shown previously, Sedriks and Kenney (1972) used Equation (2.6) as a description of bed-scale wetting, estimating wetting efficiencies from overall rate estimations for completely wetted and completely dry particles, to illustrate the importance of pre-wetting. Ruecker and Ackgerman (1987) took a similar approach, determining the reaction rates in a vapour-phase packed bed reactor to determine r_d and then in an (almost exclusively) liquid-phase packed bed reactor to determine r_w. It was possible to operate the bed in the vapour phase employing a very high H_2-to-liquid feed ratio. Realising that the methods of Sedriks and Kenney (1972) and Ruecker and Ackgerman (1987) violate the (probable) condition of internal pore filling, Llano et al. (1997) studied the hydrogenation of anthracene for different vapour-to-liquid feed ratios of the limiting reagent. The data were extrapolated to zero liquid feed to obtain an estimation of the overall rate of reaction for an externally dry, internally wetted pellet. This was used in the additive model for the estimation of wetting efficiency. The method implicitly assumes that the average surface concentration of the limiting reagent is a function of wetting efficiency only, so that no external mass transfer data were reported.

Goto and Mabuchi (1984) employed an estimate of ηk_r for the oxidation of ethanol (first-order with respect to oxygen) by measuring conversions of an upflow reactor at high

liquid flow rates. Literature correlations were used to estimate gas-liquid and liquid-solid mass transfer in trickle-flow operation so that r_w and r_d could be determined for each experimental condition, in order to estimate wetting efficiency. The disadvantage of this method is that mass transfer rates are estimated with correlations, and not determined independently. The study focuses mainly on how fractional wetting affects conversions as compared to the complete wetting obtained during upflow operation. In another gas-limited reaction study, Mata and Smith (1981) varied liquid feed inlet saturation levels in order to be able to approximate particle kinetics and fractional wetting independently without the need for further kinetic studies. They had to rely however, on correlations for external mass transfer.

Morita and Smith (1978) managed to measure mass transfer and wetting efficiency indepently by conducting experiments at the same feed flow rates with catalysts of different activity. This work has the considerable advantage that the measurements are not affected by the accuracy of correlations, although an estimation of particle kinetics is needed, as well as a gas-liquid mass transfer correlation in order to decouple gas-liquid and liquid-solid mass transfer. A very similar method was used by Herskowitz et al. (1979) for a more complete set of wetting efficiency and liquid-solid mass transfer measurements.

Whereas all previous diagnostic studies of trickle-bed reactors are based on linear kinetics, Mogalicherla et al. (2009) developed a method for wetting efficiency estimation in a reactor where Langmuir-Hinshelwood kinetics are applicable. Using internal diffusion theory for nonlinear kinetics[4], it was possible to relate overall trickle-bed efficiency to average surface concentration of the rate-limiting (volatile) reagent, and hence to f.

All diagnostic studies seem to be on a reaction where the rate is determined by a volatile reagent, though especially in the refining industry, the performance of many reactors can be expected to be determined by a non-volatile reagent (Dudukovic, 1977; Sie and Krishna, 1998). Several integrated predictive reactor studies deal with these, for example the studies of Wu et al. (1996) and Khadilkar et al. (1996). The latter study was used for the development of a criterion to identify whether the reaction rate is controlled by the gas or (non-volatile) liquid component. Based on this criterion and experimental results, recommendations could be made for the mode of operation of a three-phase packed bed reactor (upflow vs. downflow).

The predictive approach is well suited to the investigation and verfication of existing hydrodynamic theories and correlations. Whereas diagnostic studies have to be simple to enable one to correctly identify and quantify certain hydrodynamic aspects, the predictive approach can incorporate complex reaction kinetics (Khadilkar et al., 1999; Chaudhari et al., 2002) or hydrodynamic modelling at different levels (Ravindra et al., 1997b; Gunjal and Ranade, 2007). Yet, it seems that the behaviour of a trickle-bed still leads to surprising (not modeled) results: Levec and Smith (1976) had to con-

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[4]Similar to the Bischoff modulus discussed in Chapter 4.

clude that channelling occured inside the reactor, Ravindra et al. (1997b) found that liquid distribution, multiplicity and packing orientation led to unmodelled results and Gunjal and Ranade (2007) illustrated how sensitive a reactor can be to its hydrodynamics. Clearly, there is much to learn about liquid flow morphology and how it affects the performance of a reactor.

2.4 Conclusions

While trickle-bed reactors are widely used in industry and subject to numerous studies in laboratories, the research in this field are too often restricted to either reactor performance studies, hydrodynamic studies or theoretical studies. A more integrated approach coupling reaction phenomena, mass transfer and hydrodynamic characteristics with special emphasis on wetting efficiency can be highly recommended. Research opportunities that may aid in this cause include a more complete physical description of liquid-solid contacting, integration and validation of theoretical modeling with this description; and a reactor study on liquid-solid contacting that does not rely on correlations.

Nomenclature

Bi' modified Biot number, $Bi' = \frac{k_{LS}V_R}{S_p D}$

C concentration, mol/m^3

D reagent effective diffusivity, m^2/s

D_m molecular diffusivity, m^2/s

d_p catalyst pellet diameter, m

f wetting efficiency, dimenionless

k_r first-order reaction rate constant based on V_R, s^{-1}

k_{LS} liquid-solid mass transfer coefficient, m/s

Q_L liquid volumetric flowrate, m^3/s

r reaction rate based on active catalyst volume, $\text{mol}/\text{m}^3\text{s}$

Re_i Reynolds number of i-phase, $Re_i = \frac{\rho_i v_{Si} d_p}{\mu_i}$

Sc_i Schmidt number of reagent in the i-phase, $Sc_i = \frac{\mu_i}{\rho_i D_m}$

Sh_{LS} Sherwood number for liquid-solid mass transfer, $Sh_{LS} = \frac{k_{LS} d_p}{D_m}$

S_p pellet external area, m^2

V_R catalyst pellet volume or shell volume for an egghell catalyst, m^3

v_{SL} superficial liquid velocity $v_{SL} = \frac{Q_L}{A_c}$, m/s

X conversion, dimensionless

Z reactor length, m

Greek letters

ϕ_G Generalised (Aris) modulus, $\phi_G = \frac{V_R}{S_p}\sqrt{\frac{k_r}{D}}$

η pellet efficiency factor, dimensionless

η_0 overall efficiency factor, dimensionless

τ reactor residence time, s

Subscripts

bulk   refers to bulk liquid

d   refers to (externally) completely dry pellet

L   refers to liquid phase

LF   refers to liquid-filled operation

s   refers to catalyst surface

TBR   refers to downflow (trickle flow) operation

w   refers to completely wetted pellet

CHAPTER 3

VISUALISATION OF WETTING MORPHOLOGY

Colorimetric measurements of wetting effiency that will form the basis for pellet internal diffusion modelling in Chapter 4 are presented in this chapter. This work is an extract from work published in two papers (van Houwelingen et al., 2006, 2007).

Though usually well rationalised, most work on the measurement of wetting efficiency and modelling of its effect on reactor performance is based on theoretical "visualisations" of partial wetting under trickle-flow conditions: the vast majority of wetting efficiency data is inferred from tracer response curves and the influence of fractional wetting on trickle-bed efficiency is mostly modeled based on theoretical geometries and simplifying assumptions. The distribution of particle wetting efficiency is, although it was shown to potentially affect reactor performance (Beaudry et al., 1987), generally disregarded. Until recently, the literature of fractional wetting in trickle-flow suffered a definite shortage on direct wetting efficiency measurements.

This shortage was supplemented by colorimetric measurements (which is arguably the most direct measurement technique) by Baussaron et al. (2007). Also, through theoretically constructing tracer response curves based on the mass balance equations for bulk liquid dispersion and internal pellet diffusion proposed by Ramachandran et al. (1986), Julcour-Lebigue et al. (2007) have shown that the generally accepted but previously intuitive tracer method has good theoretical grounds. Baussaron et al. (2007) satisfactorily compared wetting efficiency data derived from tracer experiments and data obtained from the direct colorimetric method.

The focus of this work is therefore not predominantly on extending the existing database on direct wetting efficiency, but on obtaining insight into the morphology of wetting efficiency for a better understanding of the role that wetting efficiency can play

in a trickle-bed reactor. To this end, colorimetric experiments were conducted to obtain photos of particles that contain information about the global variation in, and the geometry of, partial wetting. Both boundaries of the hydrodynamic multiplicity of pre-wetted trickle flow as explained in Chapter 2 were explored.

3.1 Experimental

The principle behind the colorimetric evaluation of wetting efficiency/trickle flow patterns is simple: a suitable colourant is selected, which can be used to colour the particles in a packed bed as liquid flows over it. The packed bed then contains an immense amount of data on where and how the liquid contacted the solid. Not all of these data can directly be extracted and quantified and different aspects of wetting efficiency were previously reported using colorimetry, such as average wetting efficiency (Onda et al., 1967; Lazzaroni et al., 1988; Baussaron et al., 2007) or trickle-flow patterns, (Ravindra et al., 1997a)). As said, the focus in this work is on the global variation in particle scale wetting and on particle scale wetting geometry.

3.1.1 Trickle-flow setup and experimental procedure

The experimental setup is shown in Figure 3.1 and consists of a 1.0 m long, 63 mm I.D. glass column packed with 2.5 mm porous γ-alumina spheres, a low pressure N_2 feed system and two separate liquid feed systems, one for a clear water feed and one for water doped with a water-soluble colourant, Chrome-Azurol S. This colourant was previously used successfully by Lazzaroni et al. (1988) for the determination of wetting efficiency and has the advantage that it adsorbs irreversibly onto the external surface of the porous γ-alumina spheres without diffusing through the particles, thereby colouring only the surfaces that were contacted by the liquid. The clear water feed is used during start-up and for pre-wetting the packing, and is fed to the column until steady state is reached. This steady state is verified with liquid holdup and pressure-drop measurements, and visual observations through the glass column wall. Liquid holdup is measured with a weighing technique using a load cell, and pressure drop is measured with a differential pressure transmitter. Though the relative measurement of these parameters are considered good enough for the validation of steady state, absolute measurements are not considered accurate enough to be reported as experimental results.

After steady flow has been obtained, the feed is switched to the tank that contains a $0.2\,\text{g/L}$ solution of the colourant Chrome-Azurol S. Liquid recycle lines with needle valves are installed around both feed tanks, which can be used to minimise disturbances during feed switchover. For a constant Chrome-Azurol S concentration of $0.2\,\text{g/L}$, 20 minutes of contacting time is required before the colour intensity of the colourant on the particles
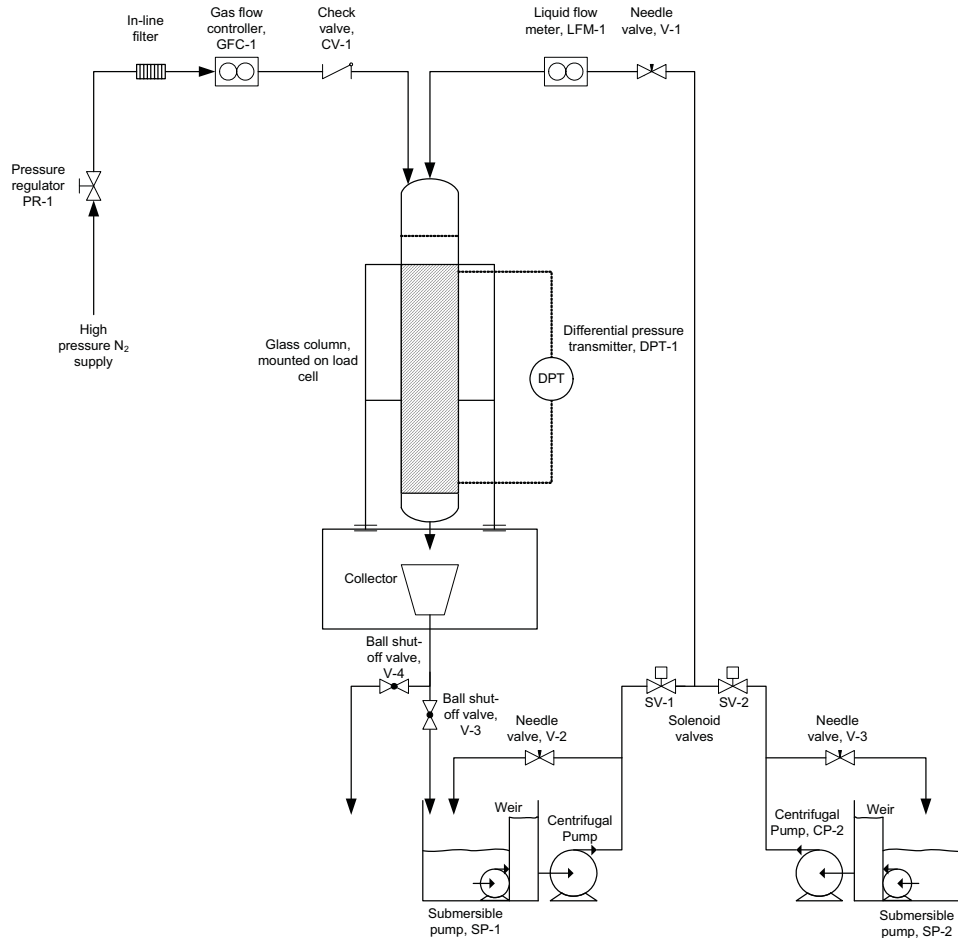
Figure 3.1: Trickle-bed experimental setup for colorimetric evaluation of wetting efficiency.

remains constant (Lazzaroni et al., 1988). After switchover, the colourant is initially stripped from the solution, and 40 minutes of steady-state colourant flow was required to avoid an axial colour intensity profile through the bed. Inherent in colorimetric methods is the assumption that trickle-flow is stable during steady state: flow fluctuations will lead to an overestimation of wetting efficiency. This assumption is supported by data from van der Merwe and Nicol (2005) and van der Merwe et al. (2007). It is also likely that flow instabilities will show in colour intensity variations of the particle surfaces that were contacted with the colourant. No significant variations were observed.

When exploring the effect of pre-wetting, startup procedures for flow experiments have to be well defined and carefully maintained. The boundaries of pre-wetted multiplicity were obtained through the following procedures:

- *Levec pre-wetting.* Prior to liquid irrigation, the bed is kept completely submersed in water for at least 3 hours to ensure complete internal saturation, and the complete external wetting of all particles. The bed is then drained under experimental gas-flow conditions until only the residual liquid holdup remains, after which liquid irrigation at the required rate is introduced.

- *Extensive pre-wetting.* After the packing has been internally saturated, the bed is drained and gas flow is set to the required rate. Liquid flow is increased until the pulsing regime is encountered and is then gradually set back to the required rate.

In both cases, coulourant is introduced only after steady state was achieved. These two pre-wetting methods represent the lower (Levec) and higher (extensively pre-wetted) hydrodynamic multiplicity cases for pre-wetting (Loudon et al., 2006). The flow conditions investigated in this work are listed in Table 3.1.

Pre-wetting procedure	L ($\mathrm{kg/m^2s}$)	G ($\mathrm{kg/m^2s}$)
Levec	1.6	0.152
-	5.35	-
Extensive	1.6	0.152
-	5.35	-

Table 3.1: Experimental flow conditions.

3.1.2 Data capturing and processing

After the bed is dry, the particles in the bed are unloaded and the whole population of particles is mixed, so that the sample particles are representative of the particles in the bed. These sample particles are captured in a plate in which a 17×17 grid of 2.7 mm holes have been drilled. Particles in the grid are retained by two clear PVC plates fastened on both sides of the grid and these are then photographed in a light box as shown in Figure 3.2 to obtain consistent images. The grid is photographed from two sides, resulting in two photos for each particle, so that the largest possible area can be evaluated. Fifteen samples of 17×17 particles were used to characterise each bed that was subjected to colorimetric flow experiments. Using software from Matlab's® Image Processing toolbox, half-particles are identified and extracted from the image and the wetted fraction of each half-particle is calculated. The imaging was designed to exploit the fact that Matlab® handles an image as a three-dimensional matrix containing the red, green and blue colour intensity for each pixel. The grid colour was blue, resulting in a good contrast between the grid and the particles when applying a red filter to the images; whereas the background colour was green for easy realignment of the image if the photographed grid was skew. Each half-particle is extracted as a separate 70×70 pixel image, and each pixel on each image is classified as wetted or non-wetted based on its colour.

The fractional wetting of an imaged half-particle was then calculated by weighting each pixel on an image according to the surface area it represented on the 3-D praticle for the given position of its 2-D projection on the image. Half particles in the two photos
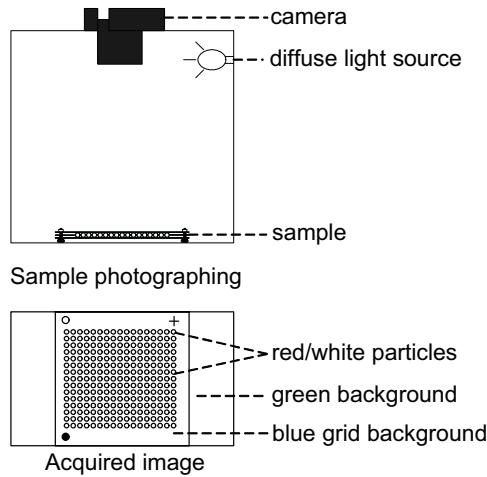
camera

diffuse light source

sample

Sample photographing

red/white particles

green background

blue grid background

Acquired image

Figure 3.2: Particle imaging.

for the same grid were then matched to give the wetting efficiency of each (complete) particle. Reference points for the matching of half-particles were supplied by markings on the grid as is shown in Figure 3.2. An example of the extracted half-particle images is shown in Figure 3.3.

For information on wetting geometry, 14 particles were hand-picked for an as-large-as-possible wetting efficiency range and each of them was captured in 2 high-resolution photographs of opposite hemispheres. These results are utilised in Chapter 4.

Data accuracy

Though the image analysis is rather straightforward, some important analysis steps are necessary to ensure that results are accurate and statistically significant. One of the major sources of possible error in wetting efficiency estimation is the fact that it is almost impossible to classify the pixels on the outer perimeter of a half-particle image due to blurriness, imperfect cropping of, and shadows on the image. Since the pixels near the outer perimeter of a 2-D projection of a 3-D sphere represent a large fraction of the spherical area, incorrect classification of these pixels can lead to large errors in wetting efficiency estimation and have to be discarded. This "boundary effect" is illustrated in Figure 3.4. Based on several images of fully wetted and completely dry half-particles, it was found that all pixels further away than $r/r_p = 0.91$ from the centre point of the image had to be discarded due to the boundary effect (the outer three rings of pixels in the 70×70 pixels image exhibit boundary errors). This means that only 60% of the total particle area can be taken into account.

The fact that only 60% of a particle's surface could be evaluated, give rise to an important question: is 60% of the surface area enough for the data on the global variation in particle scale wetting efficiency to be meaningful? For example, if only one pixel could be evaluated, a conclusion of the study would be that all particles in a TBR are
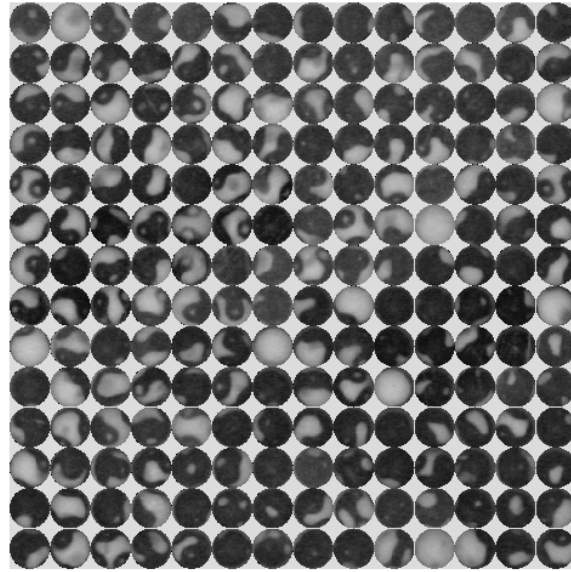
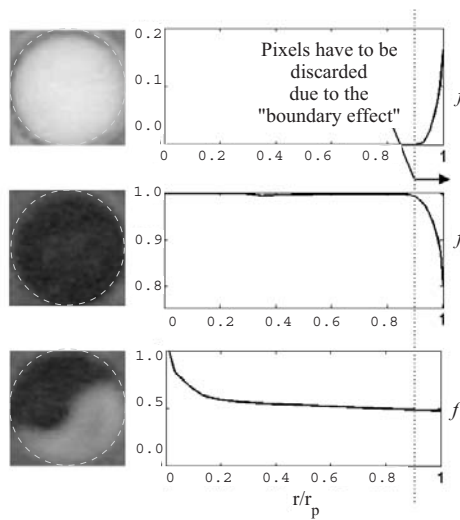**Figure 3.3:** An example of extracted half-particle images.

Figure 3.4: The boundary effect as a source of possible experimental error.
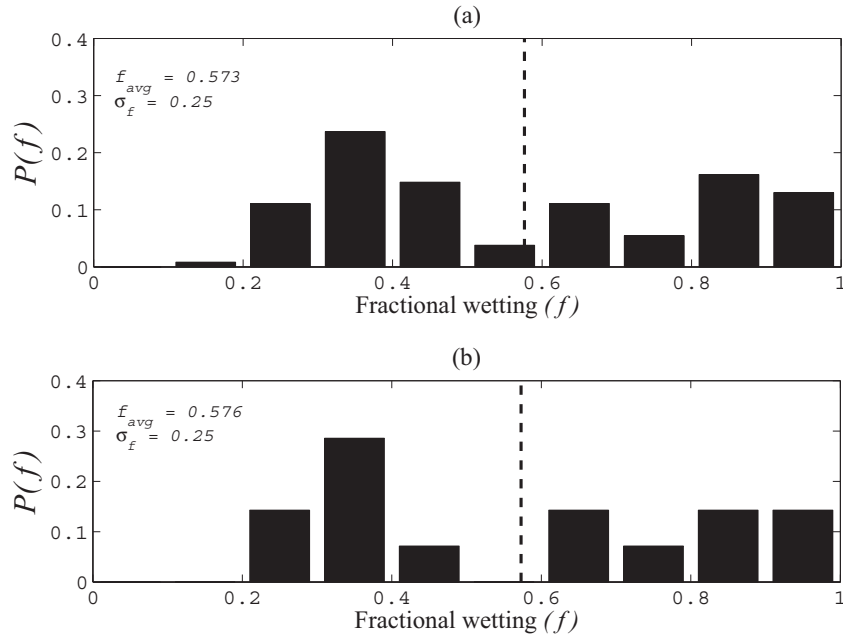
Figure 3.5: Simulated (a) 60% PWD for (b) a well characterised PWD consisting of 14 parti-
cles.

either completely wet or completely dry. The data in Figure 3.5 was generated to ensure
that 60% of the total surface area is indeed enough. Shown in the figure are particle
wetting distributions (PWDs), histograms of the distribution of particle scale wetting
efficiency. The difference between the two PWDs in the subfigures is an estimate of how
representative the PWDs are if only 60% of each particles surface can be evaluated: the
14 fractionally wetted particles that were photographed in high resolution ($> 90\%$ of
the surface can be evaluated) were characterised in detail so that wetting geometry and
extent are known for each particle. This information was built into a computer model
and each particle was then "viewed" from 500 random viewing angles. Two caps on
opposite sides of the particle (together constituting of 60% of the particle area) were
then used to estimate the wetting efficiency for each particle viewed at each angle. This
simulated image capturing is very similar to the physical method of random sampling
and photographing the opposite half-particles, and one can predict the (60%) PWD that
would be obtained for this single well-known PWD with the current photographing and
image analyis method. Since Figure 3.5(a) and (b) agree closely, the 60% PWDs are good
representations of the true PWDs.

It is also important to ensure that enough particles are photographed to be represen-
tative of the bed population. In this investigation, a packed bed contained between 300
000 and 400 000 particles, whereas a maximum of 289 particles could be photographed
and analysed in one grid. For each experiment, 15 grids were photographed and analysed.
Figure 3.6 shows the average wetting efficiencies for 15 different samples from the same
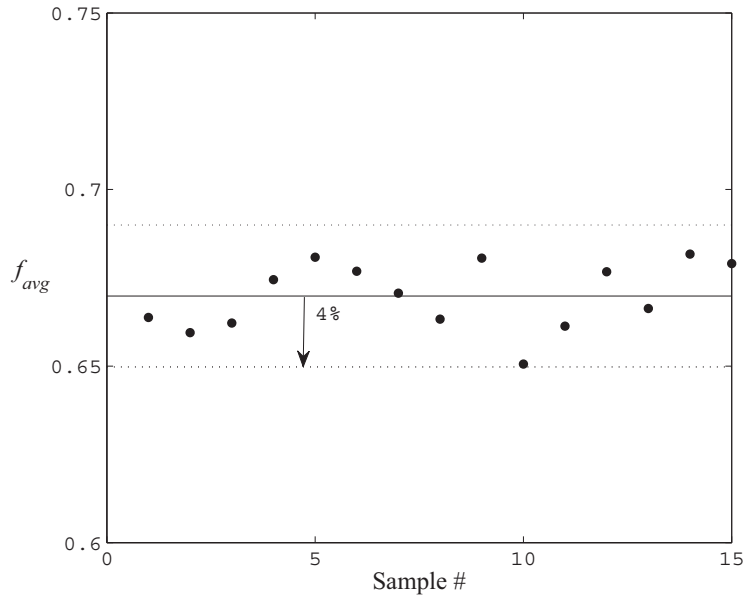bed. It is clear that even only one sample is quite representative of the bed in terms of

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Figure 3.6: Average wetting efficiencies for different samples from the same bed population. One sample consists of ≤ 289 particles, photographed in the 17×17 capturing grid

the average wetting efficiency: all values are within 4% of the mean.

This is not the case for the standard deviation of the distribution, which varied by up to 10% for different samples consisting of about 17×17 particles taken from the same bed population as is shown in Figure 3.7a. One sample is clearly not representative of the bed in terms of the standard deviation of the particle wetting efficiency distribution. For the PWDs to be statistically representative, the value of the total population standard deviation should converge within the fifteen samples that were taken from the bed. That this is indeed the case, is shown in Figure 3.7b: A total sampled population of more than 2000 particles is enough for representative distributions in terms of the standard deviation, and for all experiments $\pm 3000 - 4000$ particle were sampled.

3.2 Results and discussion

Particle wetting distributions for the two investigated pre-wetting methods are shown in Figures 3.8 (low liquid flow rate, L = 1.60 $^{kg}/_{m^2s}$) and 3.9 (high liquid flow rate, L = 5.35 $^{kg}/_{m^2s}$). The effect of pre-wetting is striking. The extensively pre-wetted beds have a fractional wetting of most particles close to the average wetting, whereas the PWD's Levec pre-wetted beds clearly show the existence two populations of particles - a significant fraction of particles is very poorly wetted or even completely dry, so that parts of a Levec pre-wetted bed may not be utilised whatsoever. This effect is more pronounced at the lower liquid flow rate (figure 3.8). Apart from the differences in PWDs, average
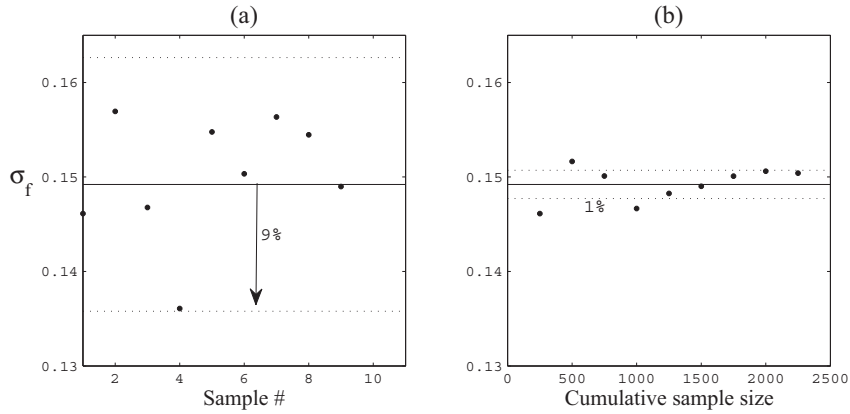
Figure 3.7: Standard deviation for (a) different samples from the same bed, and (b) as a function of the sampled population size sampled from the same bed.
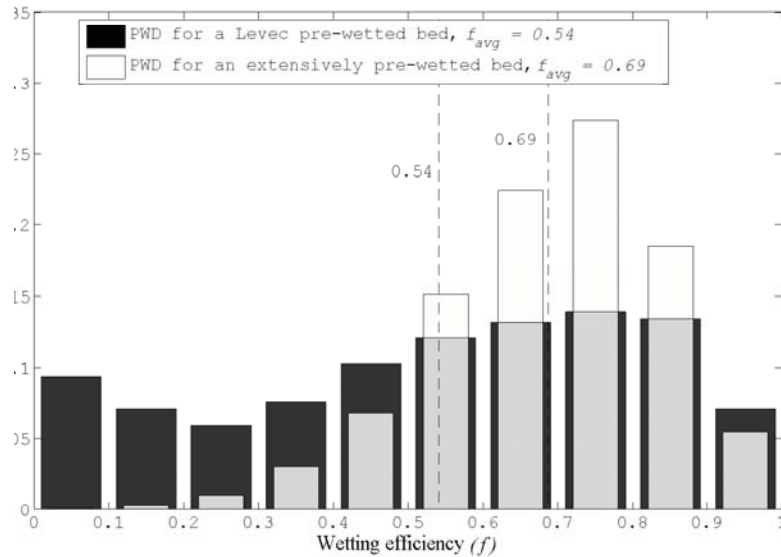

Figure 3.8: Particle wetting distributions for Levec- and extensively pre-wetted beds at L = 1.60 $^{kg}/m^2s$. Gas flow rate was G = 0.15 $^{kg}/m^2s$

wetting efficiencies are far lower for the Levec pre-wetted beds than for the Kan pre-wetted beds at corresponding liquid and gas flow rates.

One might argue that the only difference between the Levec and extensively pre-wetted beds is only in average wetting efficiency and that the PWD is only determined by the average wetting efficiency. That this is not the case, becomes clear when one compares the PWD for the extensively pre-wetted bed at L = 1.60 $^{kg}/m^2s$ (Figure 3.8) with that for the Levec pre-wetted bed at L = 5.35 $^{kg}/m^2s$: Though both beds had more or less the same average wetting efficiency, the PWDs are completely different. Where the PWD of the extensively pre-wetted bed shows a Gaussian distribution around the average wetting efficiency, the bimodal distributions in the Levec pre-wetted beds suggest two types of flow, or at least channelling/bypassing of the liquid. The average wetting is
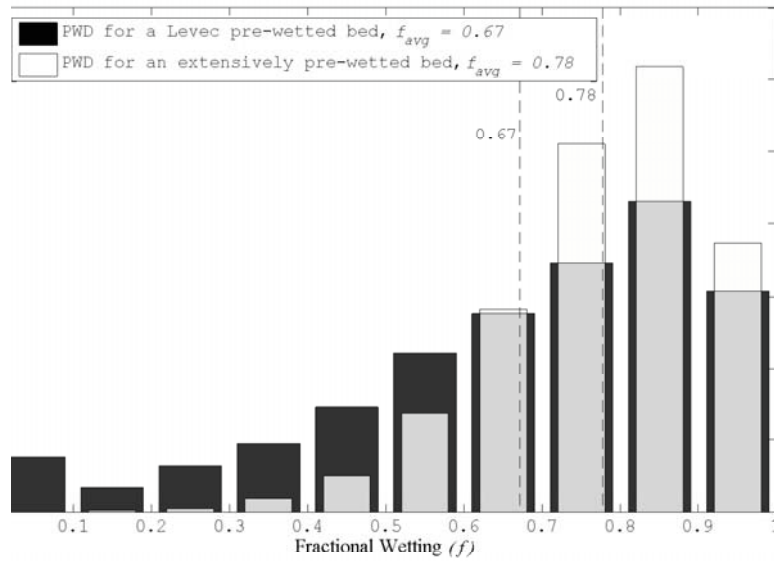
Figure 3.9: Particle wetting distributions for Levec- and extensively pre-wetted beds at L = 5.35 kg/m²s. Gas flow rate was G = 0.15 kg/m²s
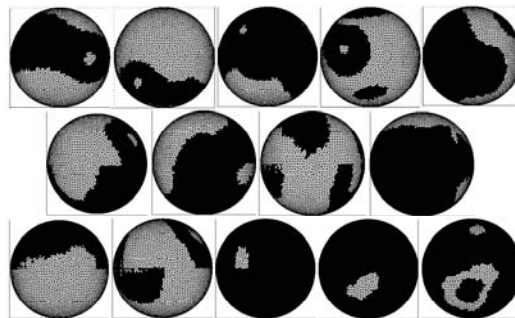

Figure 3.10: Graphic representation of obtained wetting geometry data

therefore not necessarily a good description of the PWD's.

A secondary result from the colorimetry experiments is a complete three-dimensional description of wetting geometries. A graphic representation of the 14 well-characterised particles is shown in Figure 3.10. A white colour represents dry zones, and black the wetted zones. Fractional wetting of these particles varies between $f = 0.26$ and $f = 0.97$. An interesting feature of the wetting geometry present on most particles are dry spots where the particles were in contact with one another. These can also be seen in Figure 3.3.

3.3 Summary

The work presented in this chapter suggests that different types of flow can prevail in trickle-bed reactors, depending on the hydrodynamic state and operating conditions.

The PWDs can be summarised as follows: for the extensively pre-wetted beds, all of the particles were in some fashion contacted by the flowing liquid. The shapes of the PWDs are consistent, suggesting that flow in extensively pre-wetted beds was stable and very similar for all experimental flow conditions. The Levec pre-wetted beds contain a large amount of dry and poorly wetted particles, especially at the lower liquid flow rate. The shapes of the distributions are very different from those of the extensively pre-wetted beds, and two local maxima suggest two different types of flow, or at least channelling/bypassing of the liquid flow. Visually, wetting geometries look very similar to those reported by Baussaron et al. (2007). In the next chapter, these geometries will be used for modeling of intraparticle diffusion.

Nomenclature

f	fractional wetting of particle, dimensionless
G	gas mass flux, $\mathrm{kg/m^2s}$
L	liquid mass flux, $\mathrm{kg/m^2s}$
$P(f)$	fraction of particles with fractional wetting within histogram bin, dimensionless
r	distance from centrepoint of half-particle image, pixels
r_p	half-particle radius on image, pixels