

Trickle Flow Multiple Hydrodynamic States: The Effect of Flow History, Surface Tension and Transient Upsets

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Surface Tension and Transient Upsets**

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The existence of multiple hydrodynamic states (MHS) in trickle bed operation has been proved by hysteresis observed in flow loops, as well as variation between different prewetting modes. The most common theory presented as explanation for the existence of MHS, is the film vs. rivulet concept. Based on this concept, it was suspected that in-situ upsets might promote the formations of films, thereby providing a method through which the hydrodynamic states of the Dry and Levec modes can be manipulated to perform like the Kan Liquid and Super modes.

Large performance enhancements can be obtained by altering the prewetting procedure, even for systems with a low surface tension. For the water system, the gas liquid mass transfer coefficient of the Kan Liquid and Super modes could be as much as 6 times greater than that of the Dry mode. For the low surface tension system, the gas liquid mass transfer of the Kan Liquid and Super modes could be up to 8 times greater than that of the Dry mode. Through a thorough investigation of various types of transient upsets and manipulation strategies, it was confirmed that prewetting is indeed the only way by which drastic variation in hydrodynamic states may be obtained. None of the investigated upsets (hysteresis, periodic operation or surface tension doping) resulted in changes in the liquid morphology that could compare to the significant variation that was observed by varying the prewetting mode.

Two methods were identified by which the hydrodynamic gaps between the less uniform (Dry and Levec) modes and the more uniform modes (Kan Liquid and Super) could be bridged. The first is to reduce the Levec draining time, while the second method may be seen as an in-situ type of Kan Liquid prewetting. This type of prewetting was obtained during doping with a low surface tension liquid, at a flow rate associated with the high interaction regime for the low surface tension system.

Though the hysteresis cycles did not drastically alter the predominant flow type, interesting trends were observed, some of which raised doubt about the application of the films vs. rivulet concept. One mode in particular displayed behaviour which contributed to this doubt, namely the Kan Gas mode;

- Gas liquid mass transfer on this mode decreased with an increase in liquid flow rate
- Relatively low pressure drops on this mode corresponded to relatively high liquid holdup
- It was the only mode that exhibited no hysteresis with gas flow variation, on any of the hydrodynamic parameters

The various trends and variations observed with the different types of upsets, leads to the conclusion that the concept of films vs. rivulets simply does not provide adequate explanation of the observed results. In general, two flow types may be distinguished. That which is caused by an initial increase in liquid flow rate as opposed to that which is caused by an initial increase in gas flow rate

An investigation to determine the behaviour of each of the investigated parameters near the transition boundaries on all the modes, as well as a repetition of this study with non-intrusive visual techniques is recommended.

KEYWORDS: Multiple hydrodynamic states, transient upsets, surface tension, hysteresis, trickle bed

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Nomenclature

C^*	Equilibrium oxygen concentration at 1 atm	mg/L
	Equilibrium oxygen concentration an non-standard	
C_p	pressure	mg/L
C_{L,O_2}	Concentration of dissolved oxygen in water	kmol/m ³
dP	Differential Pressure	kPa
e	Bed porosity	
G	Linear gas velocity	mm/s
H^*	Henry's constant	
H_t	Total liquid holdup	
k_{ga}	Volumetric gas-side mass transfer coefficient	s ⁻¹
K_La	Overall volumetric liquid-phase mass transfer coefficient	s ⁻¹
k_La	Volumetric liquid-side mass transfer coefficient	s ⁻¹
L	Linear liquid velocity	mm/s
m	Mass of Liquid in Column	kg
P_w	Partial pressure of water vapour	atm
P	Non standard pressure	atm
T	Temperature	K
t	Temperature	°C
u	Linear velocity	m/s
V_b	Bed Volume	m ³
Z	Bed Length	m

Greek Symbols

θ	correlating variable	
ρ_G	Gas density	kg/m ³
ρ_L	Liquid density	kg/m ³

Subscripts

e	Exit
e'	Exit of empty bed

f	Feed
f'	Feed of empty bed
G	Gas phase
L	Liquid phase

1. Introduction

Trickle bed reactors are used extensively in petroleum, petrochemical and chemical industries. These reactors are generally fixed bed catalytic reactors, in which gas and liquid flow cocurrently downward.

Understanding the phenomena that govern the performance of trickle bed reactors are essential to their design, scale up and process intensification. Some of the hydrodynamic parameters commonly encountered in trickle bed literature, include pressure drop, liquid holdup, wetting efficiency and mass transfer. Prediction of trickle bed performance is greatly complicated through the existence of multiple hydrodynamic states (MHS). The existence of MHS has been discovered as early as 1978 by Kan & Greenfield. In the early studies the MHS were reported as pressure drop and liquid holdup hysteresis loops, while it was later illustrated by following different prewetting methods.

The hysteresis behaviour have been investigated by various authors such as Kan & Greenfield 1979; Levec *et al.*, 1988; Christensen, McGovern, & Sundaresan, 1986; Lazaroni *et al.*, 1989; Wang *et al.*, 1995, and Wang *et al.*, 1999. Most of the investigations into multiple hydrodynamic states focused on flow hysteresis loops. In these, a single operating point reached in one instance by increasing the flow, is compared to the other instance where it was reached by decreasing the flow. The extent of the hysteresis depends on the pre-wetting mode and the maximum flow rates used. In these studies it was shown that these multiple steady states are very stable and the difference in obtained steady states are substantial; Christensen *et al.*, (1986) found that the pressure drop on the upper curve (decreasing path), could be as much as 100% greater than those on the lower curve (increasing path).

The initial focus on MHS (or hysteresis) was to understand the mechanism that caused the variation in pressure drop and holdup measurements. The following have been suggested as explanations:

- The difference between film and rivulet flow (Christensen et al., 1986)
- The change in tortuosity of the gas flow channels (Kan & Greenfield, 1978 & 1979)
- The difference between advancing and receding contact angles at the gas-liquid-solid interface (Levec et al., 1986 & 1988)
- The non-uniformity of the flow (Wang et al., 1995).

Each of these theories served to explain the scenarios they were obtained in well. Not one of them can however be applied satisfactorily to all of the scenarios. The exact cause for the existence of multiple hydrodynamic states is still under speculation. The film vs. rivulet concept seems to be the most popular theory.

Kan & Greenfield's (1978) explanation for increased gas tortuosity, rested upon the fact that the surface tension of the liquid was high enough to sustain the altered flow. This claim inspires the question of the effect of lowered surface tension. Lowering surface tension should enable easier formation of films and enhanced liquid spreading. If the existence of multiple hydrodynamic states is solely a consequence of converting from rivulet to film flow, multiple hydrodynamic states may not be observed in lower surface tension liquids.

Discrepancies in results of the early investigations were found to be a result of two different prewetting modes (Kan and Levec wetting). Levec *et al.* 1988 observed more pronounced hysteresis loops than the other authors. The highest flow rate utilized in their loops was situated in the pulsing regime, rendering their decreasing leg in the Kan wetted mode. The hysteresis they observed was therefore actually a consequence of a change in the prewetting mode. The full extent of the influence of different pre-wetting modes, has however only been

confirmed recently. A study by Loudon, Van der Merwe & Nicol (2006) quantified the extent of pressure drop, liquid holdup and gas liquid mass transfer variation for different prewetting methods. The prewetting modes investigated by Loudon are:

- Dry Mode
- Levec
- Kan Liquid
- Kan Gas
- Super

Loudon *et al.* (2006) found a significant amount of variation in the pressure drop and mass transfer coefficients for the different prewetted beds. He found that the lower extreme for prewetted beds was Levec prewetting, while no specific prewetting procedure could be identified as the upper extreme for all the measured variables. The Dry and Levec wetted modes were always separated by a relatively large gap from the Kan Liquid and Super modes. The Kan Gas prewetting mode exhibited interesting behaviour. High liquid holdup and relatively lower pressure drops were observed, a phenomenon which can only be explained by the change in tortuosity of the gas flow channels as suggested by Kan & Greenfield, 1978 & 1979. The extensive variation indicates that different prewetting procedures entail severe differences in the liquid morphology. Variation of the prewetting mode may hence be used to obtain substantial variation in the hydrodynamics of a single operating point.

In this work, an attempt is made to shed new light on the cause of multiple hydrodynamic states, by investigating the effect of online disturbances or upsets on the stability of the multiple hydrodynamic states (The conventional idea of films vs. rivulets is used as basis, and the aim is to create stable films via the upsets). Furthermore, the extent of variation regarding prewetting modes is extended to a low surface tension system.

With respect to this aim, the work is divided into two types of approaches to create in-situ upsets. In the first type, liquid and gas flow variations are used to improve the hydrodynamics, relying on the concept that a local velocity increase will cause the formation of stable films. In the second type, transient changes in liquid surface tension are used to improve the hydrodynamics, relying on the idea that lowered surface tension, will cause the formation of stable films.

In the first type of upsets, hysteresis behaviour and periodic operation on all prewetted modes are investigated. The hysteresis behaviour on different prewetting modes may provide some understanding in the true nature of the flow morphology of each prewetting mode. In Loudon's study, the Dry and Levec modes were always substantially lower than the Super and Kan Liquid modes. By performing these types of upsets, it may be confirmed whether the gap between these modes can be bridged, without actually altering the prewetting procedure. Furthermore, the applicability of the films vs. rivulet theory to the results is investigated.

Periodic operation has been shown to have a substantial influence on trickle bed performance. Most of the investigations have focused on reacting systems, where a continual change in the mass transfer limitations results in an increased time average conversion of the reactants. The influence of periodic operation on flow morphology has not received much attention. An enhancement of hydrodynamics due to periodic operation is expected based on the idea that a continuous change in flow will ensure the continual formation of films, a continual improvement of liquid distribution, and subsequently may be a method by which the gap between the lower and higher prewetting modes can be bridged.

The investigation of the effect of temporary lowered surface tension is preceded by an investigation of the effect of different prewetting modes with the low surface tension liquid. In relation to the film concept, lower surface tension should ensure stable film flow throughout the column even in dry mode operation. Multiple hydrodynamic states should consequently not really exist

between the different prewetting modes. Behaviour of the different prewetting modes with a low surface tension liquid, will also serve as a basis for comparison of the enhancements obtained during doping. The idea is to form films during doping with the lower surface tension liquid, that will remain stable even when the higher surface tension liquid is used, hence creating a new and improved hydrodynamic state, which may be equivalent to that obtained with the low surface tension liquid on the corresponding prewetting mode.

2. Literature Survey

2.1 Trickle Beds in General

A thorough review of trickle bed reactors, and examples of commercial applications has been presented by Al-Dahhan *et al.* (1997). Most commercial trickle-bed reactors operate adiabatically at high temperatures and high pressures. They generally involve hydrogen and organic liquids with superficial gas and liquid velocities up to 0.3 and 0.01 m/s respectively. Kinetics and/or thermodynamics of reactions conducted in trickle-bed reactors often require high reaction temperatures. Elevated pressures (up to 30 MPa) are required to improve the gas solubility and the mass transfer rates. Under these conditions, some of the reactants or products may exhibit high volatility which can have a significant affect on the reactor performance (Khadiolkar, Mills, & Dudukovic, 1999).

Typical commercial trickle bed sizes are up to 10m high, and 2 m in diameter (Boelhouwer, 2001). In these commercial situations, steady-state trickle flow is known to have pronounced liquid maldistribution and non-uniform catalyst wetting. With partial wetting in trickle bed reactors, dry zones of catalyst surface exist upon which hotspots may develop. These hotspots may lead to dangerous runaway situations in the reactor and need to be controlled (Hanika, 1999).

2.2 Flow Distribution

The distribution of flow in trickle bed reactors may be viewed on three different levels (Zimmerman & Ng, 1986)

- Flow regimes
- Flow type
- Wetting

2.2.1 Flow Regimes

Various hydrodynamic regimes can be encountered in trickle bed reactors depending on the structure of the packed bed, particle wettability, fluid physical properties and velocities (Lakota & Levec, 1990). The available data for these regimes have been summarized by Shah, 1979; Gianetto *et al.*, 1978; Satterfield 1975 and Hofmann, 1978. These regimes fall into two broad categories referred to as the low interaction regime (LIR) and the high interaction regime (HIR). While the LIR (Trickle flow) manifests itself at low gas and liquid throughputs, the HIR (pulse, spray, and mist flow regimes) takes place for moderate-to-high fluid flow rates leading to significant gas-liquid interfacial shears (Satterfield, 1975; Charpentier & Favier, 1975).

Each flow regime is related to a specific gas-liquid interaction, which in turn influences important hydrodynamic parameters such as liquid holdup, pressure drop, mass and heat transfer effects (Boelhouwer, 2001). The boundaries of these flow patterns have been determined by visual observations, sharp increases in pressure fluctuations, sudden changes in the gas-liquid mass transfer coefficients and variations in apparent electric conductivity (Satterfield, 1975). The most commonly encountered regimes are illustrated in Figure. 2.1.

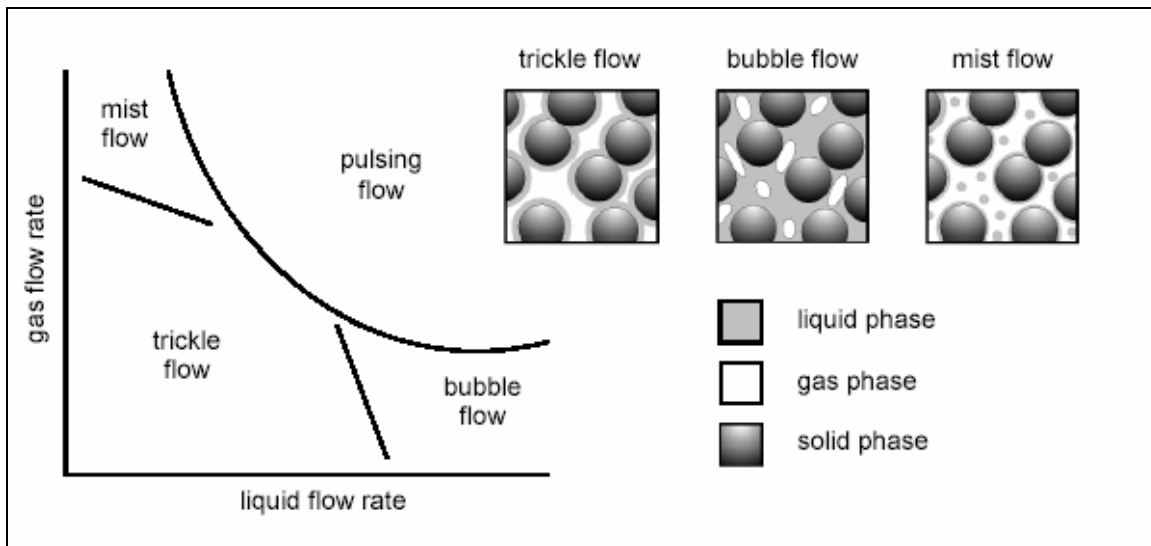


Figure 2.1 Schematic illustration of the location of the trickle, mist, bubble and pulsing flow regimes with respect to gas and liquid flow rates (Boelhouwer, 2001)

The trickle flow regime is encountered at low liquid loads, where liquid flows over the packing while gas occupies the voids. At higher gas flows, liquid droplets may be dragged along with the gas flow, resulting in a mist flow regime. At higher liquid flow rates, the liquid tends to plug the gas channels between the particles. The pressure above the plug rises; the plug is blown away and travels downward through the column with a relatively high speed ($\sim 1\text{m/s}$), and pulse frequency of approximately 1 Hz, rendering the pulsing flow regime. This regime is characterized by the successive passage of liquid-rich and gas-rich zones through the bed. With further increase of gas and liquid flow rates, the pulse frequency increases from 1 Hz up to approximately 10 Hz (Boelhouwer, 2001). The distinction between separate pulses then fade away, and a transition is reached to a liquid continuous, also called bubble flow regime (Blok, Varkevisser & Drinkenburg, 1983).

Different regimes have different characteristics, which is not only due to the flow rates that render them. Wu, McCready & Varma (1999) made a comparison between trickle and pulsing flow at the same flow rate. This can be done if it is considered that pulses are initially formed at the bottom of the column, and then moves up as the flow rates are further increased. By packing a column with

inert particles (see Figure 2.2, and confining a catalytically active region either near the inlet (where pulses have not yet formed) or near the end (where pulses have developed). Wu found that the reaction system (phenylacetylene to styrene and ethyl benzene over a platinum catalyst) had a 15% increase in conversion in the catalytic region under pulsing conditions. Therefore, the performance enhancements observed under pulsing is not merely a consequence of the flow rate, but can also be attributed to the regime characteristics. This result confirms the performance enhancement possibilities of periodic operation.

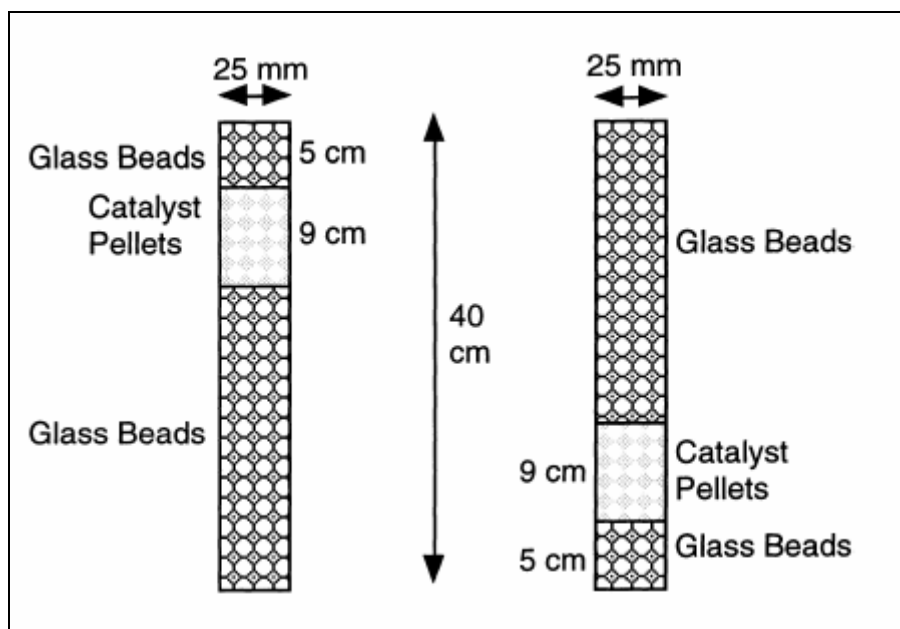


Figure 2.2 Geometries for catalyst packing used by Wu *et al.*, 1999 to compare trickle and pulsing flow at equivalent flow rates

Because the trickle and pulse flow regimes are of particular industrial interest, various investigations have focussed on the trickle-to-pulse flow transition. The current trends emerged from an analysis of the trickle-to-pulse flow transition database by Iliuta *et al.*, 1999:

- Trickle-to-Pulse flow transition is barely affected by intermediate-range bed porosity and particle sizes up to 5mm. For high porosity beds or large size particles a shift of this transition towards higher throughputs is observed.

- A significant drop of the liquid transitional velocity occurs with increasing liquid viscosity
- Low surface tension liquids exhibit a peculiar trend as higher liquid transitional velocities occur at higher rather than lower superficial gas velocities
- An increase in liquid density narrows down the trickle flow regime
- The trickle-flow domain widens at elevated pressures

2.2.2 Flow Type in Trickle Regime

It has been shown that the flow structure has a pronounced influence on the hydrodynamic state in the bed, and the existence of multiple hydrodynamic states. It has even been pointed out as a possible cause for hysteretic behaviour in the trickle regime (Christensen *et al.*, 1986). The flow structure or morphology is mainly determined by the liquid holdup within the bed. By following different prewetting methods, the dominant flow type can be altered (Loudon *et al.*, 2006, 2005).

Liquid holdup in trickle bed reactors consist of films, rivulets, pendular structures and liquid pockets (Zimmerman & Ng, 1986; Lutran, Ng & Delikat, 1991). Of the various flow structures, films and rivulets are associated with a single particle, while the others are related to two or more. A film is a thin, laminar liquid stream that covers a particle either partially or fully. A rivulet is a liquid stream flowing over the surface of a particle. Filaments (or channels) are liquid streams that flow down the bed in the channels between the particles and can be considered to be a string of liquid pockets. Pendular structures reside at the contact points of packing particles, while a liquid pocket fills the inter-particle pore space formed by more than two spheres. These flow features are illustrated in Figure 2.3.

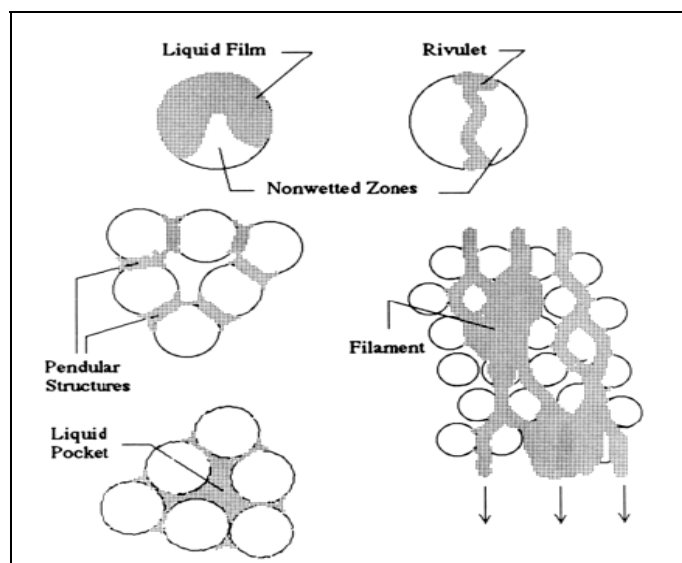


Figure 2.3 Flow features in the trickling regime: a liquid film, a rivulet, pendular structures, a liquid pocket and a filament (Zimmerman & Ng, 1986.)

If the packing is completely wetted, it is covered by liquid films while the gas travels in the interstitial void space. By decreasing the flow rate the complete films may break up into partial films, or rivulets and incomplete wetting of the packing will occur (Ravindra, Rao & Rao, 1997). The multiplicity of hydrodynamic states approached by increasing and decreasing flows respectively, could therefore relate to the changing flow types as was previously suggested by Christensen *et al.*, 1986. According to Christensen non-pretreated beds are dominated by filament type flow, whilst pretreated beds are dominated by film flow.

2.2.3 Wetting Efficiency

Wetting efficiency (sometimes referred to as the contacting effectiveness), is defined as the fraction of the catalyst pellet external area effectively wetted by the liquid flowing down the bed (Gianetto & Specchia, 1992). This is a crucial factor that influences the apparent reaction rate in TBRs, which depends not only on the partial wetting of the external catalyst surface, but also on the external liquid renewal degree.

Depending upon whether the limiting reactant is present only in the liquid phase or in both fluids, the reaction over externally incompletely wetted pellets can be greater or smaller than the rate observed over completely wetted ones. If the reaction is liquid-limited and the liquid limited reactant is non-volatile, then a decrease in the external wetting efficiency reduces the surface for liquid-solid mass transfer, thereby causing a decrease of the reaction rate. If the liquid reactant is volatile and heat effects are significant, then an additional reaction may also occur at the dry catalyst surface. Higher reaction rates can also be achieved through gas-limited reactions where the gaseous reactant can access the catalyst pores from the externally dry area (Iliuta, Larachi & Al-Dahhan, 2000).

The first investigation the existence of multiple hydrodynamic states regarding wetting efficiency was performed by Van Houwelingen, Sandrock & Nicol (2006). They developed a new technique, based on the colorimetric method for the purpose of investigating the distribution of particle wetting in trickle-bed reactors. It was shown that the method of prewetting has a major influence on average wetting efficiency and wetting distributions: Average wetting efficiencies varied by as much as 20% between the prewetting modes. Average wetting efficiencies of the Kan prewetted beds were significantly higher than those for the Levec prewetted beds at corresponding liquid and gas flow rates. They also found that Levec prewetting lead to a considerable fraction of the bed that was not used (up to 7% at the investigated flow conditions). In the Kan prewetted beds, all of the particles were in some fashion contacted by the flowing liquid. Surprisingly, not all the particles that were contacted were completely wetted.

2.3 Hydrodynamic Parameters

2.3.1 Liquid Holdup

Liquid holdup is one of the primarily important hydrodynamic parameters in trickle bed reactors. It plays an important role in the hydrodynamics, mass and heat transfer processes (Al-Dahhan *et al.*, 1997). These processes are directly related to the actual flow rates of gas and liquid through the reactor, which is determined by the holdup (Burghardt *et al.*, 1995). Knowledge of holdup is especially important in commercial trickle bed reactors with exothermic reactions to ensure safe operation by preventing hotspot formation, and reactor runaway (Al-Dahhan *et al.*, 1997).

Liquid holdup is a valuable parameter in the evaluation of flow type (morphology) through the reactor. It can be seen as an approximate measure of the contacting effectiveness of the liquid and solid, and is often used to estimate residence time (which influences reactant conversion (Goto & Smith, 1975) or average film thickness (Satterfield, 1975). By affecting the wetting efficiency, the reaction selectivity may also be affected, depending on whether the reaction takes place solely on the wetted catalyst area or on dry and wetted catalyst areas (Al-Dahhan *et al.*, 1997).

Liquid holdup data is sometimes reported as saturation values which are fractions of the void space. More commonly, total liquid holdup (H_t) is expressed as a fraction of the total volume of the bed filled with liquid. For non-porous particles, total liquid holdup can be divided into the residual and dynamic (or free draining) liquid holdup. The residual liquid holdup refers to the liquid that remains in the reactor after draining, while the dynamic holdup refers to that part of the total holdup that does drain i.e. the difference between the total and residual liquid holdup. Residual holdup typically ranges from 2-5%.

The residence time of liquid in a trickle-bed reactor is determined by the dynamic holdup (Goto & Smith, 1975). The dynamic liquid holdup is a function of the gas and liquid flow rates, the fluid properties, and the catalyst characteristics. Other factors that might influence holdup include (Satterfield, 1975):

- The liquid inlet distributor
- Shape and size of catalyst particles
- Catalyst bed height
- Wetting characteristics of packing and fluids
- Gas flow rate

2.3.1.1 General Trends

Iliuta *et. al.*, 1999, summarized the trends of liquid holdup based on a comprehensive database for the LIR and HIR:

- liquid holdup is an increasing function of liquid velocity and viscosity, as well as particle diameter;
- it is a decreasing function of gas superficial velocity and liquid surface tension;
- liquid holdup decreases as gas density increases, except for very low gas velocities where it is insensitive to gas density;
- non-coalescing liquids exhibit much smaller holdups (and much higher pressure drops) than coalescing liquids;
- gas viscosity appears to have marginal effect on liquid holdup and pressure drop;
- mixing with fines improves liquid holdup at the expense of increased pressure drops

2.3.1.2 Measuring Techniques

Liquid holdup can be measured by various techniques (Ellman *et al.*, 1990):

- weighing the dry reactor and subtracting this result from the weight of the reactor when the liquid flows through it to obtain the total liquid holdup
- simultaneously shutting off the inlet and outlet streams and then draining the reactor to obtain the dynamic or draining holdup
- RTD analysis
- Analysing the result of non-intrusive visualisation techniques

2.3.1.3 Correlations and Models

Correlations for total external or dynamic liquid holdups and two-phase pressure drops were summarized by Saroha & Nigam (1996) and Al-Dahhan *et al.* (1997), the majority of them being mostly empirical and restricted to their specific ranges of process conditions. Most of the correlations neglect to take bed prewetting into consideration. Loudon *et al.*, 2006 (2005) tested various correlations for differently prewetted beds, and showed that it is definitely necessary to include the prewetting effect in models for improved accuracy.

2.3.2 Pressure Drop

The two-phase pressure drop across the trickle bed reactor is a crucial parameter in the design, scale-up and operation of the trickle bed reactor. It is a measure of the energy required to move the fluids through the reactor (Saroha & Nigam, 1996). Fluctuations in pressure drop are often used as an indication of the operating regime. The trickle flow regime is typically characterized by a standard deviation of 2% in pressure drop. In the pulsing regime the standard deviation in pressure drop is approximately 5% (Blok *et al.*, 1983).

2.3.2.1 General Trends

Pressure drop is an increasing function of increasing gas and liquid superficial velocities, liquid viscosity, gas density, and decreasing particle diameter and surface tension (Dudukovic, Larachi, & Mills, 1999; Iliuta *et al.*, 1999 and Wang, Mao & Chen, 1995). Generally pressure drop and liquid holdup influence each other mutually, since a higher holdup will serve greater resistance to the gas flow, which will render a higher pressure drop (Saroha & Nigam, 1996). An exception to this trend is found when the bed is wetted by the Kan Gas mode (Loudon *et al.*, 2006).

2.3.2.2 Correlations and Models

Correlations that consider the mutual influence of liquid holdup and pressure drop are the modified Ergun equation and correlations using the modified Galileo number (Sai & Varma, 1988 and Wammes *et al.*, 1991). Loudon *et al.* (2006) tested various correlations for differently prewetted beds. He found that most of the correlations in general use are insufficient to account for the effects of prewetting. The large amount of scatter in literature data might be a result of the

neglect of consideration of the various prewetting procedures followed to obtain the experimental data.

2.3.3 Gas-Liquid Mass Transfer

In an industrial trickle-bed reactor, the reaction between the components in the gas-phase and those in the liquid is usually facilitated by the solid catalyst phase. The gaseous reactants must therefore be absorbed and transported across a liquid film to the outside catalyst surface, and then through the liquid-filled pores to the reactive surface where adsorption and chemical reaction may occur (Sylvester & Pitayagulsarn, 1975). The rate controlling step can then be any one of the following (Satterfield, Pelossof & Sherwood, 1969):

- The rate of mass transfer of reactants between the bulk gas phase and the gas-liquid interface (also referred to as the gas-side mass transfer)
- The rate of mass transfer between the gas-liquid interface and the bulk liquid (also referred to as the liquid-side mass transfer)
- The rate of mass transfer between the bulk liquid and the catalyst surface
- The rate of diffusion and simultaneous reaction within the catalyst pores

Since a gas must first be dissolved in the liquid for any absorption process, the gas-liquid mass transfer is one of the most fundamental steps influencing reactor performance (Charpentier, 1976). The gas-liquid mass transfer rate (especially the gas-liquid interfacial area) is strongly dependent on the flow texture. It is then no surprise that hysteresis has also been observed in gas-liquid mass transfer data (Wammes *et al.*, 1991). It is therefore also a useful parameter in the study of variations in flow texture. To ensure that only gas-liquid mass transfer influences the performance, an inert packing may be used.

According to Herskowitz & Smith (1983), the overall gas-liquid mass transfer coefficient may be expressed in terms of the liquid side and the gas side mass transfer coefficients according to Equation 2.1.

$$\frac{1}{K_L a} = \frac{1}{H^* k_g a} + \frac{1}{k_L a} \quad (2.1)$$

In the most commonly encountered situation the mass transfer limiting reagent is the gaseous species. The gaseous reactant is usually present in substantial stoichiometric excess and in relatively high fractional concentration in the vapour phase as well as being relatively insoluble in the liquid, especially in the case of hydrogen and oxygen (Satterfield, 1975). The values of H^* is then larger than unity, resulting in the term, $H^* k_g a$ being at least one order of magnitude larger than $k_L a$ over the range of liquid and gas flow rates commonly encountered in trickle-beds. Thus, $K_L a$ can be approximated as $k_L a$ (Herskowitz & Smith, 1983)

2.3.3.1 Determining the Liquid Side Mass Transfer

The volumetric gas-liquid mass transfer coefficient $k_L a$ can be determined via physical absorption or desorption techniques, or the less preferred chemical absorption techniques (Lara-Marquez, Wild & Midoux, 1994).

In the physical absorption technique, oxygen is transferred from air (eventually enriched with oxygen) to water which has been stripped of oxygen while in the desorption technique oxygen is transferred from water (previously saturated with air) to nitrogen. Desorption is preferred since the absorption is complicated by the longitudinal variation in gas-phase concentration of oxygen due to pressure drop through the bed (Hirose, Toda & Sato, 1974). The driving concentration difference $C_A \rightarrow 0$ of desorption is therefore easier to measure precisely than the driving concentration difference $C_A^* \rightarrow C_A$ of absorption (Lara-Marquez *et al.*, 1994)

2.3.3.2 Quantifying the Gas-Liquid Mass Transfer Coefficient

Goto & Smith (1975) investigated gas-liquid mass transfer by using the desorption technique. They developed a method to quantify the volumetric mass transfer coefficient based on a simple mass balance over the column, with consideration of the mass transfer effects in the end regions of the column. The end effects were considered by dividing the column into sections as depicted in Figure 2.4.

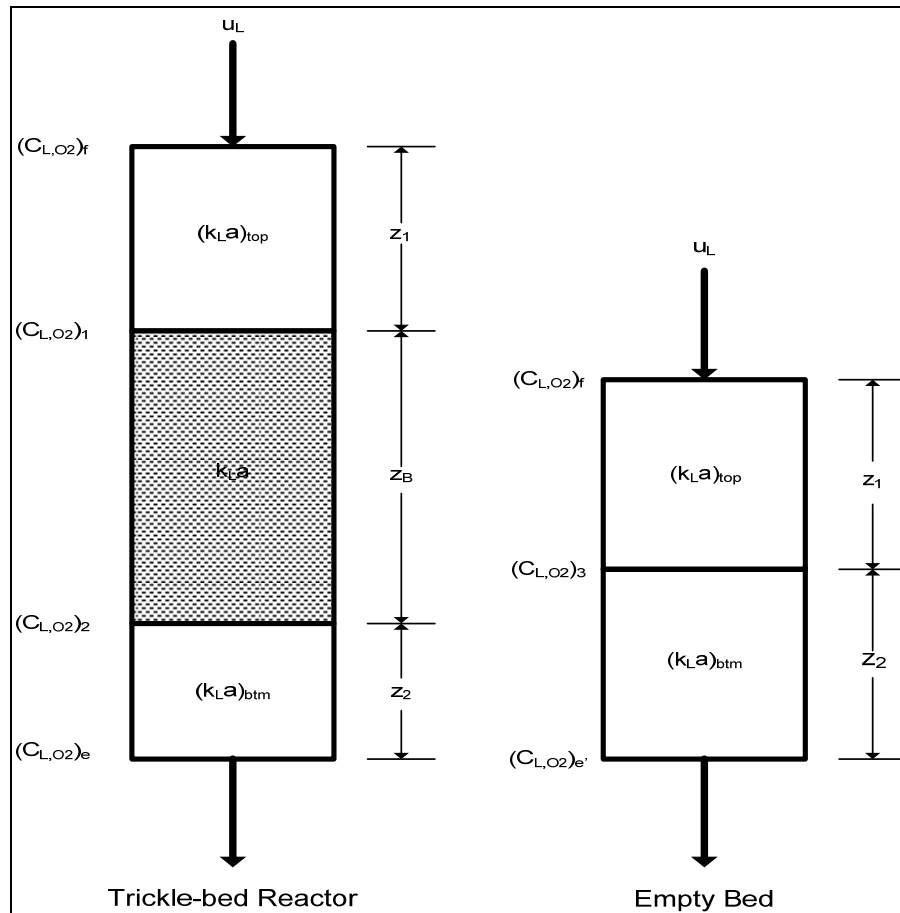


Figure 2.4: End effects in the gas-liquid mass transfer correlation are accounted for by dividing the column into sections (adapted from Goto & Smith, 1975)

By performing a mass balance over the sections as depicted in Figure 2.4, equation 2.2 can be derived (See Appendix 1 for the full derivation)

$$k_L a = \frac{L}{Z} \ln \left[\frac{(C_{L,O_2})_e (C_{L,O_2})_f}{(C_{L,O_2})_e (C_{L,O_2})_{f'}} \right] \quad (2.2)$$

2.3.3.3 General Trends

The liquid phase mass transfer rate is affected by the fluid flow rates, packing shape and size, and by the properties of the liquid and its foaming characteristics (Sarooha & Nigam, 1996). The gas liquid interfacial area increases with increasing gas density, increasing foaming characteristics, and usually increases with increasing flow rates (Iliuta, Iliuta & Thyron, 1997).

2.4 Multiple Hydrodynamic States

Multiple hydrodynamic states can exist in trickle bed reactors, depending on the mode of operation, and flow history. Hysteresis behaviour in trickle bed reactors have been reported as early as 1978, by Kan & Greenfield. Since then various investigators have reported hysteresis in pressure drop, liquid holdup and gas liquid mass transfer. It seems however that the implication of hysteresis behaviour on the research and operation of trickle beds has only recently been highlighted. Wang, Mao & Chen (1999), was one of the first authors to suggest that the large amount of scatter in liquid holdup and pressure drop correlations could be because the experimental data used in the derivation of these equations, were perhaps associated with different hydrodynamic states and operating modes. This notion has since been encouraged through the work of Van der Merwe., 2004 (regarding flow hysteresis) and Loudon *et al.*, 2006 (regarding different operating modes).

Wang *et al.* (1999) summarized the views on hysteric behaviour; in the early stage of hysteresis study, the behaviour was interpreted in terms of the difference in rivulet flow and film flow (Christensen *et al.*, 1986). Later, the bicontinuous porous medium model (Chu & Ng, 1989) and the parallel zone model (Wang *et al.*, 1995) were proposed to describe pressure drop hysteresis. Melli & Scriven (1991) proposed a two-dimensional network of passages to interpret the hysteresis of liquid holdup and mass transfer qualitatively, whilst Mao *et al.*, 1996 used a capillary model for the same purpose. Wang *et al.* (1999) concluded after consideration of the different views that these multiple hydrodynamic studies imply that the non-uniformity of gas-liquid flow induce the hysteretic behaviour. He also stated that the severity of hysteresis can be viewed as an index of poor phase contact and low reactor efficiency.

Most of the investigations into multiple hydrodynamic states focused on flow hysteresis loops. In these, a single operating point reached in one instance by

increasing the flow, is compared to the other instance where it was reached by decreasing the flow. Discrepancies in some of the early results were found to be a result of two different prewetting modes (Kan and Levec wetting). The full extent of the influence of different pre-wetting modes, has however only been confirmed recently. Loudon *et al.* (2006) conclusively showed that several operating regimes or hydrodynamic boundaries could be obtained by variation of the prewetting modes.

2.4.1 Prewetting Modes

Prewetting the bed minimizes the influence of the bed geometry on the flow distribution, and tends to reduce liquid maldistribution (Lutran *et al.*, 1991). Different modes of operation can be obtained by following different prewetting procedures.

The prewetting modes investigated by Loudon *et al.*, (2006) are:

- Non-prewetted (Dry Mode)
- Levec (Levec *et al.*, 1988)
- Kan Liquid (Kan & Greenfield, 1978)
- Kan Gas
- Super Mode (Van der Merwe, 2004)

With the Dry bed operation, the liquid and gas flows are introduced into the system at the desired flow rate without any prewetting of the bed. Dry beds are usually dominated by filament/rivulet flow (Lutran *et al.*, 1991)

A Levec bed is prewetted by flooding the packed bed or by operating in the pulsing regime for a specified time. Before actual operation commences, the bed is drained until only the residual liquid holdup remains (usually a draining time of 20min). Christensen *et al.* (1986) pointed out that the films created by flooding or pulsing rupture on draining, which results in behaviour similar to that of a dry bed.

This mode of flow is therefore characterized by rivulet (channel) flow (Van der Merwe, 2004).

Kan-wetting is performed by operating the column in the pulsing regime where after the flows are adjusted to the desired values without any interruption. The pulsing regime may be reached by increasing the liquid flow (Kan Liquid) or by increasing the gas flow (Kan Gas).

Super wetting is achieved by flooding the column, and then adjusting the flow rates to the desired operating points, without allowing draining time. Draining of excess holdup will therefore occur under irrigation. This mode is dominated by a mixture of film and filament flow (Van der Merwe, 2004).

Van der Merwe & Nicol (2004), pointed out that the Levec, and Super wetted beds can actually be seen as limiting cases of the other. In the Levec-prewetted mode a liquid “pulse” (with a length greater than the bed length) is followed by an effectively infinitely long stationary gas pulse (draining is allowed to continue until completion). In the Super mode the stationary “pulse” of liquid is followed by an infinitely short stationary gas pulse (i.e. there is no drainage before the trickle flow irrigation starts). The fact that these are limiting cases explains why authors such as Loudon *et al.* (2005) and Levec *et al.* (1988) observed a possibility of an envelope of possible operating points, and mentioned that there should be a way to get in between these modes.

2.4.2 Influence of Prewetting

Loudon *et al.* (2006) investigated the extent of influence of the various prewetting modes on the flow morphology. He evaluated the pressure drop, liquid holdup and gas-liquid mass transfer obtained with equivalent flow paths on the different prewetted beds. The results confirmed that the prewetting procedure has a pronounced effect on the obtained hydrodynamic state, and highlights the inefficiency of trickle bed models that do not consider the specific pre-wetting

procedure. The reason as provided by Wang *et al.* (1999), for the large amount of scatter in trickle bed data seems to be viable. Some of the results obtained by Loudon are summarized below:

- Pressure drop in the Kan and Super-wetted beds can be as much as seven times greater than the pressure drop in the Dry and Levec-wetted beds
- The different prewetting procedures resulted in four distinct regions for the holdup results (Kan-wetted, Super-wetted, Levec-wetted, Dry bed)
- The liquid holdup in the Kan-wetted bed was up to four times greater than the liquid holdup in the Dry bed, and thirty percent greater than the holdup in the Levec wetted bed
- The volumetric gas-liquid mass transfer coefficient in the Kan and Super-wetted beds were up to six times greater than the mass transfer coefficient in the Dry bed and two and a half times greater than the mass transfer coefficient in the Levec-wetted bed.

Loudon *et al.* (2006) briefly mentioned an effect of the draining time used in the Levec wetted bed. He found that steady state operating points nearer to those of the Super and Kan-wetted beds can be obtained by decreasing the draining time in the Levec-wetted bed. The conclusion could be drawn therefore, that the operating conditions determined from the different pre-wetting modes are only boundaries. The actual operating points could lie anywhere between these boundaries, indicating an envelope of possible operating points (which agrees well with the results of Levec *et al.*, 1988)

2.4.3 Hysteresis Loops

The hysteresis effect of flow loops have been investigated by authors such as Kan & Greenfield, 1978; Levec *et al.*, 1988; Christensen *et al.*, 1986; Lazzaroni,

Keselman & Figoli, 1989 and Wang *et al.*, 1995. The extent of the hysteresis depends on the pre-wetting mode and the maximum flow rates used.

2.4.3.1 Liquid Flow Modulation

Hysteresis loops reported by investigators up to now, for a variation in liquid flow rates, result in a general trend. A higher holdup, and pressure drop is observed if an operating point is achieved by decreasing the flow rate to that point than by increasing the rate (illustrated in figure 2.5a, b, d, and e).

Figure 2.5d represents the pressure drop hysteresis observed by Christensen *et al.*, 1986; Levec *et al.*, 1988 and Wammes *et al.*, 1991, for the Levec mode of operation. Christensen *et al.*, 1986, found that the pressure drop on the upper curve (decreasing path), could be as much as 100% greater than those on the lower curve (increasing path). They also found that the fractional difference in pressure gradient between the upper and lower curves became smaller as the gas flow rate was increased.

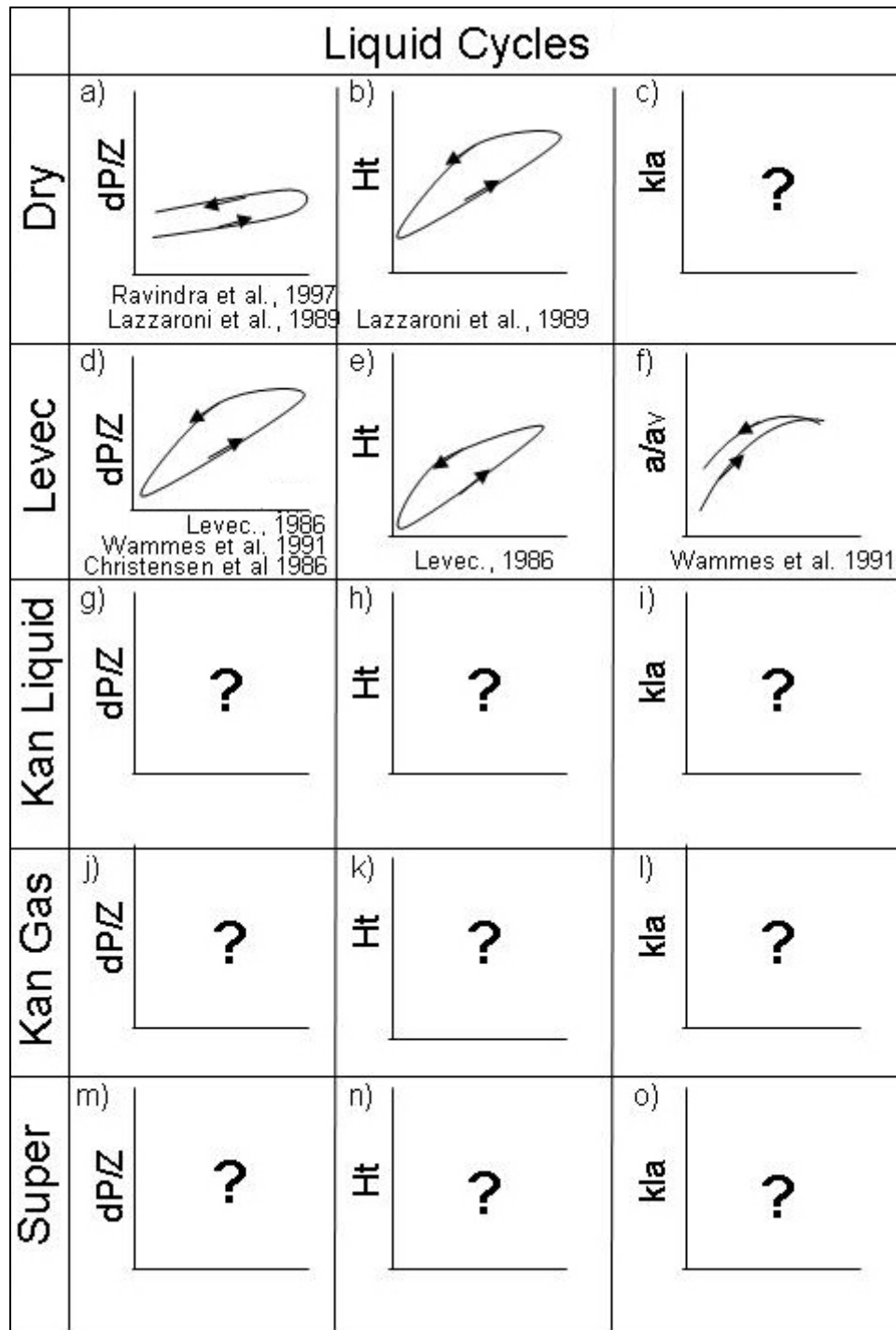


Figure 2.5 Hysteretic cycles obtained with liquid flow loops by various investigators on Dry and Levec pretreated beds.

Lazzaroni *et al.*, (1989), obtained similar trends for pressure drop, and liquid holdup on a Dry bed. They contributed the increase in pressure drop and liquid holdup to a decrease in cross-sectional area for the gas to flow through; an

increase in flow rate, resulted in liquid spreading to new parts of the bed, which would tend to remain in these sections when the flow was decreased.

Based on the visual observations on the reactor wall, Christensen *et al.* (1986) concluded that at increasing flow rates, the liquid phase flows in the form of rivulets through the packing. This results in relatively low values of the holdup and pressure drop. As the liquid throughput increases, the holdup becomes larger. Sederman & Gladden (2001) observed that number of rivulets increased with increasing liquid flow rate, until a superficial velocity of about 1.5-2mm/s. A further increase in flow rate was taken up by the size of existing rivulets. At a particular throughput a transition to film flow occurs. If the throughput is decreased again, the film flow pattern remains stable down to a lower throughput before the films break up into rivulets. This results in the hysteresis for the holdup and the pressure gradient.

The difference in the liquid film stability between the modes of operation has been attributed to contact angle hysteresis (Levec *et al.*, 1986); The difference between both modes of operation lies in the fact that in the increasing flow mode the three-phase contact line is advancing over a dry surface, whereas in the decreasing flow mode the contact line is receding from a wet surface. It is a well known fact that the contact angle of a three-phase system is larger when the contact line advances than when it recedes. A larger contact angle means that a larger force has to be exerted in order to cause a change in the location of the three-phase contact line. In terms of the process under consideration, this implies that a larger fraction of the bed will remain dry in the increasing flow mode than in the decreasing flow mode at the same operating conditions. The results of Wammes *et al.* (1991) support the visual observations of two flow patterns. In case of rivulet flow at equal flow less gas-liquid contact area is created in comparison to film flow at equal flow rates.

Levec *et al.* (1988) observed more pronounced hysteresis loops than the other authors. This can be understood if the pre-wetting effects as explained in section

2.4.1 and 2.4.2 are considered. Although the bed is originally flooded, some of the films over the particles are broken, and parts of the bed behave similarly to a dry bed (Ravindra *et al.*, 1997). When the flow rate is increased, the liquid distribution is enhanced. The highest flow rate utilized in their loops was situated in the pulsing regime, where the films would be re-established. A reduction in flow rate causes these regions to drain under irrigation. Their decreasing leg is therefore in the Kan wetted mode, (which has higher holdups than the Levec-mode, due to the increased liquid-solid shear stress associated with film flow). Levec also observed that if the liquid flow rate is reduced at an intermediate flow rate, values within the maximum loop can be obtained, indicating an envelope of possibilities. This observation hints that with each increase in flow rate, a certain amount of enhancement in liquid distribution is obtained.

Wammes *et al.* (1991) are the only investigators who reported the hysteresis on gas liquid interfacial area thus far (figure 2.5f). They found that the interfacial area is larger when the liquid flow rate is decreased from a higher value than the value obtained when the liquid flow rate is only increased. It is important to note that if the liquid flow rate is increased to the point of flooding and then decreased, the return leg is actually as a result of operating the bed in the Kan-wetted mode. The higher interfacial area may be explained if the commonly adapted theory of the transition from rivulets to film flow is considered. In the case of rivulet flow, less gas-liquid contact area is created in comparison to film flow at equal flow rates. Wang *et al.*, 1999 also observed similar trends in hysteretic behaviour with RTDs. An interesting observation by Wang was made with the RTD experiments. In flow modes, usually assumed to have uniform liquid distribution, the distribution results from the RTDs showed that non-uniformity actually exists.

2.4.3.2 Gas Flow Modulation

For gas modulation the same trend is not always observed. This can clearly be illustrated by comparing equivalent gas flow paths on Kan and Levec pre-wetted beds, Figures 2.6 d and g.

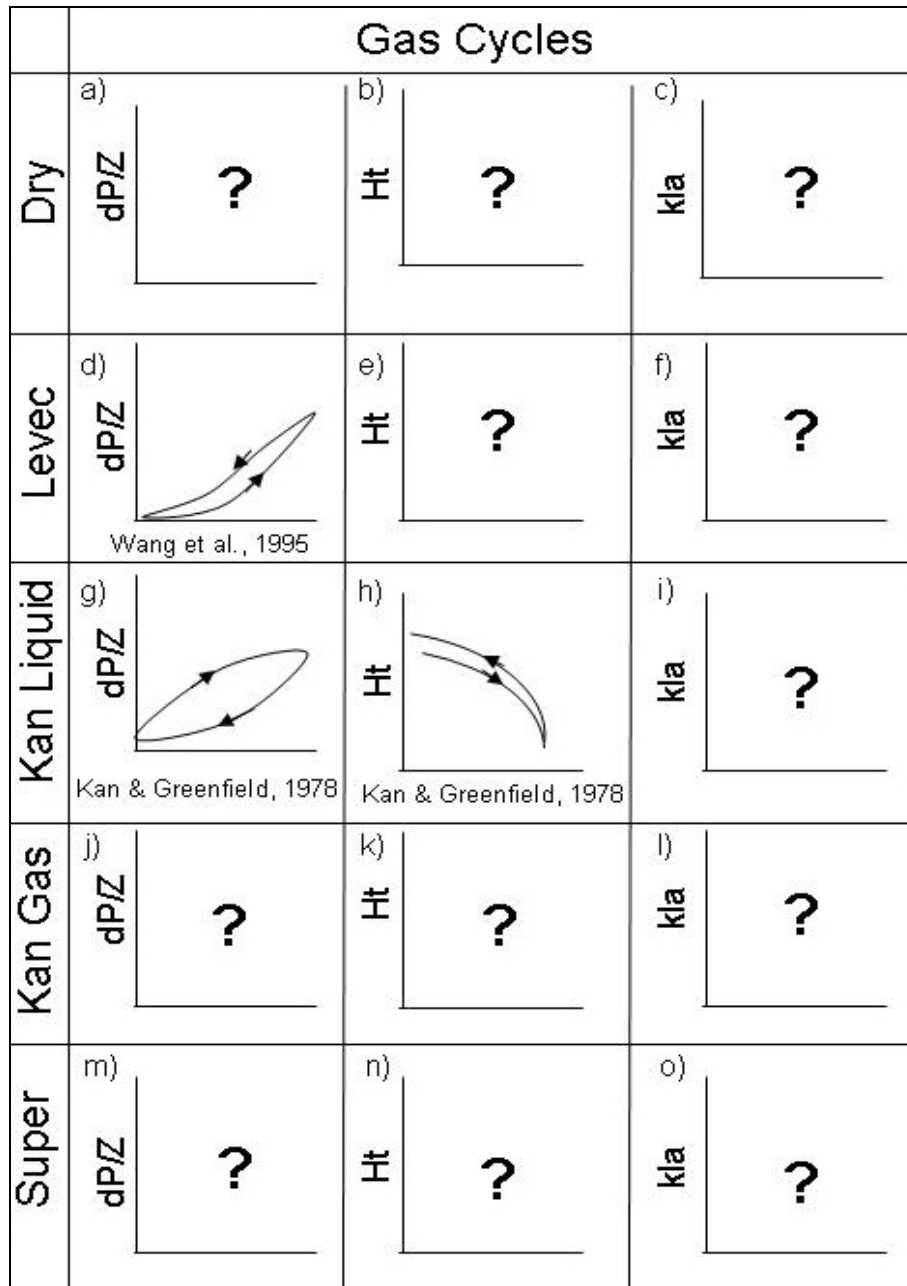


Figure 2.6 Hysteric behaviours for gas flow modulation on the different prewetting modes

Kan & Greenfield (1978) found that for a given gas flow rate, the pressure drop, and holdup are lower if the flow has been reduced from a higher value (Figure 2.6g). Wang *et al.* (1995) observed the opposite behaviour (Figure 2.6d). They found that for a Levec-wetted bed, the pressure drop was higher if the flow was reached by reducing the flow. It is important to note that if the gas flow rate was increased to the point of pulsing, the return leg would actually be on the Kan Gas wetted mode.

Figure 2.6 g and h corresponds to the Reduced Gas Flow rate condition of Kan & Greenfield (1978). They found that for a given gas flow rate, the pressure drop is lower if the flow has been reduced from a higher value. The steady-state value attained for a given gas flow rate is dependent on the maximum gas flow rate that the bed was subjected to. The reason for the difference in pressure drop, according to Kan & Greenfield, is that in a prewetted bed, in the absence of gas flow, the liquid bridges are orientated randomly. As the gas flow rate is increased the liquid bridges transverse to the general flow of the gas tend to be broken down, thereby decreasing the gas flow path density and tortuosity. Due to the high surface tension, even when the gas flow rate is reduced, this flow pattern is retained and results in a lower pressure drop. The decrease in the gas flow path density and tortuosity also results in a higher liquid holdup due to the fact that the liquid holdup is directly affected by the gas velocity acting on the liquid surface (Kan & Greenfield, 1978).

Figure 2-6d) is based on the experimental findings of Wang *et al.* (1995) for a Levec wetted bed. Their results show the opposite trend to what was seen in the Kan wetted bed. They found that the pressure drop for a given gas flow rate that has been reached by decreasing the gas flow rate from a maximum value, was higher than the pressure drop recorded for the run where the gas flow rate was always increasing. This could be explained by considering that a Levec wetted bed is said to be dominated by rivulet flow. An increase in gas flow rate may in this case spread the liquid more, and cause more uniform liquid distribution, which will result in a higher pressure drop due to decreased flow path for the gas.

According to Wang *et al.* (1995) a lower pressure drop is related to less uniform distribution of gas-liquid flow in the trickle-bed, while the upper branch of the hysteresis loop corresponds to more uniform distribution of gas-liquid flow.

2.5 Periodic Operation

Various forms of periodic operation have been used with great success; Concentration variation (Lange *et al.*, 1994) as well as periodic flow reversal (Zagoruiko *et al.*, 1992 and Matros, 1990) has been implemented on an industrial scale to eliminate or control hotspot formation. Periodic flow modulation is a newer concept, and as yet has not been implemented industrially. The prospects for this type of operation are however promising (Khadilkar, Al-Dahhan & Dudukovic, 1999; Lange *et al.*, 2004; Turco *et al.*, 2001).

The principle of periodic operation is to force a system to operate continuously in a transient mode as opposed to allowing the system to relax to steady-state operation (Boelhouwer, Piepers & Drinkenburg, 2001). This exploits the non-linearity of chemical reactions (which often appear as inertial effects) and its associated heat effects. An abrupt increase in an input variable might then have a larger effect on the reaction rate or selectivity of a reaction than the return process to the original state. The net effect of the change is therefore a greater time-average rate or selectivity (Silveston & Hanika, 2002).

2.5.1 Modes of Periodic Operation

Periodic flow modulation can be achieved in two different modes of operation (Boelhouwer, 2001):

- Slow mode of operation (Periodic variation of feed rate in a time interval in the order of minutes)
- Fast mode of operation (short pulses of liquid, externally induced in a time interval of a few seconds)

These can be achieved by either flow interruption (Haure *et al.*, 1990; Lange *et al.*, 1999 and Turco *et al.*, 2001), or flow variation (Khadilkar *et al.*, 1999 and Boelhouwer, Piepers & Drinkenburg, 1999) of the gas or liquid flow rate.

According to Boelhouwer (2001), the fast mode of operation can be seen as an extension of the natural pulsing regime, in a range of gas and liquid flow rates normally associated with the trickling regime. Gas flow rates necessary for pulse formation are about 15% lower compared to natural pulsing flow at equivalent liquid flow rates. The character of the induced pulses, are equivalent to that of the natural pulsing regime near the transition boundary. Based on the properties of pulses, both gas and liquid limited reactions should benefit from this type of operation. Experimental investigations for liquid limited conditions under the fast mode of periodic operation have not yet been reported. In the fast mode of operation, the pulsing frequency can be controlled externally. Frequencies lower than 1Hz can be obtained, making it possible to match the time constant of pulsing with the time constant of reaction. According to Wu *et al.* (1999) this ought to ensure maximum performance.

During the slow mode of operation, the gas or liquid phase is cycled (by either flow interruption or variation) with relatively long periods (the order of minutes). This results in the alternation of liquid and gas rich zones through the column. This mode reaches a pseudo steady state, subsequently alternating between two constant steady states.

The parameters used to characterize the periodic cycles, are the cycle split and period. Cycle split is defined as the fraction of time for which the high liquid flow rate is passed through the bed, while cycle period is the total time of a full cycle.

2.5.2 Enhancements Achieved by Periodic Operation

Periodic operation has been shown to increase conversion, selectivity, catalyst lifetime and hot spot control (Silveston & Hanika, 2002). These consequences render it a tool for process intensification (Nigam & Larachi, 2005) and improved process control (Lange et al., 1994).

Two reactions systems have enjoyed considerable attention in the investigations of periodic flow modulation; the catalytic hydrogenation of α -methylstyrene (AMS) to cumene (usually over palladium catalyst) and the oxidation of SO_2 . Both of these are usually gas reactant limited. Haure, Hudgins & Silveston (1989) and Lee, Hudgins & Silveston (1995) investigated the effects of periodic operation by flow interruption on the oxidation of SO_2 to sulfuric acid. They reported increases in oxidation rates of up to 50%, which was contributed to enhanced temperature profiles, and reduced mass transfer resistance. Lange *et al.* (1994) and Khadilkar, Al-Dahhan & Dudukovic (1999), reported performance enhancements up to 60% for catalytic hydrogenation of α -methylstyrene (AMS) to cumene over palladium catalyst.

Under liquid limited conditions, catalyst wetting and liquid supply to the particles is crucial. Flow interruption under liquid limited conditions does not produce any enhancement, in actual fact; it may result in lower conversion. This is due to the competition between the positive effects of periodic liquid flow modulation (increased liquid distribution, uniform wetting), and the aggravation of the liquid limitation caused by interruption of the liquid flow. At extremely low flow rates, a small enhancement may be observed. A superior flow modulation strategy seems to be the alteration of the gas flow rate. Under these conditions, the liquid limitation will be reduced, while more uniform wetting will still be promoted. This has however not been investigated yet.

2.5.3 Motivation for Achieved Enhancements

The initial motivations for enhancements observed during periodic operation, focused on evolvment of temperature fronts, and reduced mass transfer limitations.

Haure *et al.*, 1989 found that only about 50% of the increases in their study, could be explained by the enhanced mass transfer rates, and contributed the rest to an increase in temperature. The liquid flush regenerates the catalyst and flushes out the inhibiting product. With shorter flushing periods, the maximum temperature is reached more rapidly during the *Off* part of the cycle (Metzinger *et al.*, 1992). This is an indication that the catalyst has not been fully regenerated during the *On* part. This suggests a minimum flushing time for the liquid to ensure catalyst regeneration. This explains why both cycle split and period both have an optimum value.

The complex interplay between enhancing mass transfer, prevention of reactant starvation, and the time needed for catalyst regeneration influences the choice for optimum cycle split and period; at low cycle periods the liquid reactants may be supplied at shorter time intervals than needed for their consumption by the gaseous reactant, leading to gas reactant starvation; at large cycle periods, the opposite behaviour is observed due to longer gas access time than needed to consume the liquid reactants (liquid reactant starvation). On the other hand, a minimum flush time is necessary to ensure catalyst regeneration (Khadilkar *et al.*, 1999).

Lange *et al.*, (1994) and Turco *et al.*, 2001 investigated the influence of periodic operation under isothermal conditions. The conversion during liquid flow modulation could be increased by up to 52%, while gas flow modulation did not significantly affect performance. The enhancements could be attributed to either mass transfer, liquid distribution or wetting efficiency, since cycling of the liquid feed modifies the holdup.

Liquid holdup in packed beds mainly consists of two parts: dynamic and residual. The latter depends upon the mode of cycling, flow rate, catalyst shape and catalyst properties such as porosity, roughness, and wettability. Cycling also influences the contact time of the liquid and catalyst and the interfacial area. By variation of the liquid flow rate, the catalyst wetted area increases, and decreases. A decrease in the liquid film at the catalyst surface allows hydrogen, the limiting reactant, more ready access to the catalytic sites, which leads to increase in local reaction rate. The variation in the liquid loading may also influence the liquid solid mass transfer coefficient. The cycling may open new channels that were otherwise closed and that contained so called liquid pockets, thereby increasing the specific liquid solid area (Lange *et al.*, 1994).

Most of the investigations in periodic operation have focused on the enhancements obtained in reacting systems, where gas and liquid limitations play an important role. As discussed previously, the main reasons for these improvements tend to revolve around the alteration of mass transfer limitations during the operation. A secondary effect, commonly mentioned in these types of investigations, is an increased uniformity of wetting and liquid distribution. Not many experimental investigations have however been done to prove this claim. Investigators such as Boelhouwer (2001), and Xiao *et al.* (2001), have mentioned experimental evidence of the enhanced liquid distribution obtained due to periodic operation. Xiao *et al.*, (2001) showed that cycling of the liquid feed, resulted in more uniform liquid distribution both radially and axially. In fact, their experiments indicated that they could achieve more uniformity with forced gas pulsing than the natural flow regime at an equivalent gas flow rate. Lim *et al.*, 2004 showed by using MRI that though periodic modulation of the liquid feed had a negligible impact on the macroscopic gas-liquid distribution, the local distribution at specific points along the column was improved; Minor changes in the liquid distribution as a function of time were observed and these took the form of, for example, minor growth of one or two rivulets within the image but these had negligible effect on the values of surface wetting and holdup extracted from the images.

According to Lim, the rapidly changing gas-liquid distribution imposed by the liquid flushes will result in wetting of the entire catalyst surface.

Borremans, Rode & Wild (2004) did not observe an enhancement in liquid distribution, due to periodic operation. They reported instead, that the maldistribution factor increased due to periodic operation. The increased maldistribution factor was attributed to the increased central flow. It has to be considered that the flow rates they investigated, is actually very close to the natural pulsing flow regime, and therefore it is to be expected that a significant improvement won't be achieved by periodic operation. A further pitfall of their investigation is the fact that they considered only bed scale distribution, while it has clearly been shown by investigators using MRI techniques, that the average bed scale distribution, is in actual fact a bad presentation of the actual distribution in the bed

These experimental investigations regarding the liquid distribution effect, were all performed with a type of fast mode of operation, and cannot explain what the transient effect has during the slow mode of operation on liquid distribution. These initial studies do not suggest however, that such transient operation necessarily modifies the macroscopic gas-liquid distribution within the bed for a given set of operating conditions in the trickle-flow regime. It is therefore not certain whether the enhancements obtained during periodic operation, are solely due to continually changing mass transfer limitations, and product flushing, or improved liquid distribution. Another effect which has not been considered in any of the investigations mentioned, is the hysteresis behaviour encountered in pressure drop and liquid holdup. This is quite surprising, as periodic operation can actually be seen as a repetition of a flow loop, and should therefore have a certain extent of hysteresis included.

3. Experimental

3.1 *Experimental Setup*

The experimental setup was designed to enable dynamic monitoring of the bed average hydrodynamic parameters; pressure drop, liquid holdup and gas-liquid mass transfer. All data was logged onto the DeltaV operating system with the use of a continual historian. All experiments were performed at atmospheric pressure and ambient temperature. Two experimental setups were used (Figures 3.1 and 3.2). Experimental setup 1 was used in all the water/nitrogen experiments, while setup 2 was used in the low surface tension liquid/nitrogen experiments.

The reactor consisted of an 85cm long Perspex column (id 67mm), designed with a pressure release valve (V-2). The valve provides a gas outlet when the column is flooded. The bed was packed with 3mm glass beads. A constant bed porosity of 0.36 was maintained, through using a constant mass and height of packing.

In experimental setup 1, tap water is enriched with oxygen by mixing the water with air in TK-1. A weir and submersible pump (SP-1) is used to ensure a constant pressure head. The gas and liquid are fed cocurrently into the bed. The liquid flow rate was adjusted with the use of parallel valves. Needle valve (V-1) was used to adjust the bulk flow rate, while metering valve (V-3) enabled fine tuning. Three way valve V-4 was used to direct the liquid back to the feed tank when the column was being drained. Load cell WT-1, differential pressure transmitter DPT-1 and oxygen analyzer AN-1 enabled measurement of the hydrodynamic parameters hold up, pressure drop and gas-liquid mass transfer.

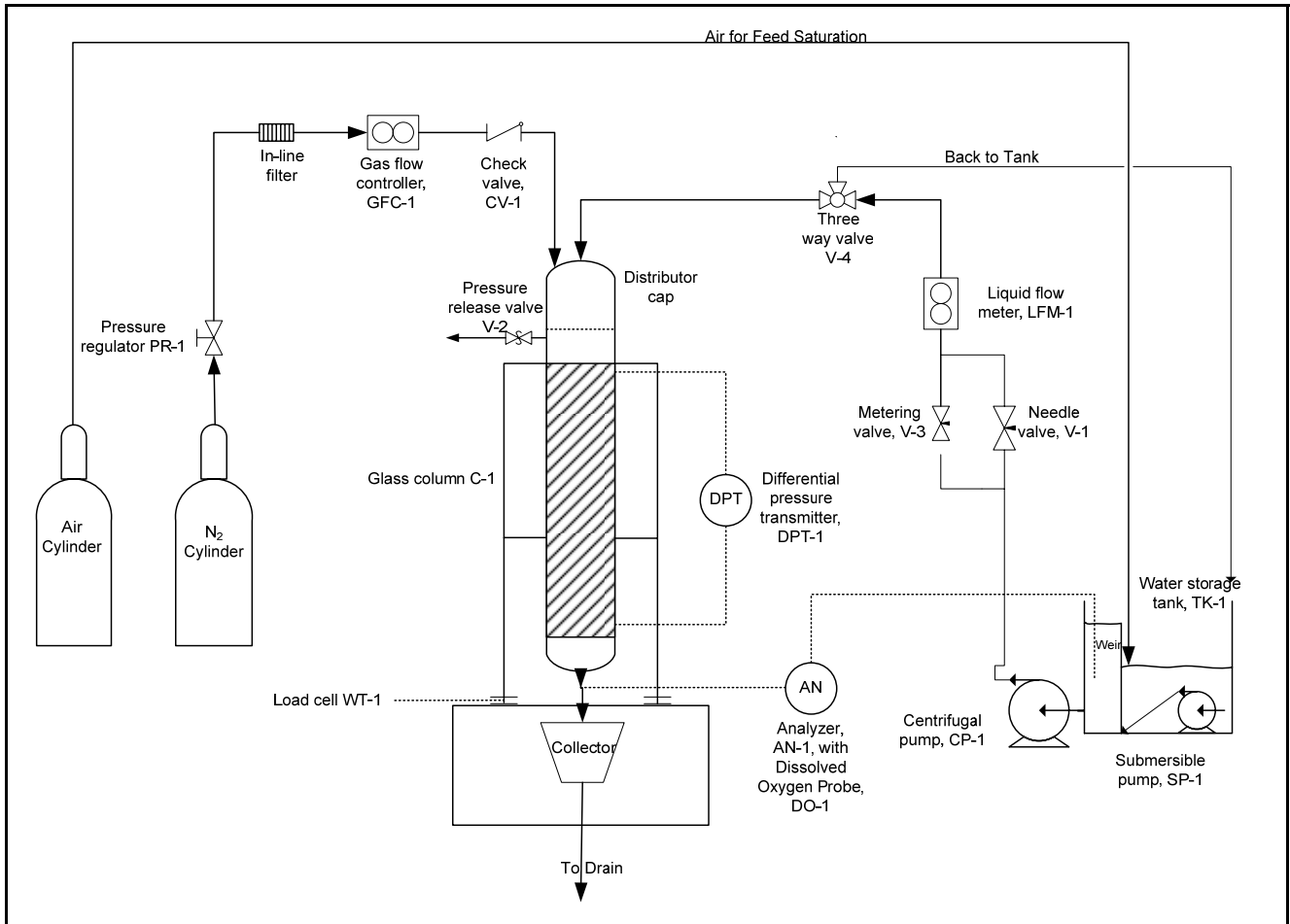


Figure 3.1 Experimental Setup 1 as used for water /nitrogen system. The setup enables dynamic monitoring of hydrodynamic parameters pressure drop, liquid holdup and gas liquid mass transfer.

Low surface tension (LST) liquid experiments were performed on experimental setup 2. Two separate feed tanks were used. TK-1 was still used for tap water, while TK-2 contains a LST liquid (mixture of ethanol and water). Gate valves V-5 and V-6 were used to switch between the different feed tanks. A recycle stream transported the oxygen poor LST liquid mixture back to the feed tank where it was once again enriched with oxygen. Both feeds were pre-saturated with oxygen by bubbling air through the feed. Once the saturation value was reached, the value was kept constant by continually bubbling air through the liquid.

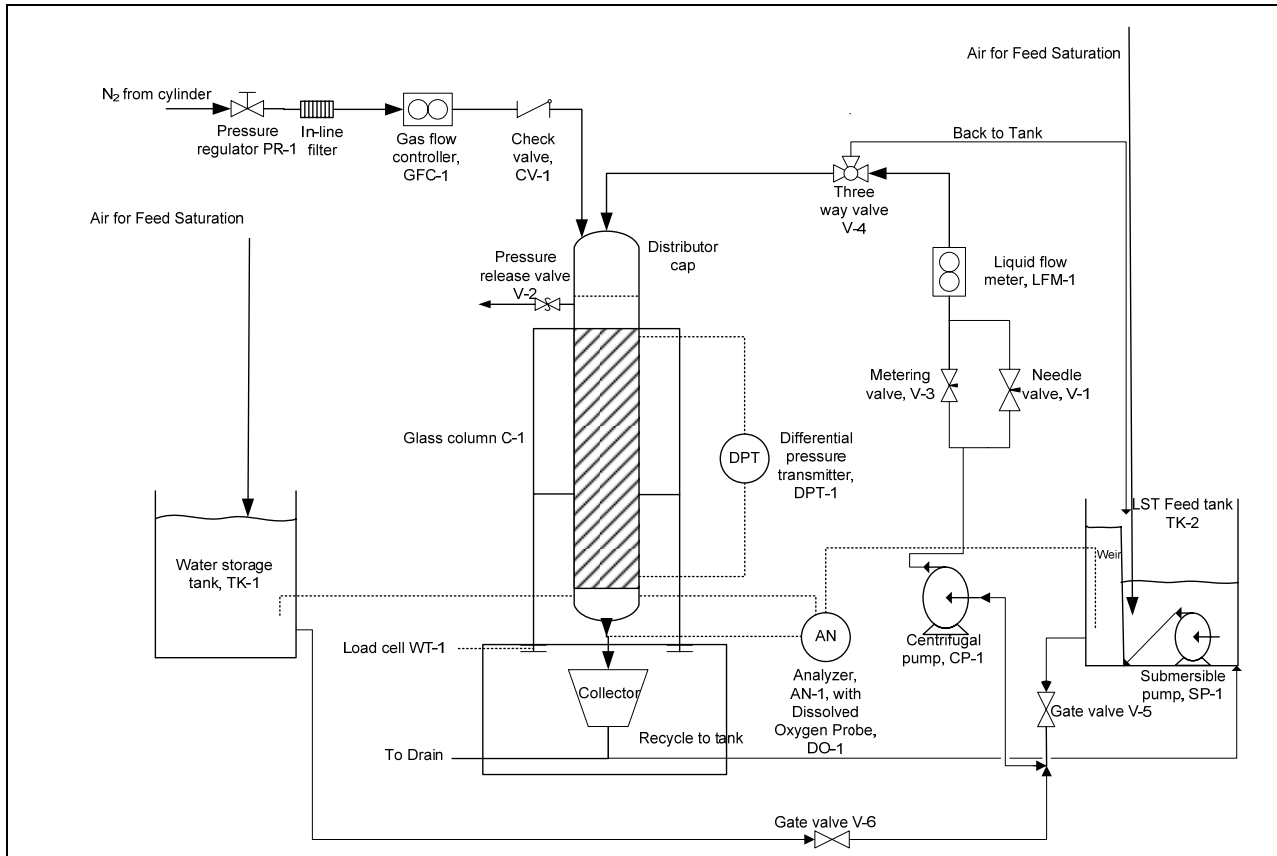


Figure 3.2 Experimental setup 2 as used for LST liquid experiments.

One distributor was used for all of the experiments and is shown in Figure 3.3. The holes in the distributor plate are 0.5mm in diameter and spaced in a square pitch arrangement, 8mm apart. This results in a hole-density of 16000points/m², which is more than adequate according the study of Burghardt *et al.*, 1995. The cap contains three ¼" stainless steel tubes through which the gas is fed into the column. This ensures that liquid distribution will remain as uniform as possible even at high gas flow.

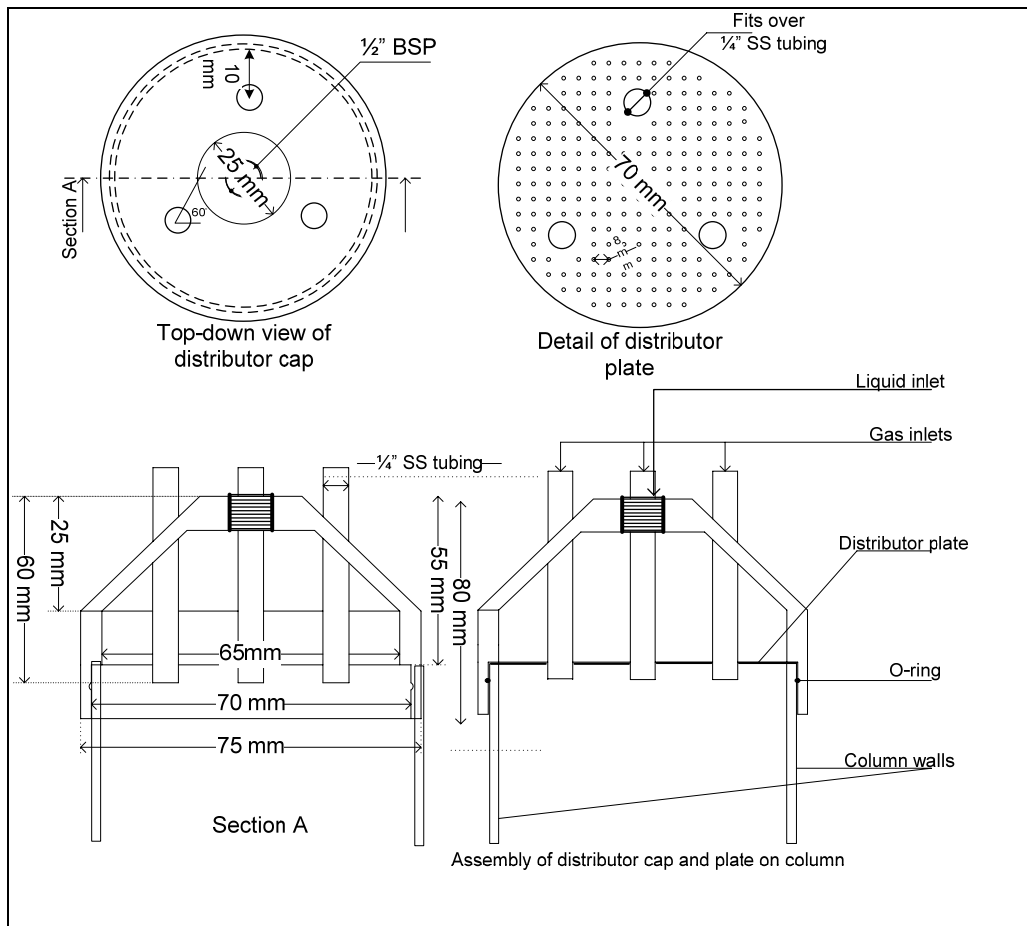


Figure 3.3 The gas and liquid distributor design ensures uniform distribution at the top of the column for both phases.

Liquid accumulates in the distributor, which has to be subtracted from the total measured weight. To ensure that this amount is constant, the feeding tube has to be liquid filled during all the experiments. This was especially a problem in the Levec wetted beds; when the pump is shut of, some of the liquid in the distributor drained, and would not fill up until higher flow rates. The original experimental setup as used by Loudon *et al.* (2005) was modified to correct this problem. A three way valve (V-4) was included to recycle the feed to the column during draining periods, without suspending the flow from the pump itself. The mass of liquid in the filled distributor was determined to be 133g.

3.2 Experimental Equipment

The pressure drop over a section of the bed was measured by a Rosemount Model 3051CD Pressure Transmitter. The accuracy of the transmitter was 0.1% of the range and under normal operating conditions translates to an accuracy of approximately 6Pa.

The liquid holdup was continually measured by a weighing method. This was achieved by mounting the column on a high accuracy load cell (WT-1), type 642C3 from Revere Transducers Europe. The accuracy of the load cell is 0.02% of the span, rendering an accuracy of approximately 4g.

The dissolved oxygen in the feed tank and outlet stream was measured with Dissolved Oxygen Sensor 499ADO from Rosemount Analytical. The range of the probe is 0 – 20 ppm and has a reported accuracy of 0.2ppm and a repeatability of 0.05ppm at 25°C. The analyzer used was the SOLU COMP II analyzer from Rosemount Analytical (AN-1). The oxygen sensor needed to be calibrated for a zero standard (no dissolved oxygen) and air calibration. The zero standard was obtained by placing the probe in a solution of 5% sodium sulphite in water. Air calibration was performed by keeping the probe 1cm above a glass beaker filled with water while waiting for the reading to stabilize. The electrolyte solution in the probe was regularly replaced.

The liquid flow rate was monitored with an Electromagnetic Flow Measuring System (LFM-1), the PROline promag 10H from Endress + Hauser. The flow meter has an accuracy of 0.5% of the rate when the flow is above 1l/min and an accuracy of 1.5% of the rate when the flow is between 0.2 and 1l/min.

The gas phase flow rate was monitored and controlled with a Brooks Smart Mass Flow (GFC-1) Model 5851S. The range of the flow meter is 0 – 100l/min, calibrated for Nitrogen with an accuracy of 0.7% of the range.

Ethanol concentration in the LST liquid was monitored with a Brix portable digital refractometer.

3.3 Experimental Method

3.3.1 Determining Liquid Holdup

The Liquid holdup was determined by using a weighing method. The load cell was zeroed before liquid is introduced into the column. The total mass of liquid in the column was then continually recorded throughout an experiment. After the column is drained, the residual mass of liquid can be noted. The liquid in the distributor was then subtracted from the measured mass before it was converted to liquid holdup with equation 3.1.

$$H_t = \frac{m}{\rho_l V_b} \quad (3.1)$$

3.3.2 Determining Gas Liquid Mass Transfer

A desorption technique was used to determine the gas liquid mass transfer coefficient. Oxygen is transferred from water, pre-saturated with air, (by bubbling air continuously through the feed tank), to nitrogen, which is fed cocurrently into the column with the oxygen rich water. The magnitude of the gas liquid mass transfer coefficient is determined by the amount of oxygen stripping that occurs. For each operating point, the feed ($C_{LO_{2f}}$) and exit ($C_{LO_{2e}}$) dissolved oxygen concentrations were measured. Each experiment was mimicked in a small (10cm) glass column (of same diameter) to determine the end effects. The dissolved oxygen concentration of the feed ($C_{LO_{2f}}$), and exit concentration ($C_{LO_{2e}}$) were hence measured in the small column for the same pairs of flow rates used in the normal experiments. These concentrations were used in equation 2.2 to calculate the gas liquid mass transfer coefficient.

To ensure that the feed was indeed saturated, equation 3.2 to 3.4 was used to estimate the saturated dissolved oxygen concentration at a specific

temperature. No experiment would commence before the particular saturation value was observed on the oxygen probe in the feed tank.

$$C_p = C^* \times P \left[\frac{(1 - \frac{P_w}{P})(1 - \theta P)}{(1 - P_w)(1 - \theta)} \right] \quad (3.2)$$

where P_w is the partial pressure of water vapour at the specific temperature as calculated from equation 3.3, while θ is calculated from equation 3.4

$$\ln P_w = 11.8571 - (3840.70/T) - (216.961/T^2) \quad (3.3)$$

$$\theta = 0.000975 - (1.426 \times 10^{-5} t) + (6.436 \times 10^{-8} t^2) \quad (3.4)$$

During a single experiment, the temperature never varied by more than 2°C.

3.4 Experimental Procedures

Two types of experiments were performed in each category. In one type, the gas was varied at a constant liquid flow rate (termed constant liquid flow rate experiments), in the other liquid flow rate was varied while the gas flow rate was kept constant (termed constant gas flow rate experiments). At each operating point three parameters were noted namely: pressure drop, liquid holdup and dissolved oxygen concentration in the exit stream.

3.4.1 Start Up

The glass beads were randomly packed into the column, noting the mass and height. The distributor cap was mounted onto the column, and sealed. The column was then mounted onto the load cell (WT-1), after which the scale was zeroed. With each new packing, the pressure drop at various gas flow rates were noted on the dry bed to enable determination of the Ergun constants. The liquid in the feed tank was saturated with air. The saturated dissolved oxygen concentration of the feed was noted. The temperature variation was kept small so that it did not significantly affect variations in dissolved oxygen concentration. Once the feed was saturated with oxygen, the prewetting procedure of interest was executed.

Liquid flow rates of 5, 7 and 9mm/s were evaluated at a constant gas flow rate of 20mm/s, while gas flow rates of 20, 40 and 70mm/s were evaluated at a constant liquid flow rate of 9mm/s. These values were chosen to ensure comparability to the results of Loudon *et al.* (2005). The prewetting hysteresis experiments were performed on the same bed to minimize the effects of repacking on the different prewetting procedures.

The prewetting modes were used in the following order:

- Dry
- Levec
- Kan Liquid
- Super
- Kan Gas mode

3.4.2 Dry Bed Operation

In the constant gas experiments, the gas flow rate was set to the desired flow rate (20mm/s). The liquid was then introduced at the lowest flow rate. Time was allowed for the system to reach steady state (10 min) before the hydrodynamic parameters were noted. The liquid flow rate was then increased to next set-point.

The constant liquid flow rate experiments were performed by once again introducing the lowest gas flow rate into the dry column. The liquid flow rate was then introduced at 9mm/s. After reaching steady state, and noting the parameters, the procedure was repeated for all of the necessary gas flow rates at the specific liquid flow rate.

3.4.3 Levec Pre-Wetting

The gas flow rate was set to the lowest flow rate, whilst valve V-2 is open to allow the gas to escape from the column. The column outlet was closed, and the liquid flow rate adjusted to a high flow rate to ensure proper filling of the distributor. After the column was properly flooded, valve V-4 was adjusted to recycle the liquid flow to the feed tank, whilst simultaneously opening the column exit. The column was then allowed to drain for 20min. After draining, V-4 was switched back to its original position, thereby allowing the liquid into the column. V-2 was

closed, and time was allowed for the system to reach steady state at the desired set-points. The parameters were noted, and the flow increased to the next operating point of interest. This procedure was repeated for all the flow rates of interest.

3.4.4 Kan Liquid Pre-Wetting

The gas flow rate was introduced at the lowest flow rate, V-2 closed. The liquid flow rate was gradually increased until pulsing could be observed over the whole length of the column (The point of pulse inception is usually in the bottom part of the column. With a further increase in flow rate, the point of pulse inception moves up, and eventually pulsing can be observed over the whole length of the column.) The pulsing regime was maintained for 20 seconds, before lowering the liquid flow rate to the desired set point. Time was allowed for steady state to be reached at each operating point before the parameters were noted.

3.4.5 Super Wetting

Valve V-6 was opened, while the gas flow rate was set to the desired set-point. The liquid was introduced at the lowest flow rate, while the column exit was shut, thereby flooding the column. Once the column was properly flooded, V-2 was closed whilst simultaneously opening the column exit, and keeping the liquid flow rate at the desired set point. The column therefore drained under irrigation. Once steady state was reached, the parameters were noted and the flow rate was adjusted to the next operating point.

3.4.6 Kan Gas Wetting

The gas and liquid flow rates were set to the desired set-points. Due to equipment limitation, pulse inception by gas flow could only be reached at a minimum liquid flow rate of 9mm/s. The constant gas flow experiments were therefore performed with liquid flow rates of 9, 9.7 and 10mm/s, at a gas flow rate of 20mm/s.

The gas flow rate was gradually increased (while keeping the liquid flow constant at the desired set point), until pulsing was induced. It was ensured that pulsing occurs over the whole length of the column. The column operated in the pulsing regime for 20seconds, before lowering the gas flow rate to the desired operating point. Once steady state was reached, the parameters were noted, and the flow rate was increased to the next operating point. This procedure was repeated for all the operating points.

3.4.7 Levec Draining Time

This experiment was used to investigate the effect of draining time on the Levec mode of operation. If it is considered that Levec and Super modes are two extremes, one with a long draining time, and the other with an infinitely short draining time, it should theoretically be possible to operate anywhere between these modes purely by decreasing the draining time of the Levec wetted mode.

Liquid flow rates of 5, 7 and 9 mm/s were used at a constant gas flow rate of 20mm/s. The bed was flooded by closing the column exit, while valve V-2 is open. Valve V-2 was then closed to allow the liquid to return to the feed tank while the column is drained. Time was allowed for the column to drain. Draining times of 0, 0.5, 1, 10, 15, 20 min were tested. After draining, V-4 was closed, while simultaneously switching V-2 to allow the liquid into the tank. 10 min was allowed at each flow rate for the system to reach steady state before the

hydrodynamic parameters were noted. The same bed was used for all the draining times investigated.

3.4.8 Hysteresis Flow Loops

The objective of this experiment was to investigate whether hysteretic behaviour occurs on all the prewetting modes, and what the nature of the behaviour is. Hysteretic behaviour may provide a better understanding of the true nature of each prewetting mode.

Constant gas flow rate ($G=20\text{mm/s}$) and constant liquid flow rate ($L=9\text{mm/s}$) experiments were performed. The same prewetting procedures as explained previously were followed. At each pair of flow rates, 10min was allowed for steady state to be reached, after which pressure drop, liquid holdup and dissolved oxygen was noted. Instead of only increasing the flow (as done in the prewetting experiments explained previously), the flow rate was lowered once the highest flow rate was reached along the same flow path, back to the starting operating point. In the constant gas flow experiments, the liquid was varied according to the flow loop: $5>7>9>7>5\text{ mm/s}$. In the constant liquid flow rate experiments, a gas cycle of $20>40>70>40>20\text{ mm/s}$ was used. Each flow loop was repeated to investigate the behaviour of a secondary loop on the same flow cycles.

3.4.9 Periodic Operation

Hysteresis loops were created on each of the prewetting modes, once again with two types of experiments (constant gas, and constant liquid.) The liquid was cycled between 5 and 7mm/s at a constant gas flow rate of 20mm/s , while the gas flow was cycled between 20 and 40mm/s at a constant liquid flow rate of 9mm/s . Periodic operation was performed with a cycle split of 0.5, and a period

of 6min (slow mode of periodic operation). Periodic operation was only initiated after the system obtained steady state at the lowest flow rates in each cycle. The system was monitored under periodic operation for 1 hour, while noting the parameters on each operating point just before adjusting the flow rate.

3.4.10 Low Surface Tension (LST) Liquid

All these experiments were performed with a low surface tension liquid, with a surface tension of 42.3 dynes/cm (nearly half that of water). The LST liquid was prepared by adding ethanol to water (see figure 3.4). These experiments were performed on experimental setup 2.

A recycle stream was included to retain the ethanol. The ethanol concentration was monitored throughout the experiments with a Brix digital refractometer.

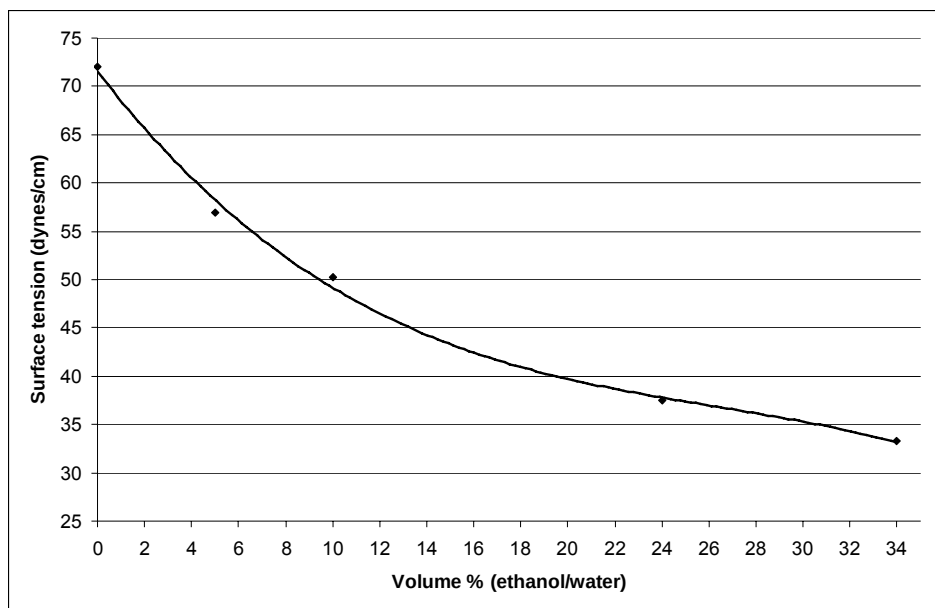


Figure 3.4 Surface tension of water can be drastically lowered with the addition of ethanol.

The prewetting experiments for the LST liquid were performed as described for the water system. The flow rates used differ a little from those used in the water

experiments, since the high interaction regime is encountered much earlier with the low surface tension liquid. Figure 3.5 illustrates the approximate difference in regime transition for the LST liquid, as opposed to the water system.

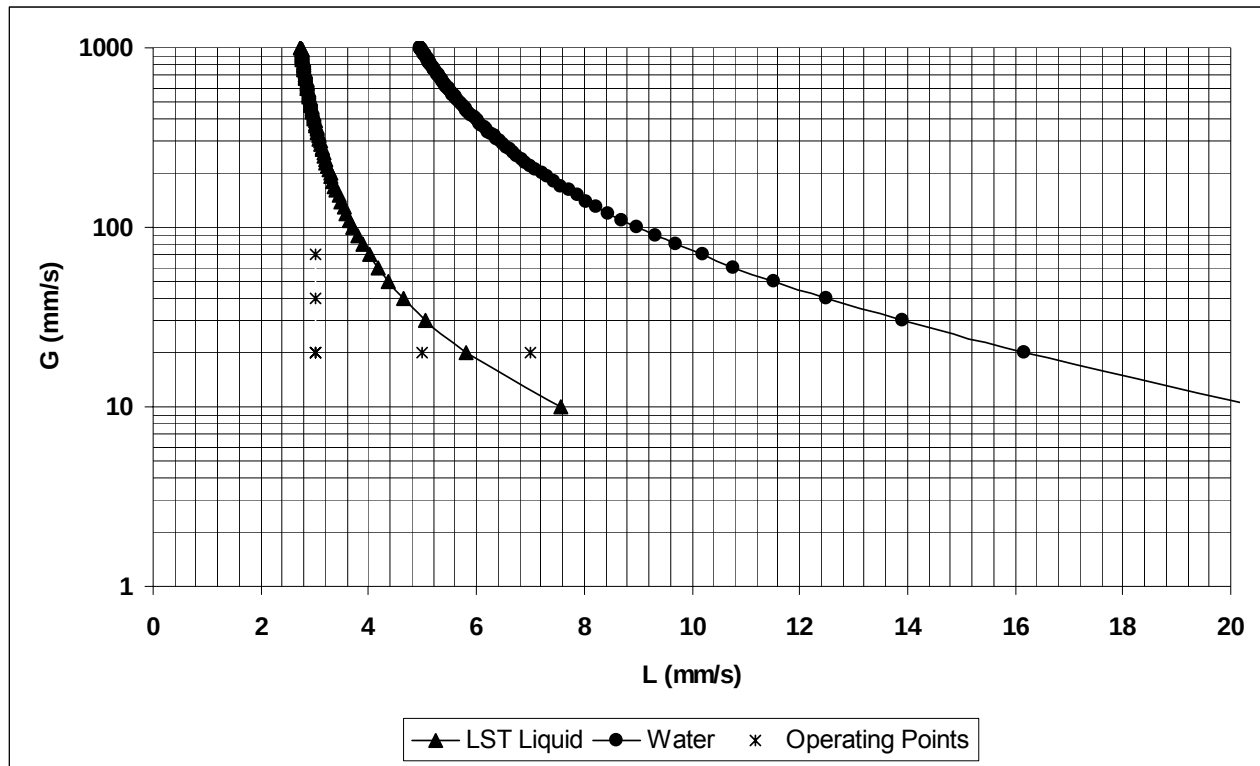


Figure 3.5 Estimated regime transitions for the low surface tension (LST) liquid in comparison with that of water. (Estimated from the Larachi et al., 1999 Simulator)

Liquid flow rates of 3, 5 and 7mm/s at a constant gas flow rate of 20mm/s were used, as well as gas flow rates of 20, 40 and 70mm/s, at a constant liquid flow rate of 3mm/s. Instead of performing the different prewetting modes on the same bed, the bed was repacked every time to cancel a lasting effect that a LST liquid might have. All of the prewetting modes as discussed for the tap water experiments were evaluated.

3.4.11 Low Surface Tension Doping

Doping effects were tested on a steady state water/glass system for all the different prewetting regimes, at liquid flow rates of 5 and 7mm/s, and a gas flow rate of 20mm/s. Experimental setup 2 (Figure 3.2) was used. The bed was repacked for each of the evaluated operating points, to ensure that the effect observed would only be due to the amount of low surface tension (LST) liquid used during that particular run. It could be expected that the repacking will cause more variation in the results.

A newly packed bed would thus be wetted with the tap water (V-6 open, V-5 closed) in a particular mode (Dry, Levec, Kan Liquid, Super and Kan Gas as explained previously), and then set to the desired flow rates. The water system would then be allowed to obtain steady state, where pressure drop, liquid holdup and the dissolved oxygen concentration would be noted. Once the system obtained steady state, V-6 was closed whilst V-5 was simultaneously opened. The LST liquid was therefore fed into the system for a certain amount of time (hereafter referred to as the doping time) while ensuring that the flow rate was maintained at the desired set-point. Various doping times were initially evaluated, after which a doping time of three minutes was chosen for consecutive experiments. After doping, the valve positions were reverted, and the water system was once again allowed to obtain steady state (still at the desired set point). The new hydrodynamic parameters were then noted. Before repacking the bed, the glass beads were thoroughly washed and dried in an oven to remove all traces of ethanol.

4. Prewetting

Van der Merwe & Nicol (2005) was the first to propose that the limits of variation regarding multiple hydrodynamic states in trickle bed reactors can be defined by specific prewetting procedures. The extent of variation in the hydrodynamic parameters (pressure drop, liquid holdup and gas liquid mass transfer) between the various prewetting procedures was quantified by Loudon *et al.*, 2006, and Loudon, 2005.

This work may in a sense be seen as a continuation of the work of Loudon (2005). Although the basic experimental setup was the same as he used, minor modifications was applied to the system. Furthermore, the setup was out of use for a period of nearly four months. To ensure that the setup was performing correctly, a few data points of Loudon was repeated. These results would also serve as a basis for comparison during the consecutive experiments. The modes investigated were:

- *Dry Mode*: a bed packed with completely dry particles. The liquid and gas are introduced into the system at the desired flow rates.
- *Levec Mode*: The bed is prewetted by flooding the packed bed. Once prewetted, the liquid flow is shut off and the liquid is allowed to drain under gravity for 20min. Liquid is then introduced into the system.
- *Kan Liquid Mode*: The bed is prewetted by operating in the pulsing regime by increasing the liquid flow rate to the point of pulsing. The flow rates are subsequently decreased to their operating set points.
- *Super Mode*: The bed is flooded completely with liquid. The flow rates are adjusted to the specific operation points without allowing the column to drain (the bed drains under irrigation)
- *Kan Gas Mode*: The bed is prewetted by operating in the pulsing regime by increasing the gas flow rate to the point of pulsing. The flow rates are subsequently decreased to their operating set points.

4.1 Prewetting Modes with Water

The multiple hydrodynamic states obtained with the different prewetting methods for liquid holdup, pressure drop and gas liquid mass transfer, confirm that there is a large difference in the performance of the various prewetting modes. In the results figures, the average data point is shown along with error bars that represent the maximum and minimum values obtained during repetitions of the same experiment. The data markers corresponding to a single flow rate were in some cases off-centred to eliminate overlapping error bars.

4.1.1 Pressure Drop

These results agree very well with that of Loudon, 2005. Two distinct regions are seen with high pressure drop (Kan Liquid and Super modes) and lower pressure drop (Dry and Levec modes). The pressure drops obtained with liquid variation on the different prewetting modes are shown in figure 4.1.

Kan Gas seems to fill in the gap between the higher and lower pressure drop modes. Kan Liquid has the highest pressure drop, being as much as four and a half times greater than the pressure drop on the Dry mode. The gas flow restriction is the highest in this mode, which in turn reflects that liquid distribution should be very uniform, thereby agreeing well with the results obtained for Liquid Holdup.

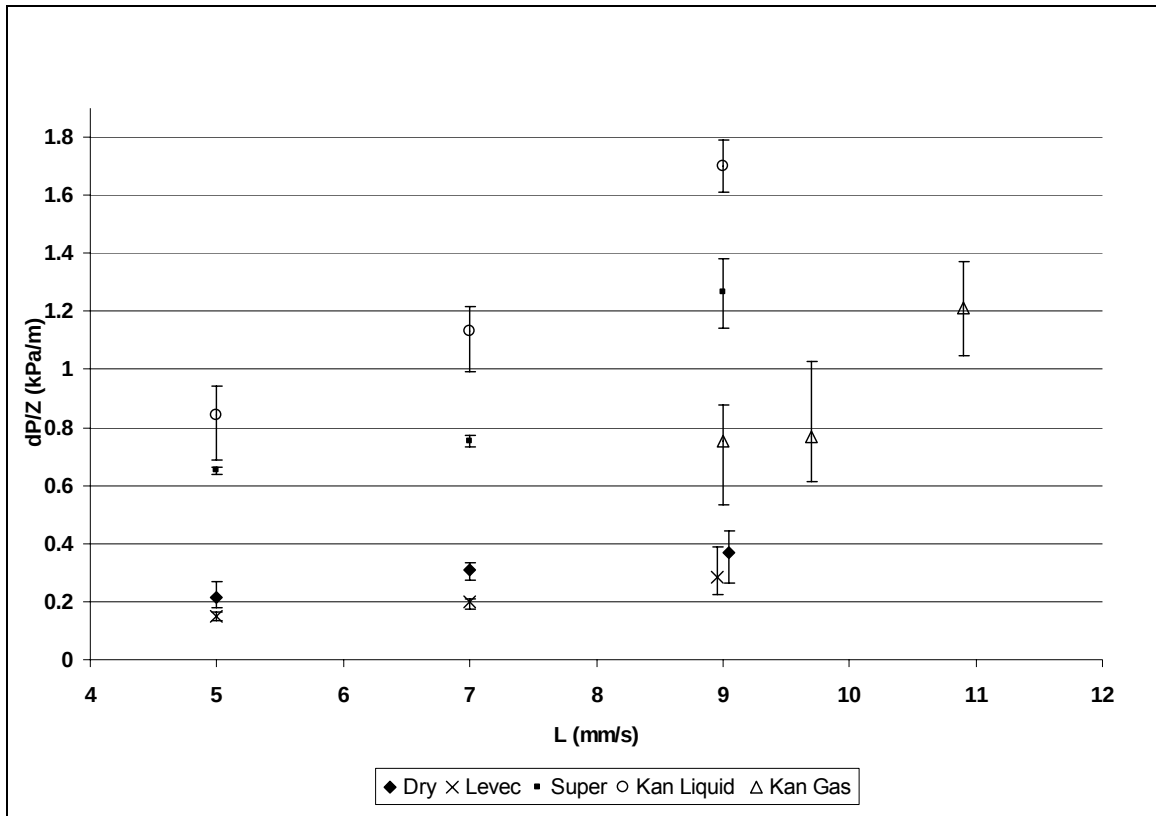


Figure 4.1 Pressure drop hysteresis as a result of different prewetting procedures ($G=20\text{mm/s}$). Kan Liquid wetting provides the highest pressure drop.

The variation in pressure drops for the different modes increase with increasing flow rate. Pressure drop is very sensitive to the specific regime. Liquid holdup increases gradually with increasing flow rate to the pulsing point on all the modes, except for the Dry and Levec modes. The incline on these modes is initially very small. A sudden increase in pressure drop occurs if the point of pulsing is reached.

The pressure drops obtained for gas flow variation on the different prewetting modes, are shown in figure 4.2.

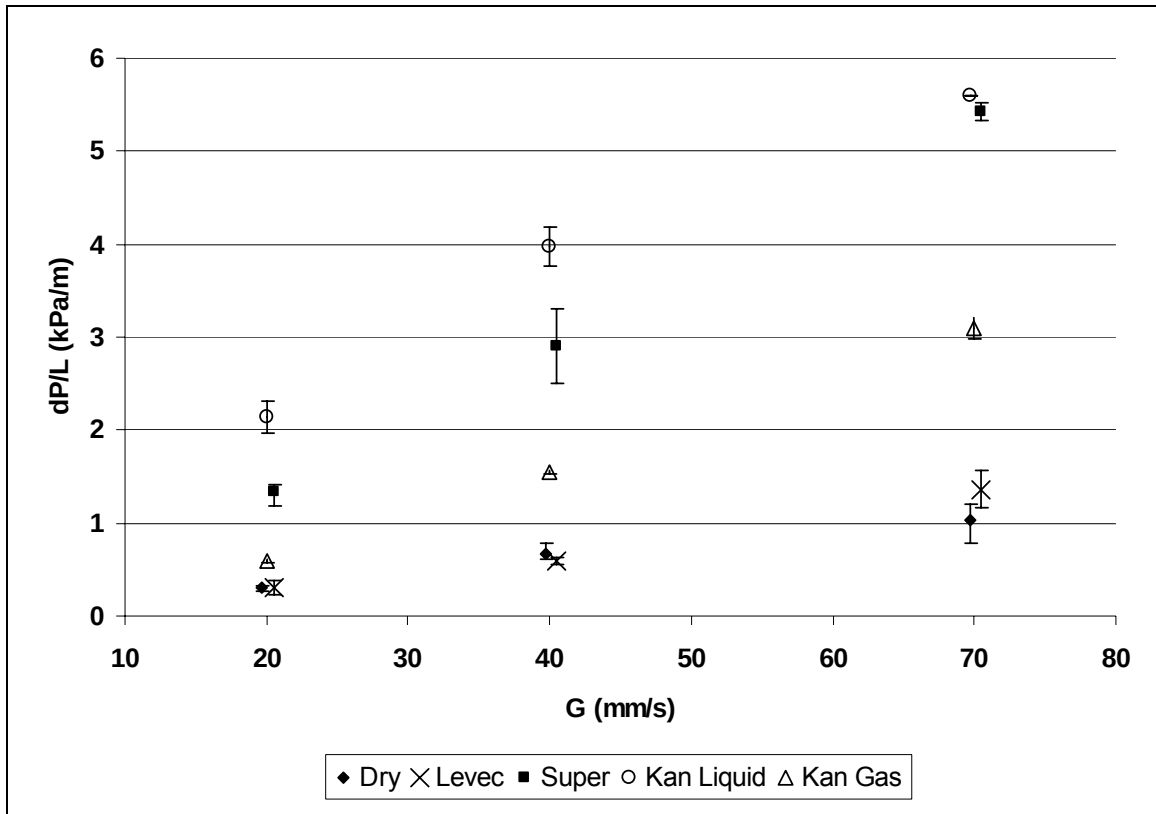


Figure 4.2 Pressure drop hysteresis obtained as a result of different prewetting methods, by varying the gas flow rate at a constant liquid flow rate of 9mm/s.

Pressure drop is an increasing function of gas flow rate regardless of the operating mode. Three regions can be distinguished, with Dry and Levec having the lowest pressure drop, and Kan Liquid and Super having the highest pressure drops, whilst Kan Gas mode is in between. Pressure drop of the Kan Liquid mode can be as much as seven times greater than that of the Dry mode.

The variation once again increases with an increase in flow rate. For the gas flow variation, it can be seen that Kan Liquid and Super mode's pressure drop will have to decrease to the Kan Gas mode if the gas flow rate is increased to the point of pulsing. This reflects that there is indeed a substantial difference between the flow types of the Kan Gas mode vs. the Kan Liquid and Super modes.

4.1.2 Liquid Holdup

The results obtained for Liquid holdup confirm the trends observed by Loudon, 2005. Their liquid holdup was however always greater than the holdup measured at equivalent operating conditions in this study. The difference seems to be the result of a partially filled liquid distributor in Loudon's study. The agreement between the holdup was better at higher flow rates, as the distributor would tend to be full at the highest flow rates.

The MHS obtained in liquid holdup for the constant gas flow experiments, are shown in figure 4.3. It can be seen that each of the prewetting modes are associated with a specific holdup margin. The liquid holdup of the Kan Liquid mode can be as much as three times greater than that of the Dry mode. A lower holdup is associated with less uniform liquid distribution. In the Dry and Levec wetted beds, liquid flows in the form of rivulets, leaving a large percentage of the column dry. In the Kan Liquid and Super wetted beds, the liquid is more uniformly distributed, giving rise to higher holdups. The dominant flow type in these modes appears to be film flow. The film thickness is not constant throughout the bed; and in certain parts of the bed the liquid still seems to be stagnant.

Generally, the correct trend of increasing liquid holdup with increasing liquid flow rate is observed. Although it seems that the Kan Liquid holdup decreases at 9mm/s according to the average, the error bars on this operating point is too high to substantiate the appearance, and the liquid holdup may well be equivalent to that of the Super mode at the same operating point.

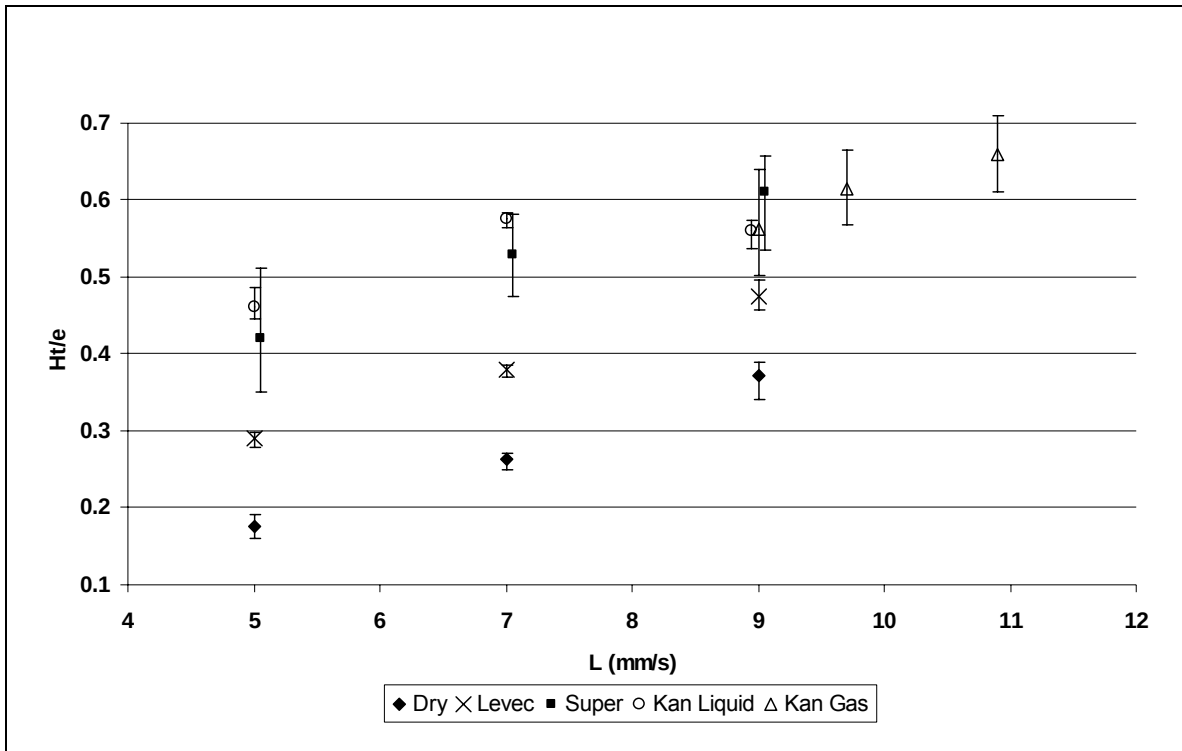


Figure 4.3 Holdup hysteresis as a result of different prewetting modes ($G=20\text{mm/s}$). The Kan Liquid and Super modes provide the highest holdup.

The Kan Gas mode could only be obtained from a liquid flow rate of 9mm/s onward. An evaluation of the different modes at 9mm/s indicates that the Kan Gas holdup is higher than the Dry and Levec wetted beds, but less than Kan Liquid and Super. The Kan Gas liquid distribution seems to be less uniform than that of the super wetted bed. It was observed that the flow type in this mode does not look like that of the Super and Kan Liquid modes. It seemed as if the gas movement was more prominent than the liquid movement.

It is evident that the liquid holdup obtained by different prewetting modes, are located nearer each other at higher flow rates. This is to be expected since higher flow rates are associated with more uniform distribution. Furthermore, it is to be expected; if the liquid flow rate is increased to pulsing on any of the prewetting modes, the operating mode will evolve into the Kan Liquid mode.

The liquid holdup obtained for constant liquid experiments on the different prewetting modes, are shown in figure 4.4. Kan Liquid and Super modes are

almost equivalent, having the highest holdups of all the modes. Kan Gas has a higher holdup than Levec mode, but less than Kan Liquid and Super.

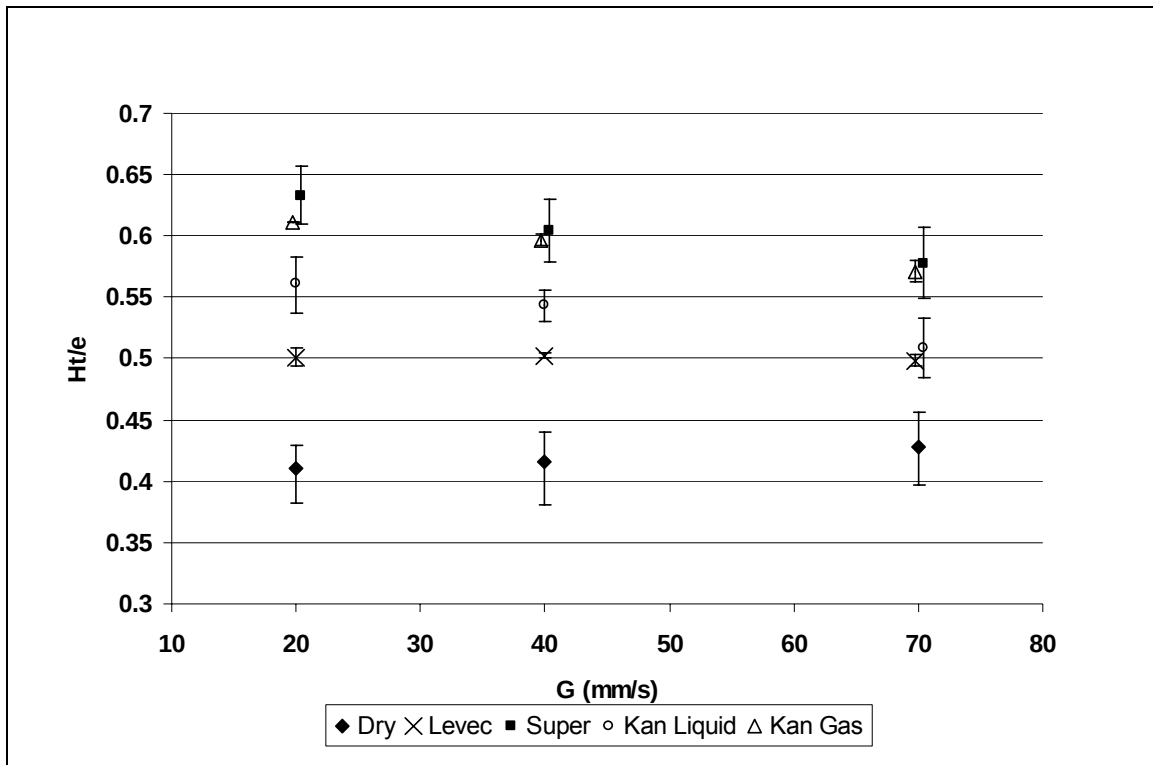


Figure 4.4 Liquid holdup hysteresis obtained as a result of different prewetting methods, by varying the gas flow rate ($L=9\text{mm/s}$).

Liquid holdup in the Super mode can be as much as one and a half times greater than that of the Dry mode. As the flow rate is increased, the distinction between the different modes once again declines. This behaviour could be expected; if the gas flow rate is increased to the point of pulsing on any of these modes, it will evolve into the Kan Gas mode. From figure 4.4 it can be seen that the different modes will converge to the Kan Gas mode as pulsing is approached.

The general trend of decreasing liquid holdup, with increasing gas flow, is observed on all of the modes, except for the Dry mode. It seems like the Liquid holdup in the Dry mode actually increases slightly with an increase in gas flow rate. This could possibly be the cause of the initial rivulets in the dry bed. In this mode, an increase in gas flow rate does not serve to smear the films, or make

them thinner. Instead, the gas serves to spread the liquid so that new rivulets may be formed, leading to a higher holdup.

4.1.3 Gas Liquid Mass Transfer

Great performance enhancements can be obtained by altering the prewetting procedure. Loudon *et al.*, 2006 showed that the gas liquid mass transfer coefficient of the dry mode can be increased by up to 400% if Super or Kan Liquid prewetting is used. These results agree well with their observations.

The results for the Gas liquid mass transfer coefficient on the different prewetting methods are shown in figure 4.5. Once again, two regions can be observed with Dry and Levec modes having much lower gas liquid mass transfer coefficients than the Kan Liquid and Super wetted modes. Gas liquid mass transfer of the Kan Liquid and Super modes, were up to 5 or 6 times greater than that obtained on the Dry mode. Kan Gas once again occupies the region between these.

Gas liquid mass transfer of the Dry mode seems like it initially decreases with an increasing liquid flow rate. If the error bars of the first two data points are however considered, it should rather be concluded that there was very little change. This can be understood, if it is considered that the Dry mode only has rivulets flowing through the bed. An initial increase in flow rate leads the creation of a few new rivulets, and eventually the expansion of existing ones. With the addition of a few small rivulets, no significant change in the gas liquid interfacial area will occur. Once the rivulets start expanding, more gas liquid interfacial area will be created.

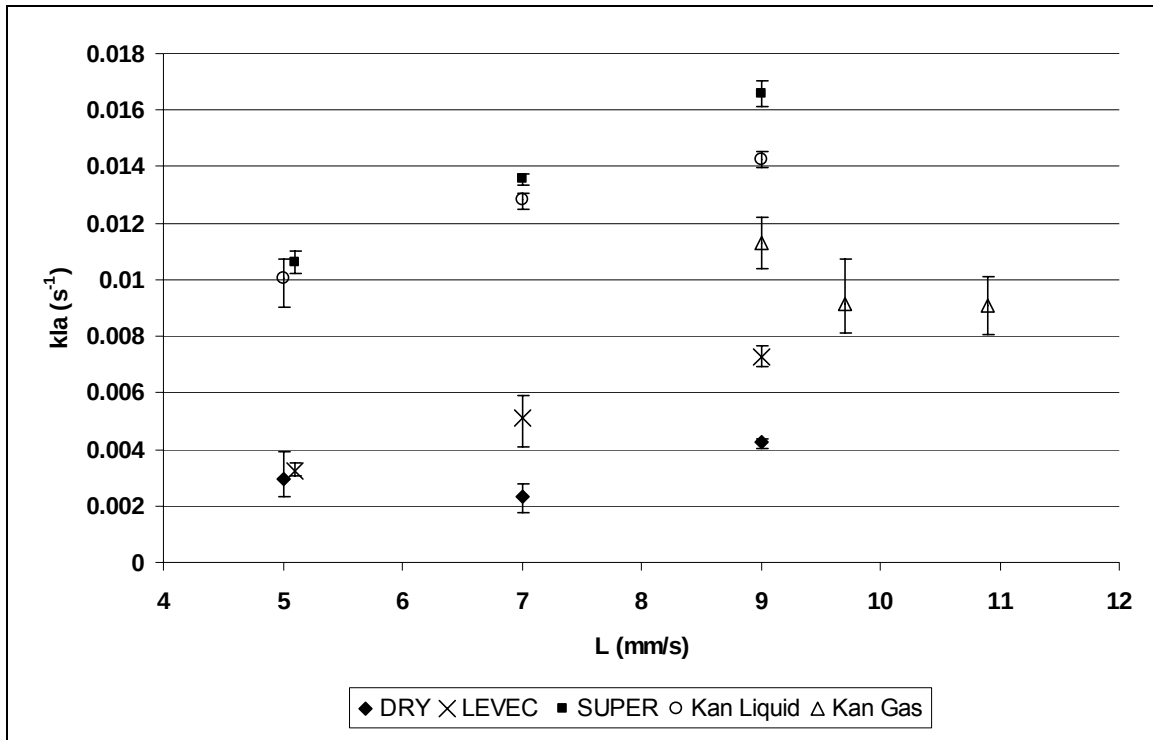


Figure 4.5 Gas liquid mass transfer hysteresis as a result of different prewetting methods obtained with a constant gas flow rate of 20mm/s.

An interesting behaviour is observed with for the Kan Gas mode. The gas liquid mass transfer for the Kan Gas mode does not conform to the expected behaviour, showing gas liquid mass transfer a decreasing function of liquid flow rate. A large discontinuity should therefore exist if the liquid flow rate for this mode is increased until the point of pulsing (moving to the Kan Liquid mode). This shows that the gas liquid mass transfer areas in these modes are different, which in turn indicates that the flow morphology of these two modes should differ drastically. As mentioned previously, visual observation confirmed that the flow type of Kan Gas mode is not like that of the Super or Kan Liquid mode.

The question then arises; if the Kan Liquid mode is dominated by film flow, what type of flow dominates the Kan Gas mode? Visual observation confirms it is certainly not rivulet flow. According to conventional thinking, it should be dominated by film flow, but the flow structure has to be different if the large discontinuity between the two modes is to be understood. This raises the

question whether or not a simple distinction between film and rivulet flow is truly sufficient to describe all the flow types in the trickle regime.

In the Kan Gas mode, pulsing is induced by increasing the gas flow rate. This can only be reached at relatively high liquid flow rates, indicating that a relatively large resistance to the gas flow is necessary. With the increasing gas flow, gas flow paths are literally blown open, orientating the liquid bridges, thereby reducing tortuosity. This explains why the pressure drop in this mode is lower than that of the Kan Liquid and Super bed. At the same time, the gas will promote more uniform wetting by distributing liquid channels through the column, giving rise to higher pressure drops than that of the Dry and Levec wetted modes. An increase in liquid flow rate, may possibly block some of the gas channels, thereby causing a rather large increase in liquid holdup, and pressure drop (increased resistance to gas flow in existing channels), whilst at the same time causing a decrease in gas liquid interfacial area.

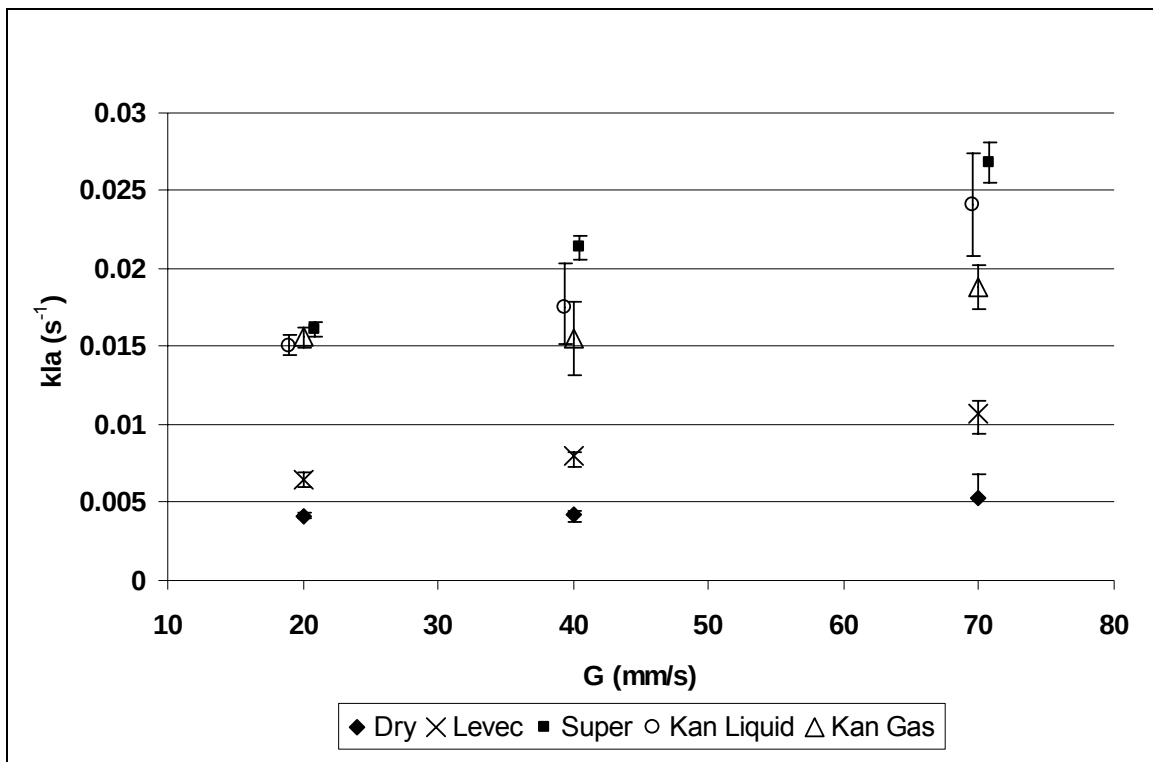


Figure 4.6 Gas Liquid Mass Transfer hysteresis obtained with gas flow variation on different prewetting modes, at a constant liquid flow rate of 9mm/s.

Once again, it can be seen from figure 4.6 that a discontinuity is bound to exist in the extrapolation for the Kan Liquid and Super modes, as a function of gas flow rate. It was initially suspected that all the modes would tend toward the Kan Liquid mode with liquid variation, and toward the Kan Gas mode in the gas flow variation. The fact that this does not happen, could indicate that there will be a large discontinuity in the transition boundary of some of the modes (based on the assumption that the transition boundary are at equivalent flow rates for all the prewetting modes). On the other hand, it could be an indication that the transition boundaries are different on the different prewetting modes. This phenomena has not yet been investigated in literature, and might well be worth exploring. Both of these occurrences will however confirm that a drastic difference must exist in the flow texture of the Kan Gas mode, vs. the Super and Kan Liquid modes.

4.1.4 Levec Draining Time

Loudon *et al.* (2006) briefly mentioned that varying the Levec draining time may have a substantial influence on the outcome of the Levec mode. They looked only at a draining time of 1 min, in comparison to the normal Levec draining time. In this study, the full extent of the time influence was investigated for the gas liquid mass transfer.

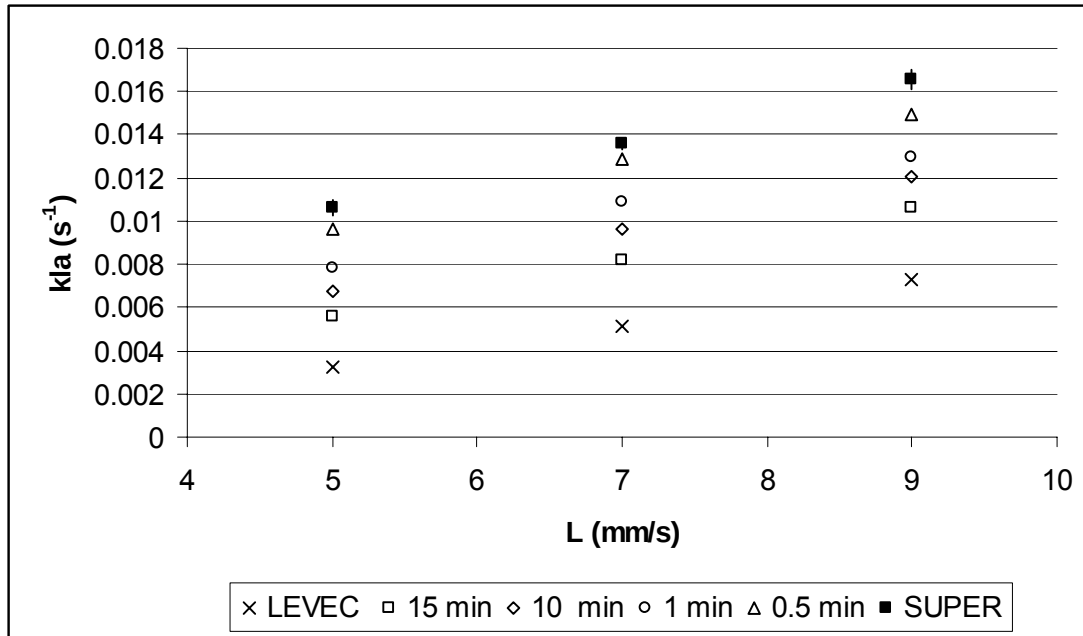


Figure 4.7 By merely decreasing the Levec draining time from 20min, the whole gap between the Levec and Super modes can be filled in.

The Levec and Super modes are limiting cases of each other. In the Levec mode a long time is allowed for the bed to drain, while in the Super mode an infinitely short time is allowed for the bed to drain. Figure 4.7 clearly affirms that this is the case. The gap in between these two modes can be filled by merely shortening the draining time from the original 20 min for the Levec mode.

It can be seen from figure 4.7, that the operating mode is not directly proportional to the draining time. With only one min of draining time, the gas liquid mass transfer decreases nearly to that obtained within 10 minutes draining time. One would suspect that the bed divides into two sections, with the top part being in the Levec mode, while the bottom part will function as the Super mode. This was however not clearly observable.

4.2 Prewetting Modes with a Low Surface Tension Liquid

One of the earliest proposed theories for the existence of multiple hydrodynamic states, implicitly suggest that the multiple hydrodynamic states may not be observed in low surface tension liquids (Kan & Greenfield, 1978). Furthermore, if the film vs. rivulet concept is applied to a low surface tension system, it is to be expected that no substantial variation between the different prewetting modes will be observed. This is due to the fact that a low surface tension liquid will spread rapidly on the packing, thereby promoting film formation. It was suspected therefore, that film flow would prevail in all the modes, thereby eliminating the cause for variation (regarding films vs. rivulets). This was investigated by using a low surface tension liquid (42.3 dynes/cm), which is approximately half that of water.

In the results figures, the average data point is once again shown along with error bars that represent the maximum and minimum values obtained during repetitions of the same experiment. The repeatability of the LST liquid experiments was not as good as that of the water experiments. The large scatter may be related to the fact that each of these experiments was performed on a newly packed bed.

The flow rates used in the water experiments could not be used in the LST liquid experiments, since the high interaction regime is encountered at low flow rates (see figure 3.5). Liquid flow rates of 3, 5 and 7mm/s at a constant gas flow rate of 20mm/s were used, as well as gas flow rates of 20, 40 and 70mm/s, at a constant liquid flow rate of 3mm/s.

In the constant gas flow experiments the high interaction regime was reached at the highest flow rate, on all the prewetting modes. In the constant liquid flow rate experiments this was not the case. The high interaction regime was only reached on Super, Kan Liquid and Kan Gas modes. This observance

substantiates one of the speculations presented in section 4.1.3. It was considered that the reason the modes do not tend toward each other, could be because the transition boundaries are different on the different prewetting modes. In the LST liquid experiments, this was clearly observed for gas flow variation experiments. The Dry and Levec mode's transition boundaries were not located near that of the Super, Kan Liquid and Kan Gas modes.

The high interaction regime obtained by an increase in liquid flow rate, was observed to be different than that obtained with an increase in gas flow. In the constant liquid experiments, a type of pulsing flow was observed, with a long pulse length (nearly half of the bed length). In the liquid slug of the pulse, fine bubbles occurred. The high interaction regime in the constant gas flow experiments consisted of fine bubbles (almost a foam type of flow) throughout the bed, indicating a very large gas liquid mass transfer area. In this regime almost all of the oxygen was stripped by the nitrogen, confirming that a large gas liquid interfacial area was created.

4.2.1 Pressure Drop

Hysteresis was also observed in the pressure drop results for the different prewetting modes. Careful consideration of figures 4.8 and 4.9 draws attention to a subject which has perhaps not received adequate attention up to now. If the results at the lowest flow rate in figure 4.9 are considered, it seems that there is not really any difference between the different modes. With a small increase in flow rate, the difference increases substantially, and, at the highest flow rate, the difference subsides again.

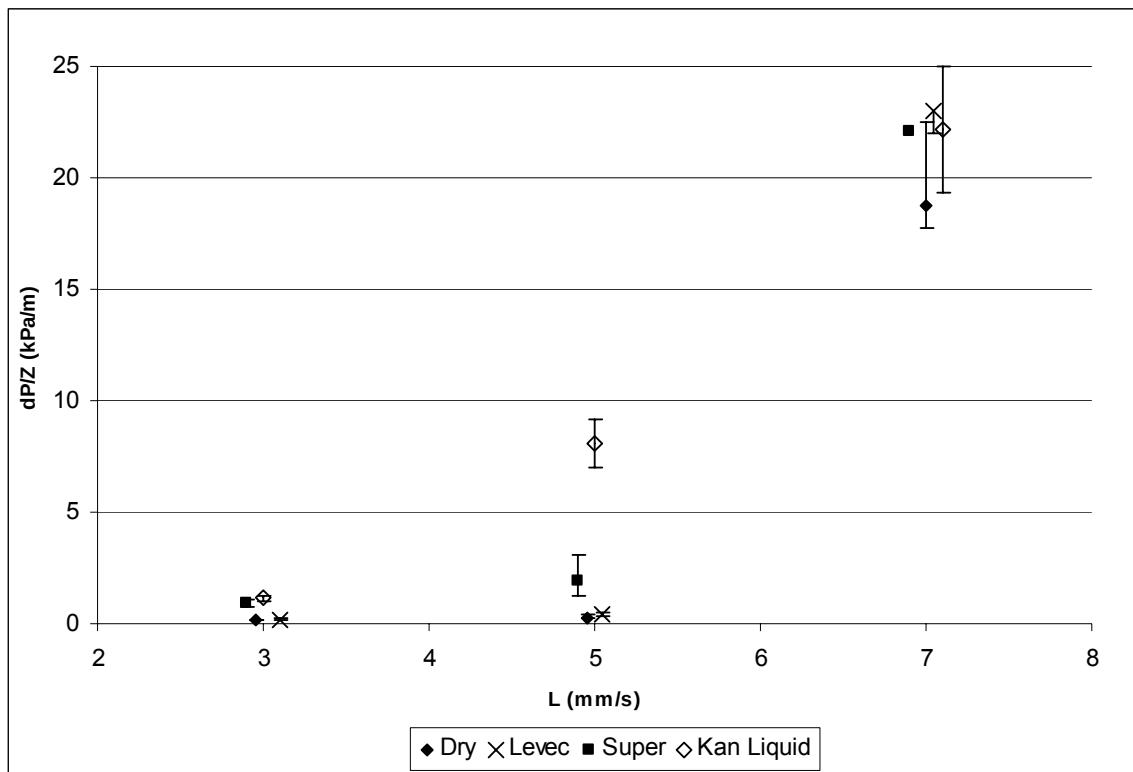


Figure 4.8 Pressure drop hysteresis is observed for liquid variation on different prewetting modes with a LST liquid ($G = 20 \text{ mm/s}$). A rapid increase in pressure occurs when the high interaction regime is reached.

If the results at the lowest flow rate in figure 4.9 are considered, it seems once again that there is not really any difference between the modes. With an

increase in gas flow rate, the differences between the modes become substantial. This indicates that the variation between the different prewetting modes is a function of the specific flow rate, and that the transition boundaries for the different modes vary.

Two clear regions of pressure drop can be seen in both the constant liquid (figure 4.8) and constant gas results (figure 4.9), with the Levec and Dry modes having the lowest pressure drop.

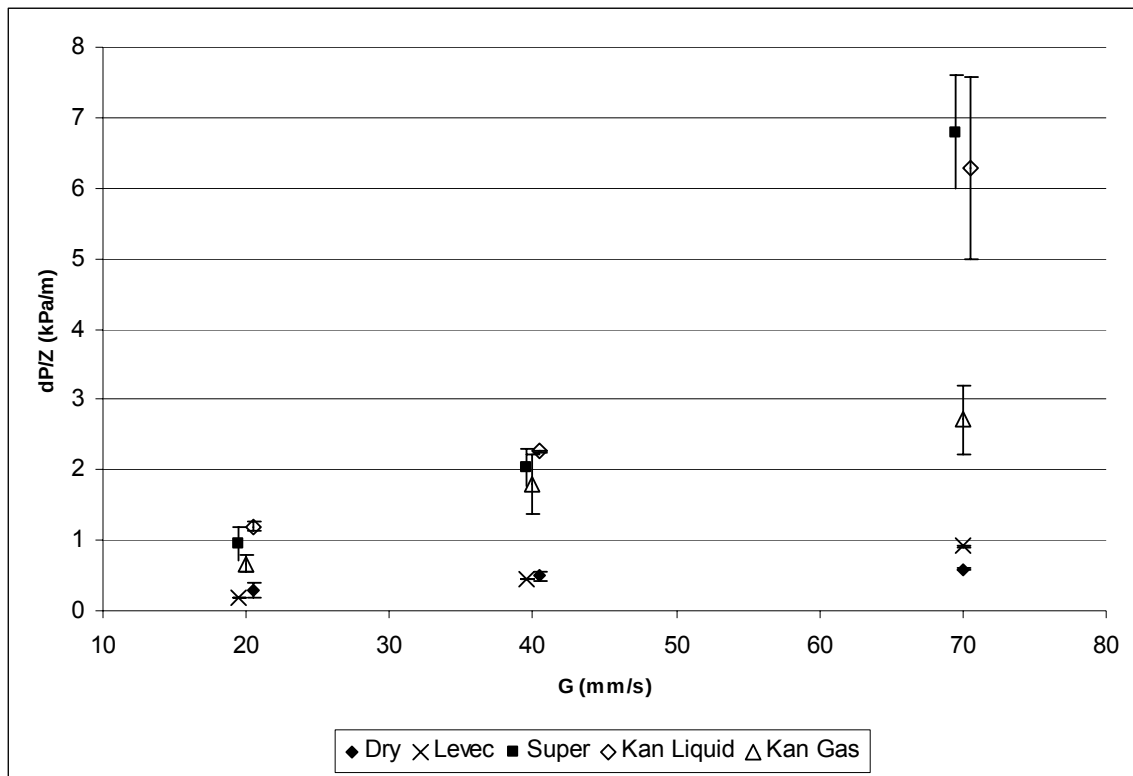


Figure 4.9 Different prewetting procedures exhibit pressure drop hysteresis with a LST liquid at a constant liquid flow rate ($L=3\text{mm/s}$). Two distinct regions are observed separating the Levec and Dry modes from the rest.

The awkward behaviour of the Kan Gas mode is even more evident within the low surface tension liquid experiments. The Kan Gas mode has relatively low pressure drops (lower than Kan Liquid and Super), while the liquid holdup of the Kan Gas mode was the highest. The effect of gas tortuosity is therefore just as influential if a low surface tension liquid is used.

The measured variables were more sensitive to liquid variation than gas variation in these experiments. This is clear from a comparison of the variation in pressure drop and gas liquid mass transfer obtained respectively in the constant gas and liquid flow rate experiments.

The difference in the pressure drops obtained with the constant liquid flow rate experiments, increase as the flow rate is increased. This can be attributed to the fact that at a flow rate of 70mm/s, the Kan Liquid, Kan Gas and Super modes, showed a transition toward the high interaction regime, while the Dry and Levec modes did not. Subsequently, there is a definite difference in flow structure of the Dry and Levec modes vs. the Kan Liquid, Super and Kan Gas modes, contrary to the initial suspicion that the Dry and Levec modes would also be dominated by film flow and therefore be equivalent to that of the Super and Kan Liquid modes.

The Kan Liquid mode's pressure drop was as much as 28 times greater than that of the Dry mode in the constant gas flow experiments, while pressure drop of the Super mode was up to 11 times greater than that of Dry mode in the constant liquid flow experiments.

4.2.2 Liquid Holdup

It is clear from figure 4.10, that a large amount of scatter was obtained in the liquid holdup data for the liquid variation experiments. Even with this amount of scatter, a clear distinction can be made between the Dry mode vs. the rest of the modes. At the highest flow rate, where the high interaction regime is encountered, this distinction fades away.

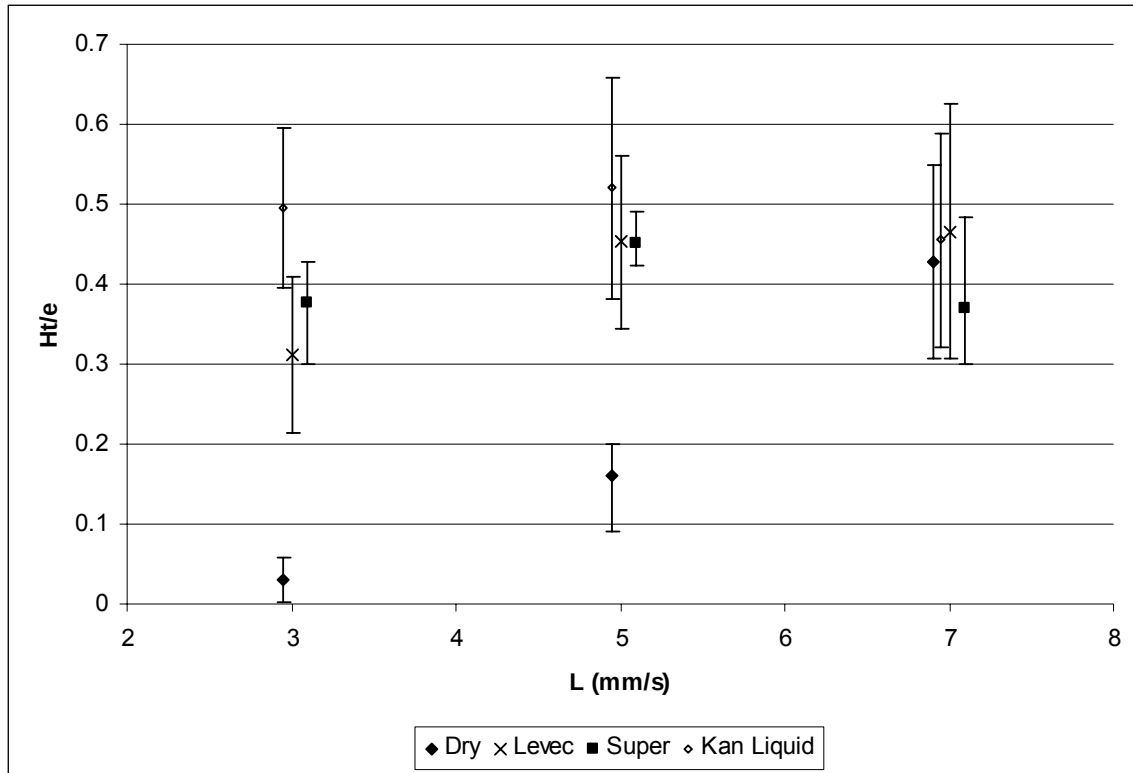


Figure 4.10 Holdup hysteresis for different prewetting procedures obtained with a LST liquid, at a constant gas flow rate ($G=20\text{mm/s}$). The differences between the modes fade away at higher flow rates when the high interaction regime is encountered.

For the Levec and Dry beds, the liquid holdup is an increasing function of the liquid flow rate. For the Kan Liquid and Super modes, the same behaviour is not observed. In fact, the liquid holdup for these modes decreased a little when the high interaction regime was reached.

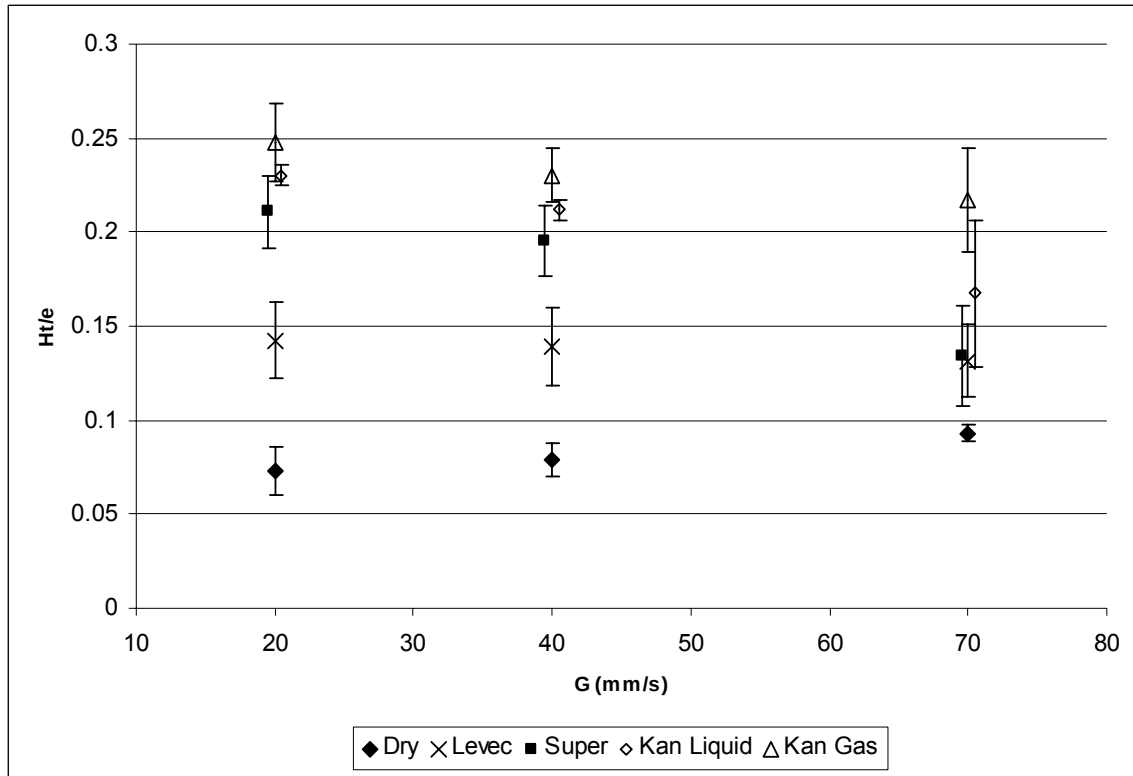


Figure 4.11 Holdup hysteresis for different prewetting procedures obtained with a LST liquid, at a constant liquid flow rate ($L=3\text{mm/s}$).

Three regions of liquid holdup were obtained with gas flow variation (figure 4.11). The distinction between the modes once again declines at the highest flow rate.

Liquid holdup in the liquid flow variation experiments were up to 17 times greater than that of the Dry mode, while in the gas flow variation experiments, Kan Gas mode was up to 3.4 times greater than the Dry mode.

4.2.3 Gas Liquid Mass Transfer

The results for the gas liquid mass transfer coefficient confirm that multiple hydrodynamic states exist, even if a liquid with a very low surface tension is used. Three regions of gas liquid mass transfer could be distinguished; Dry, Levec and the rest (figure 4.12 and figure 4.13). Levec and Dry modes initially have lower gas liquid mass transfer coefficients, which drastically increase once the high interaction regime is reached. Almost all the oxygen was removed from the feed once the high interaction regime was reached.

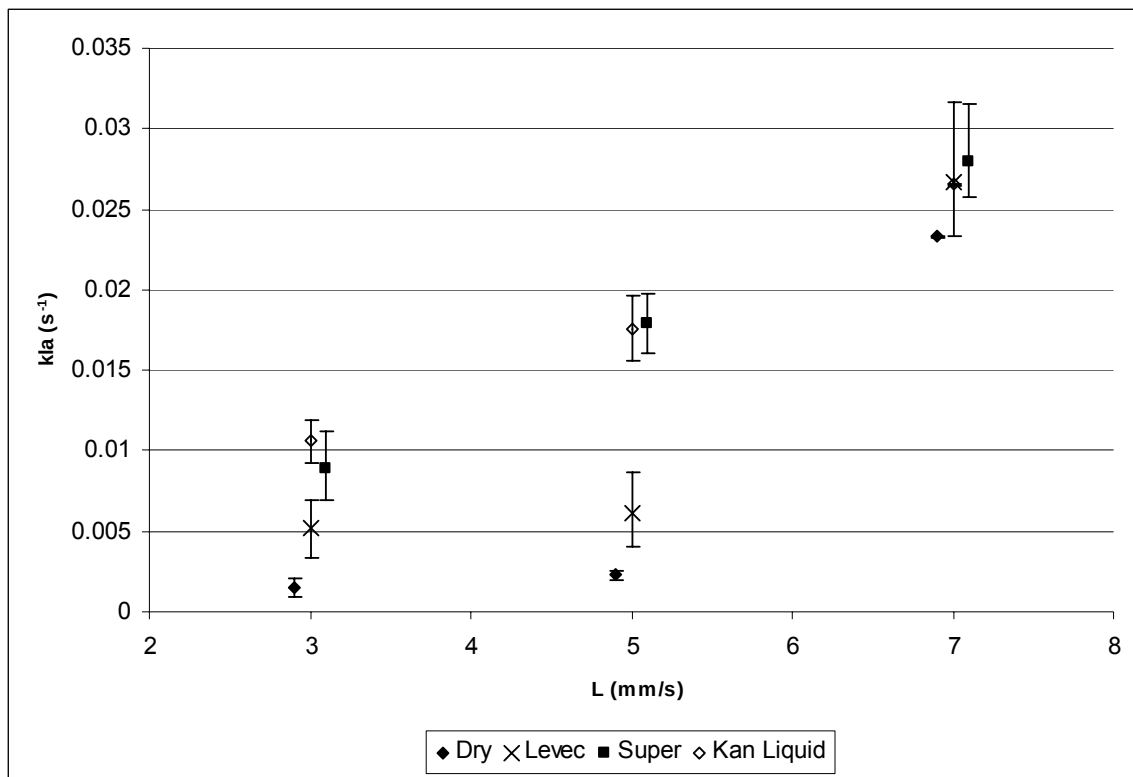


Figure 4.12 Gas liquid mass transfer hysteresis for different prewetting modes with a LST liquid at a constant gas flow rate ($G=20\text{mm/s}$). At 7mm/s a transfer to the high interaction regime occurs for all the prewetting modes.

The Kan Liquid mode's gas liquid mass transfer was as much as 7 times greater than that of the Dry mode in the constant gas flow experiments, while gas liquid mass transfer of the Super mode was up to 8.6 times greater than that of Dry mode obtained in the constant liquid flow experiments.

With gas flow variation three regions of gas liquid mass transfer coefficients were obtained, Dry, Levec and the rest (see figure 4.13). Gas liquid mass transfer on the Levec mode was as much as 2.3 times greater than that of the dry mode. Gas liquid mass transfer on the Super and Kan Liquid modes were as much as 5 times greater.

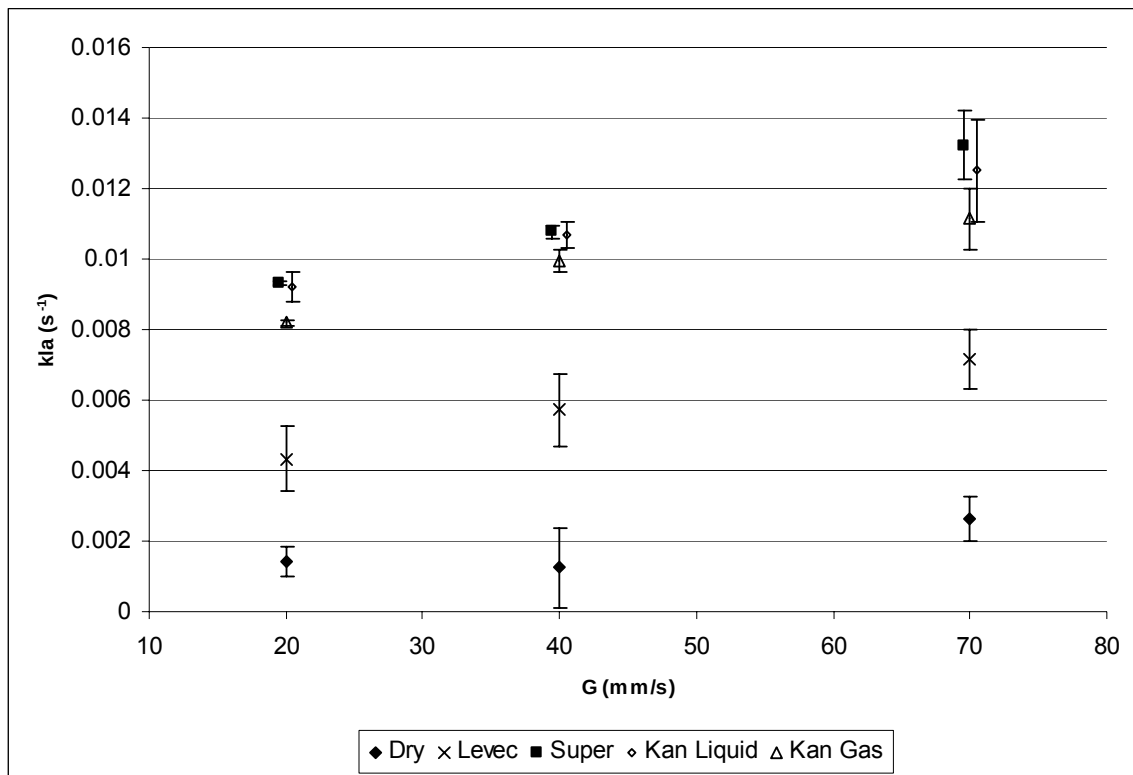


Figure 4.13 Gas liquid mass transfer hysteresis for different prewetting modes with a LST liquid at a constant liquid flow rate ($L=3\text{mm/s}$). A regime transition did not occur on all the modes.

The clear distinction between these modes cannot be explained by merely considering that the Dry and Levec modes are usually dominated by rivulet flow, while the Kan Liquid and Super mode are dominated by film flow. Due to the fact

that the surface tension is almost half that of water, the liquid should spread over the packing (wherever it is contacted) in a film type of flow. It seems therefore, that even though film flow may prevail, it does not necessarily indicate that all the particles are contacted, nor that those that are, are completely covered (a similar observation was made by Van Houwelingen *et al.*, (2006). The sufficiency of using a simple distinction between rivulet and film flow to explain the existence of multiple hydrodynamic states is thus once again questionable.

5. Flow Hysteresis

Most of the investigations into multiple hydrodynamic states focused on flow hysteresis. In these, a single operating point reached in one instance by increasing the flow, is compared to the other instance where it was reached by decreasing the flow. The extent of hysteresis depends on the maximum flow rate used in the loop, as well as the method of prewetting. Discrepancies in some of the early results were found to be a result of two different prewetting modes (Kan and Levec wetting).

The full implication of hysteresis behaviour on the research and operation of trickle beds has only recently been highlighted. Wang *et al.* (1999) suggested that the large amount of scatter in liquid holdup and pressure drop correlations could be a consequence of experimental data associated with different hydrodynamic states and operating modes. The hysteresis behaviour in trickle bed reactors is therefore important to understand before accurate predictive tools for the various hydrodynamic parameters can be developed. With the realization of the full extent of the influence of the different prewetting modes, arises the need to understand possible hysteresis behaviour on each of the operating modes.

5.1 Hysteresis with Liquid Flow Variation

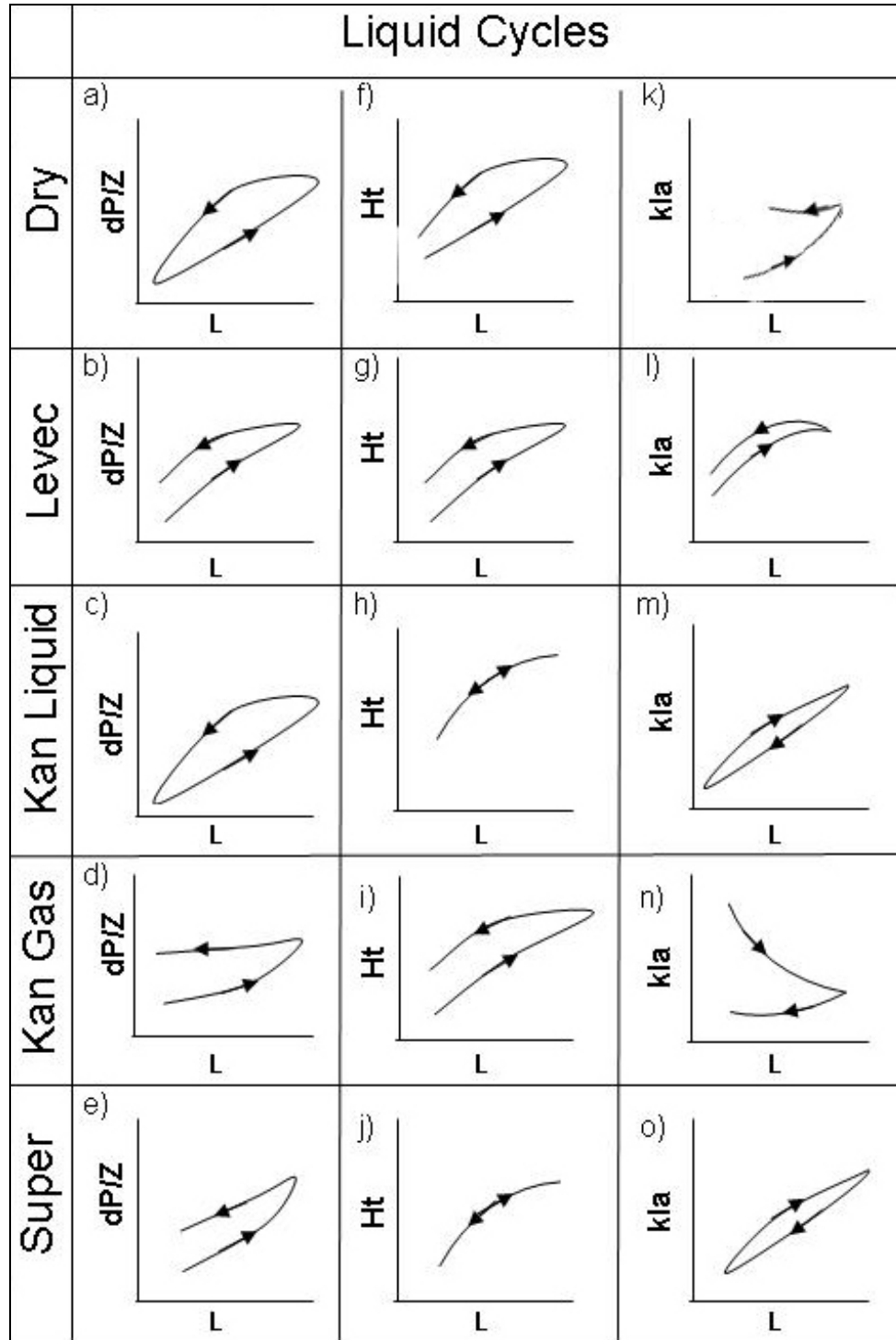


Figure 5.1 Hysteretic behaviour of the hydrodynamic parameters on different prewetting modes obtained by cycling the liquid flow rate.

Figure 5.1 is a representation of the hysteretic trends observed for liquid flow cycles, performed on all the prewetting modes. The flow rates used in the liquid flow cycle was 5-7-9-7-5mm/s. Each cycle was repeated to investigate secondary behaviour. The experimental data used to derive the trends, can be seen in Appendix 2.

5.1.1 Pressure Drop

Every prewetting mode exhibits pressure drop hysteresis with liquid variation. It should be noted that in these experiments the flow rate was not increased to the point of pulsing. If the flow loops would have been increased to the point of pulsing, the return leg would actually be in the Kan Liquid mode.

With an inspection of figures 5.1 a-e, it can be confirmed that the same hysteresis trend is observed as noted in literature (see figure 2.5) for Levec and Kan Liquid modes. A higher pressure drop is observed for the decreasing leg than the increasing leg.

The pressure drop loops for the Kan Liquid and Dry modes, revealed closed loops, while the Levec, Super and Kan Gas modes showed potential for creeping behaviour. The maximum variations gained in pressure drop by liquid variation hysteresis is shown in table 5.1

Table 5.1 Maximum deviation in Pressure drop, caused by hysteresis with liquid variation at each operating point

Mode	5mm/s	7mm/s
Dry	0.89 %	15.28 %
Levec	44.33 %	22.21 %
Kan Liquid	38.03 %	24.95 %
Super	12.39 %	26.72 %
Kan Gas	28.61 %	21.75 %

It is evident that pressure drop variations are much larger than that obtained in liquid holdup, and in actual fact also that of gas liquid mass transfer (table 5.3).

5.1.2 Liquid Holdup

Trends for liquid holdup hysteresis with liquid flow variation are shown in figure 5.1 f-j. Hysteresis behaviour is not observed on all of the pre wetting modes. The Kan Liquid and Super modes (figure 5.1h and 5.1j) do not exhibit hysteresis behaviour. Those that do exhibit hysteresis, follows the trends mentioned in literature. The liquid holdup on the decreasing leg is higher than that of the increasing leg.

In the Dry, Levec and Kan Liquid modes, closed loops were not formed. In fact the repetition of the same cycle indicated possible creeping behaviour.

Table 5.2 is included to gain some perspective on the magnitude of the variation caused by hysteresis. From the table it is evident that the only hysteresis here that is truly significant is that of the Dry and Levec modes. If these are compared to variations gained between the separate operating modes, it is clear that this hysteresis will not be sufficient to change the operating mode to that of another prewetting mode.

Table 5.2 Maximum deviation caused by hysteresis with liquid variation at each operating point

Mode	5mm/s	7mm/s
Dry	86.31 %	27.27 %
Levec	22.79 %	9.35 %
Kan Liquid	0 %	0 %
Super	0 %	0 %
Kan Gas	5.81 %	4.32 %

5.1.3 Gas Liquid Mass Transfer

The gas liquid mass transfer hysteresis provided interesting results. Though hysteresis is observed on all the modes (figure 5.1 k-o), the same hysteretic behaviour is not observed on all the modes. The trends obtained with an increase in liquid flow rate also vary on some of the modes.

The Dry and Levec modes have higher gas liquid mass transfer in the decreasing leg than in the increasing leg (figure 5.1 k & l). Here the Dry mode showed a clear increase of gas liquid mass transfer, indicating that the suspicion raised in the previous section with regard to figure 4.5 was grounded. However, the observed increase is not as significant as the increase at the corresponding flow rate in the Levec mode.

On the Levec mode, an increase in liquid flow rate increases the gas liquid mass transfer area. Once the Levec bed is drained, stagnant liquid pockets are left in the bed. With an increase in flow rate, it will be easier for the liquid to spread over these liquid pockets than it will be to spread through the completely dry particles. This explains the difference between the Dry and Levec wetted modes. On both these modes, the newly formed rivulets add gas liquid interfacial area which remains stable when the flow rate is decreased again. The gas liquid mass transfer is therefore higher on the decreasing leg. The increases in gas liquid interfacial area is substantial for both these modes as can be seen from table 5.3. The Dry mode shows a large increase but it still does not bring the mode near that of the Kan Liquid or Super.

Kan Liquid, Kan Gas and Super modes all show similar hysteresis trends, with the gas liquid mass transfer being lower in the decreasing leg than in the increasing leg.

If the hysteretic behaviour of the Kan Liquid and Super modes are considered for all the hydrodynamic parameters, it is very clear that these modes are similar,

and should actually have equivalent flow structures. In both of these, no hysteresis is observed in the liquid holdup, but pressure drop does exhibit hysteresis. An increase in pressure drop should be relatable to an increase in resistance to the flow of the gas. In both of these modes, the decreasing path is associated with higher pressure drop, while gas liquid mass transfer area is lower than it was in the increasing path. Closed loops are observed for both modes, the gas liquid interfacial area that is lost initially, is re-established by repetition of the same cycle.

The Kan Gas mode has a decline in the gas liquid mass transfer area with an increase in liquid flow rate (as was also observed in figure 4.5). With an increase in liquid flow rate, a rather large decline in the gas liquid mass transfer is observed. If the flow is decreased again, the gas liquid mass transfer decreases further. This means that the area initially lost, can not be regained by decreasing the flow, which once again reaffirms the difference in flow structure between the Kan Gas mode vs. the Super and Kan Liquid modes. It can be seen from table 5.3, and Appendix 2 that the decrease in the Kan Gas mode is more significant than that observed for the Kan Liquid and Super modes (the negatives indicate a decrease in gas liquid mass transfer area).

Table 5.3 Maximum deviation in gas liquid mass transfer, caused by hysteresis with liquid variation at each operating point

Mode	5mm/s	7mm/s
Dry	183.49 %	61.15 %
Levec	49.04 %	8.86 %
Kan Liquid	-9.25 %	-8.03 %
Super	-3.12 %	-2.87 %
Kan Gas	-24.64 %	-14.90 %

5.2 Hysteresis with Gas Flow Variation

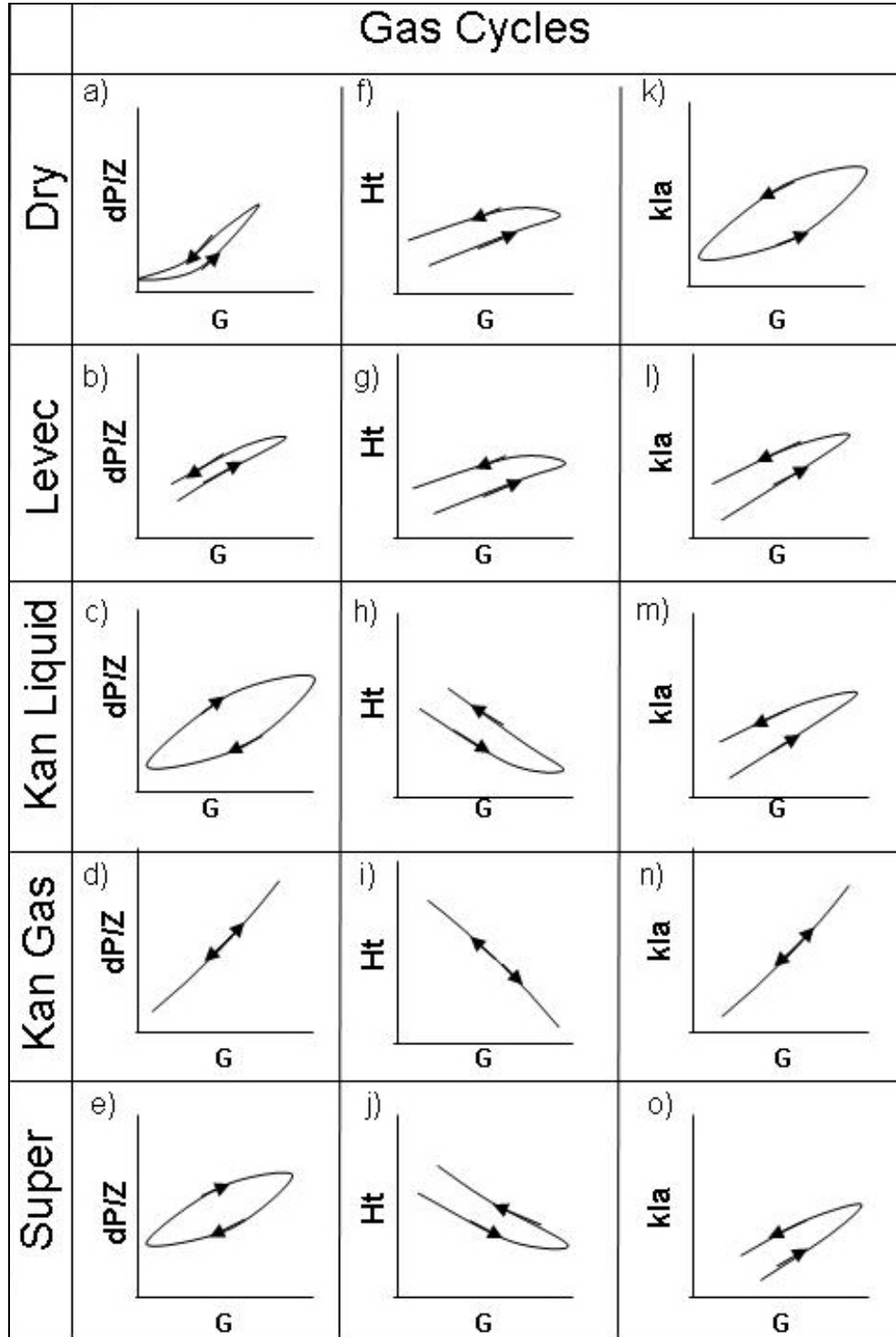


Figure 5.2 Hysteretic behaviour of the hydrodynamic parameters on different prewetting modes obtained by cycling the gas flow rate.

Figure 5.2 is a representation of the hysteretic trends observed for gas flow cycles, performed on all the prewetting modes. The flow rates used in the cycles were 20-40-70-40-20mm/s, at a constant liquid flow rate of 9mm/s. The experimental data used to derive the trends, can be seen in Appendix 3. The hysteresis trends which have not been reported in literature (figure 2.6) have been filled in.

5.2.1 Pressure Drop

Figures 5.2 a-e show the trends obtained for pressure drop through gas cycles. Not all of the modes show hysteresis behaviour, nor are the same trends observed for those that do.

For both the Dry and Levec modes, very small hysteresis was observed. Both of these shows a higher pressure drop on the decreasing path than that of the increasing path, agreeing with results of Wang *et al.*, 1995. According to Wang a lower pressure drop is related to less uniform distribution of gas-liquid flow in the trickle-bed. The increased gas flow rate on these modes, therefore serve to promote more uniform liquid distribution. The gas may spread the liquid so that rivulets are formed in new places, and the stagnant liquid pockets in the Levec mode become active.

Wang's description does however not conform well to the hysteresis behaviour observed for the Kan Liquid and Super modes. In figures 5.2 h & j, lower pressure drops are observed on the decreasing leg than on the increasing leg. According to Wang's explanation, an increase in the gas flow rate on this mode, actually leads to less uniform liquid distribution. In our opinion, this is not the case. The gas flow rate does however have different functions in these modes. The liquid holdup hysteresis trend on the Kan Liquid and Super modes is the opposite of the pressure drop trend. An increased liquid holdup is always associated with more uniform distribution. The gas may orientate the liquid

bridges (as suggested by Kan & Greenfield, 1978), and spread the film more evenly through the bed, which could also indicate thinning of the films. If these orientations are maintained with a decrease in gas flow, the resistance to the gas flow rate will be less, meaning lower pressure drop, and more uniform liquid distribution.

The Kan Gas mode, showed no hysteretic behaviour with gas variation on any of the hydrodynamic parameters. The initial orientation gained by increasing the gas flow rate to the point of pulsing (during prewetting), seems to remain stable throughout the cycles.

Table 5.4 Maximum percentage deviation in Pressure drop, caused by hysteresis with gas flow variation at each operating point

Mode	20mm/s	40mm/s
Dry	2.14%	2.38%
Levec	16.82%	3.23%
Kan Liquid	-33.04%	-18.64%
Super	-14.68%	-10.49%
Kan Gas	-1.82%	0.00%

5.2.2 Liquid Holdup

The only mode not exhibiting hysteresis is the Kan Gas mode. For the rest of the modes (figure 5.2 f-j), the same type of hysteresis behaviour is observed, with a higher liquid holdup on the return leg than on the increasing leg, which agrees with the trend observed by Kan & Greenfield, 1978. The gas flow rate promotes more uniform liquid distribution, by spreading liquid films, or new rivulets through the bed. This flow structure remains stable upon the decrease, leading to an increase in liquid holdup.

The liquid holdup was observed as a decreasing function of liquid flow rate in all the modes, except for the Dry mode, agreeing with the results of figure 4.2 (also see Appendix 3).

The variation in liquid holdup with gas flow variation is much less than that observed with liquid flow variation (compare table 5.5 to 5.1). The greatest variation in Liquid holdup is observed on the Dry mode. A comparison of table 5.5 to figure 4.4 will confirm that the variations obtained in the hysteresis loops are not as significant as that obtained by altering the prewetting procedure.

Table 5.5 Maximum deviation in liquid holdup, caused by hysteresis with gas flow variation at each operating point

Mode	20mm/s	40mm/s
Dry	24.36 %	8.08 %
Levec	2.79 %	1.39 %
Kan Liquid	2.73 %	2.39 %
Super	2.18 %	1.87 %
Kan Gas	0.00 %	0.00%

5.2.3 Gas Liquid Mass Transfer

Only the Kan Gas mode does not exhibit hysteretic behaviour for the gas liquid mass transfer. For all the other modes, the hysteretic behaviour entails a higher gas liquid mass transfer on the decreasing leg than on the increasing leg. No hysteresis in gas liquid mass transfer has been reported for gas flow cycles (figure 2.6), yet the hysteresis is just as prominent in this parameter as it is for liquid holdup and pressure drop. A 50 % increase (table 5.6) can be obtained on dry mode by performing a hysteresis cycle.

The Super and Kan Liquid modes are indeed equivalent, since the hysteretic behaviour on these modes are equivalent for all the parameters, with both gas

and liquid flow cycles (see Appendix 2 and 3). The percentage deviation on these two modes is also similar (see table 4.6).

Table 5.6 Percentage deviation in gas liquid mass transfer, caused by hysteresis with gas flow variation at each operating point

Mode	20mm/s	40mm/s
Dry	53.35%	34.59%
Levec	27.13%	12.32%
Kan Liquid	18.64%	9.37%
Super	17.83%	7.96%
Kan Gas	0.00%	0.00%

6. Transient Upsets for MHS manipulation

An attempt was made to shed new light on the cause of multiple hydrodynamic states, by investigating the effect of online disturbances or upsets on the stability of the multiple hydrodynamic states. The conventional idea of films vs. rivulets is used as basis, and the aim is to create stable films via the upsets.

Two types of upsets were investigated. In the one, gas and liquid flow rate variations were used to promote formation of films. In this regard, the effect of hysteresis (section 5) and periodic operation were investigated. In the second category, the transient changes in surface tension was used, based on the idea that a temporary lowered surface tension would cause the formation of stable films, that could remain stable even after the surface tension increased again.

If these upsets do promote formation of stable films, it could be expected that the hydrodynamic states could be manipulated, and perhaps prove to be a method by which the hydrodynamic states associated with the Kan Liquid and Super modes can be achieved through transient upsets.

6.1 Periodic Operation

The principle of periodic operation is to force a system to operate continuously in a transient mode as opposed to allowing the system to relax to steady-state operation (Boelhouwer *et al.*, 2001). Periodic operation has been shown to have a substantial influence on trickle bed performance. Most of the investigations have focused on reacting systems, where a continual change in the mass transfer limitations results in an increased time average conversion of the reactants.

The influence of periodic operation on flow morphology has not received much attention. Lim *et al.*, 2004 suggested however that the rapidly changing gas-liquid distribution imposed by liquid flushes during periodic operation may result in wetting of the entire catalyst surface.

Considering the substantial variation in multiple hydrodynamic parameters obtained with different prewetting methods, and the suspected effect of periodic operation (regarding the film concept), it was suspected that some of the performance enhancements related to periodic operation, may also be related to the different prewetting modes. Subsequently, it was suspected that periodic operation might be a transient method by which the gap between the less uniform (Dry and Levec) and the more uniform modes (Kan Liquid and Super) could be bridged.

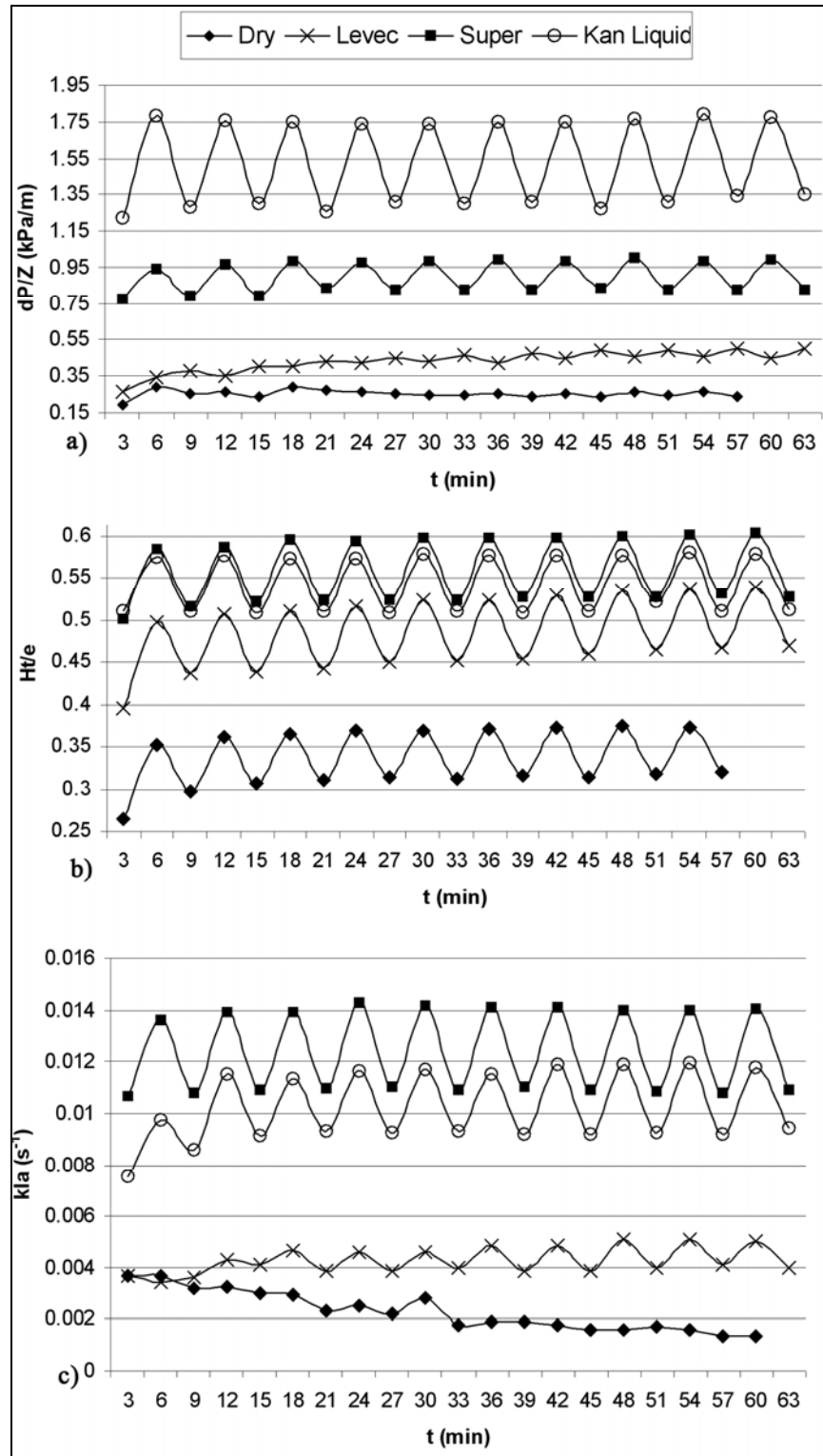


Figure 6.1 Hydrodynamic parameters obtained during one hour of periodic liquid flow cycling for a) Pressure drop, b) Liquid holdup and c) Gas liquid mass transfer

The variations obtained for the various hydrodynamic parameters during one hour of liquid cycling are shown in figure 6.1. Periodic operation was performed with a 3 min period, and a cycle split of 0.5 between 5 and 7mm/s at a constant gas flow rate of 20mm/s. The system was allowed to reach steady state before periodic operation commenced. The period was short enough to ensure that steady state was not reached at each operating point before adjustment, to capture the transient behaviour.

Pressure drop of the Levec mode increases initially, but rapidly evolves into a pseudo steady state, alternating between the same pressure drops. Most of the other modes reach their pseudo steady state almost immediately. It is clear from figure 6.1a that the modes stay separate and distinct from one another.

If the liquid holdup is considered (figure 6.1b), it is once again only the Levec mode which reaches a pseudo steady state near the end of the observation period. The other modes, reach a pseudo steady state within approximately three cycles.

The separation between the more uniform modes (Kan liquid and Super), and the less uniform modes (Dry and Levec) is clearly visible in figure 6.1c. The gas liquid mass transfer initially increases for all the modes, but then reaches a plateau, or even declines as in the case of the Dry mode. The Kan Liquid and Super modes reach their pseudo state quickly, while the Levec mode only stabilizes near the end of the observation period. The increase in gas liquid mass transfer gained by periodic operation does not promote the performance of the Levec mode nearer that of the more uniform modes. Therefore, even if continual disturbances are applied, there is a limit to the flow deformation obtainable between two specific flow rates. Similar results were obtained in the gas flow cycles (figure 6.2).

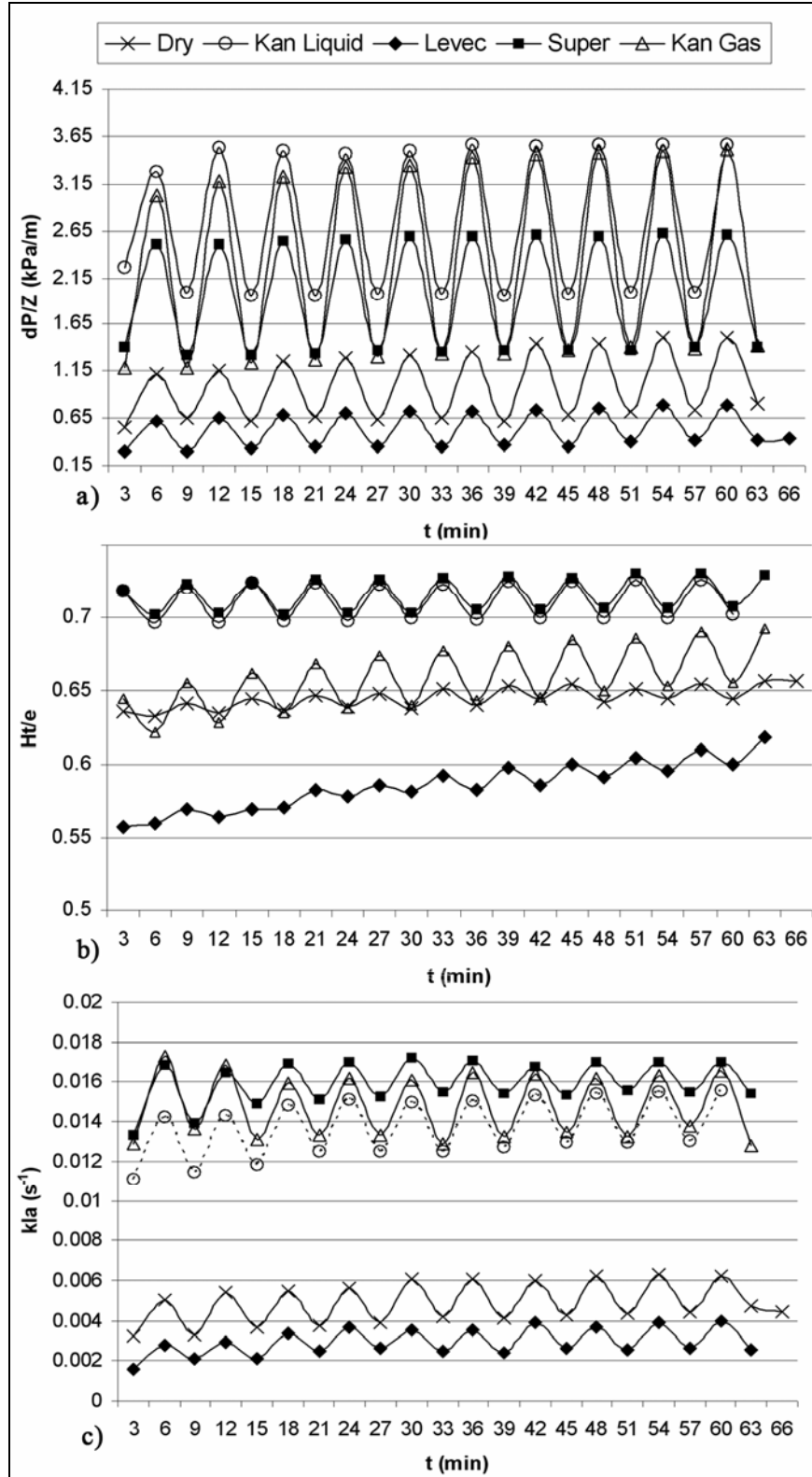


Figure 6.2 Hydrodynamic parameters obtained during one hour of periodic gas flow cycling for a) Pressure drop, b) Liquid holdup and c) Gas liquid mass transfer

Periodic cycling of the gas flow rate had nearly no effect on the pressure drops of each mode. The Levec mode displayed a minor incline, but nothing significant. The Kan Liquid and Super modes displayed a minor decline during the first cycle, which is attributable to hysteresis.

The liquid holdup in the dry mode of operation is rather unstable. With continuous periodic operation, the performance of the Dry mode may be promoted to that of the Levec mode. Surprisingly, the same type of performance enhancement was not observed for the gas liquid mass transfer in the Dry mode (figure 6.2c).

The Kan Gas mode displayed behaviour that seems contrasting to previous observations. During the hysteresis cycles with gas flow variation (figure 5.2d,i & n) no hysteresis was observed. In figure 6.2 the Kan Gas mode does however reveal minor hysteresis and even a significant increase in liquid holdup due to periodic operation. Even though the incline initially seems rather steep, it can be seen that the slope declines near the end of the observation period. Even if the observation period would be extended, it is doubtful that the Kan Gas mode's liquid holdup would move into the region of the Kan Liquid and Super modes. The apparent contrasting behaviour may be explained if the transient behaviour is considered. During the gas flow hysteresis cycles, time was allowed at each operating point for the system to reach steady state. During this time, the increased gas flow would therefore have enough time to orientate the liquid bridges, and properly form the gas channels. In the periodic experiments, time wasn't allowed for the system to reach steady state at each operating point. Therefore, the gas channels may not be fully formed, and since they were not fully established, may be lost during the decrease.

It becomes clear from these results that there is a definite and substantial difference between the various modes; especially when the Dry and Levec modes are compared to the rest. This is most clearly illustrated in the gas liquid mass transfer (figure 6.1c and 6.2c), where the two distinct regions of interaction can be observed. The Dry and Levec modes have substantially less gas liquid

interaction than the Kan Liquid, Super and Kan Gas modes. Furthermore, it is clear that periodic operation between two flow rates does not cause significant enough creep to move from the less uniform mode region to that of the more uniform modes. The suggestion of Lim *et al.*, 2004 that the catalyst will eventually be completely wet due to the periodically changing environment cannot be substantiated by these results. In fact, such transient operation may not necessarily modify the macroscopic gas liquid distribution within the bed, except for that which is caused primarily by the repetition of two or three cycles due to hysteresis.

The only mode's behaviour that indicated a possibility to grow closer to another mode through periodic operation is the Dry mode, which may eventually evolve into the Levec mode (see figure 6.1 and 6.2). This can be attributed to the instability of the Dry mode. It is therefore possible that many industrial reactors started up on the Dry mode - after a few upsets or months of operation - may actually have crept to the Levec mode of operation..

6.2 Temporary Surface Tension Variation

During the doping experiments, a low surface tension (LST) liquid (42dynes/cm) was momentarily fed into the system after the original water system reached steady state. The LST liquid was fed into the column for 3min, while ensuring that the flow rate remained constant. The feed was then switched back to the water enriched with oxygen.

No significant advantage was gained by temporarily lowering the surface tension for either the Kan Liquid or Super modes. Examples of the dynamic signals recorded on the DeltaV operating system for pressure and dissolved oxygen during doping experiments on the Kan Liquid (figure 6.3) and Dry (figure 6.4) modes are shown below. A sudden decrease in surface tension causes a step disturbance in the pressure drop and dissolved oxygen concentration. On the Kan Liquid mode, the system reverts back to the original steady state it had before doping.

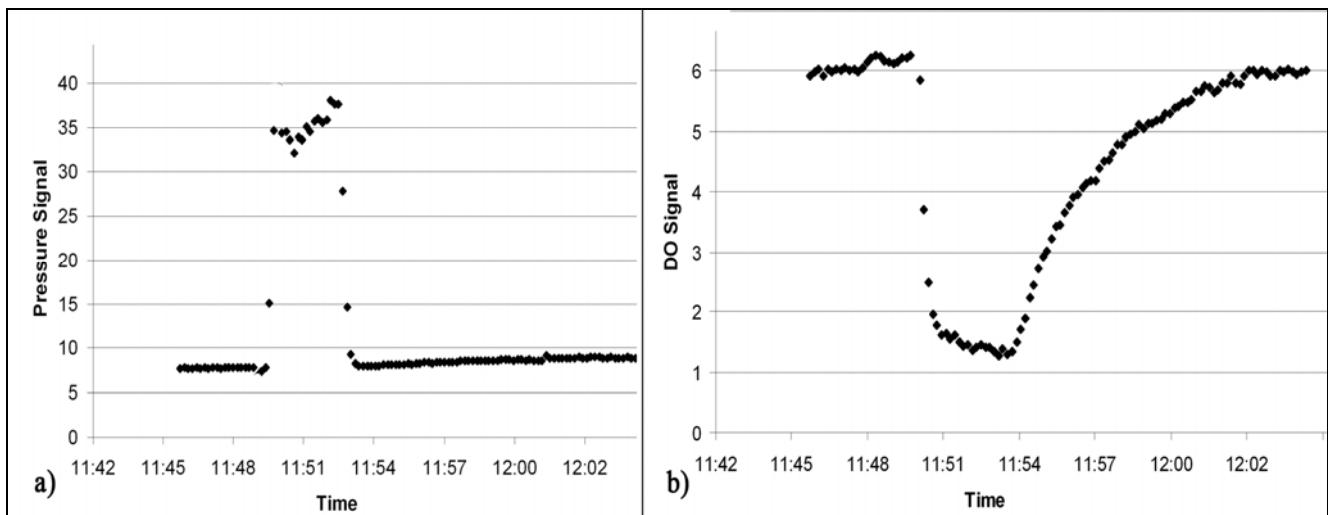


Figure 6.3 Dynamic a) Pressure and b) Dissolved oxygen signals obtained during doping on a Kan Liquid mode. Doping has a negligible influence on the Kan Liquid and Super modes.

On the Dry or Levec modes, the system does however not revert back to the original steady state, but some steady state in between those of the two different systems.

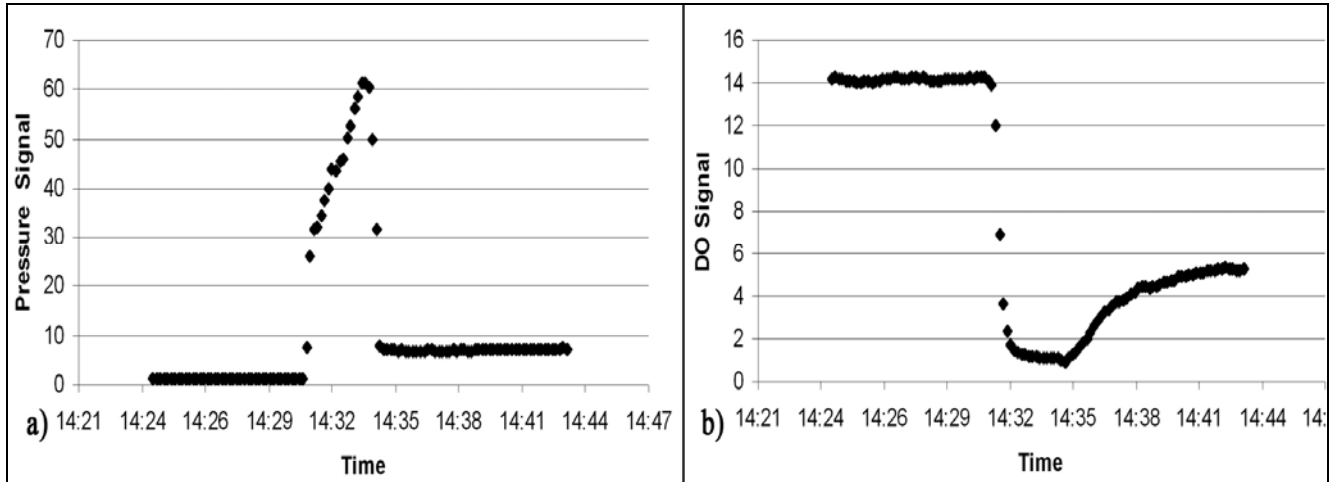


Figure 6.4 Dynamic a) Pressure and b) Dissolved oxygen signals obtained during doping on the Dry Mode. A new steady state is reached after doping.

It should be noted that at a liquid flow rate of 7mm/s, the low surface tension system moved into the high interaction regime (see section 4.2). During the doping time, a shift toward this high interaction regime occurred, briefly maintaining a foamy type of flow through the bed (indicated by the drastic increase in the pressure signal in figure 6.4a). Once the doping stopped, the foam type of flow did not prevail, but obviously altered the gas liquid mass transfer area permanently. In actual fact, doping at this flow rate might be seen as an in-situ, Kan Liquid type of prewetting procedure.

Both the Dry and Levec modes displayed a possibility of improvement. The effect of transient surface tension variations were therefore investigated on both these modes.

6.2.1 Pressure drop

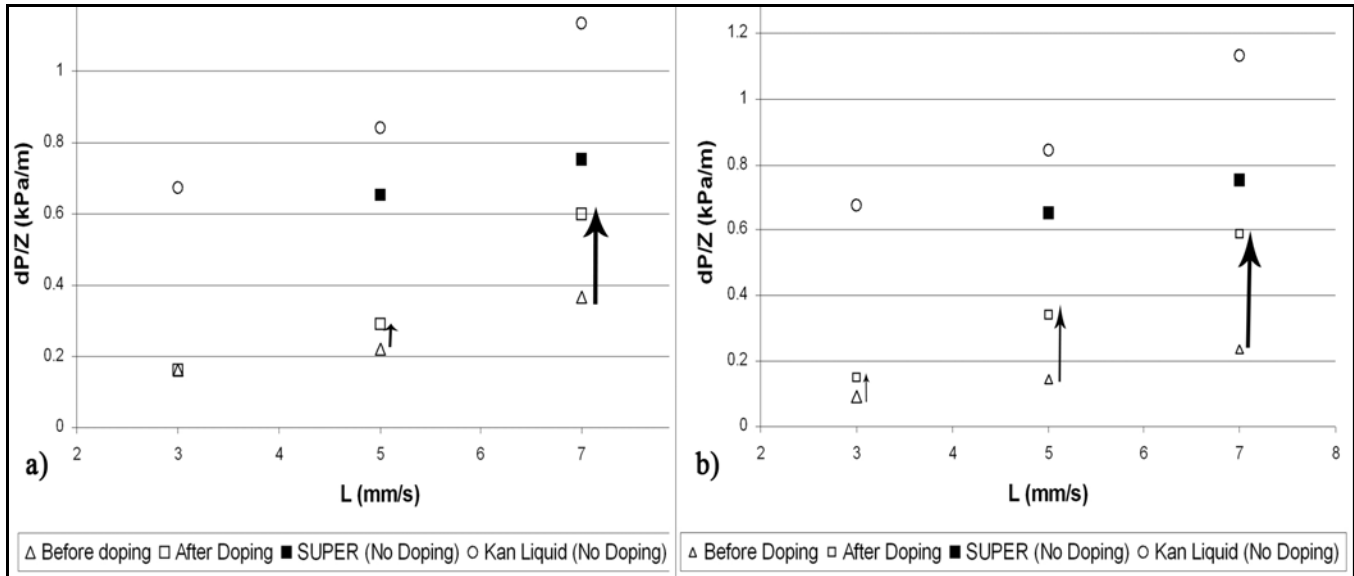


Figure 6.5 Pressure drop obtained by doping on a) Dry mode and b) Levec mode, compared to Super and Kan Liquid modes obtained in section 4.1.

At the lower flow rates, small increases are observed in pressure drop. The enhancement obtained on the Levec mode is more substantial than that of the Dry mode, which can be attributed to the fact that the liquid distribution in the Dry mode is very poor, and the lowered surface tension will have a smaller area of influence.

At the highest flow rate, a substantial increase in pressure drop is observed for both the Dry and Levec modes. These enhancements can be attributed to the in-situ prewetting caused by the temporary lowered surface tension. These increases change the steady state value of the Dry and Levec wetted modes nearer to that of the Super and Kan Liquid modes.

6.2.2 Liquid Holdup

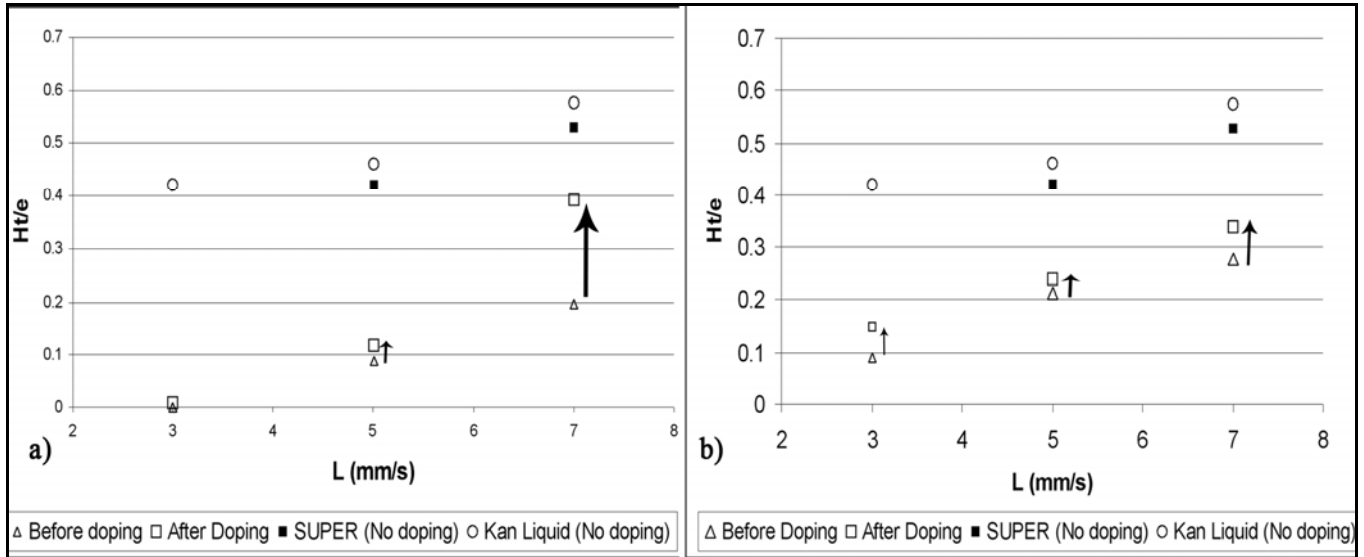


Figure 6.6 Liquid holdup obtained after doping on a) Dry mode and b) Levec mode, compared to that of Kan Liquid and Super modes obtained in section 4.1. The liquid holdup is not drastically altered even at the highest flow rate.

The liquid holdup displayed behaviour similar to that of the pressure drop. The greatest increase was observed only at the highest flow rate, where the in-situ prewetting was performed. However, the increase in liquid holdup is not as drastic as the corresponding pressure drop and gas liquid mass transfer enhancements. This may be explained if the characteristics of the high interaction regime as discussed in section (4.2.2) are considered; the regime transition was not accompanied by a sharp increase in liquid holdup, but in fact, decreased a little. Based on the characteristics of the in-situ prewetting mode, it is to be expected that drastic increases in liquid holdup will not be observed.

6.2.3 Gas Liquid Mass Transfer

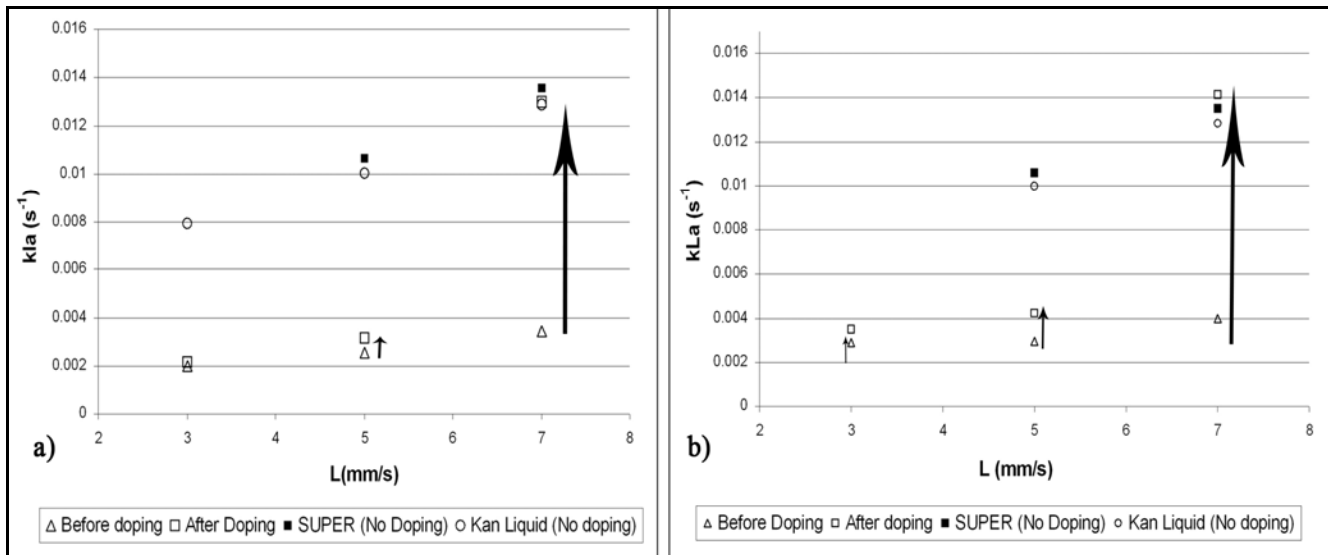


Figure 6.7 Gas liquid mass transfer coefficient obtained by doping with a LST liquid on a) Dry mode and b) Levec modes compared to that of Kan Liquid and Super modes obtained in section 4.1. A large improvement of the gas liquid mass transfer was obtained.

On both the Dry and Levec wetted modes, small enhancements were obtained on the two lower flow rates. On the highest flow rate, the enhancement is substantial, actually placing the operating mode on the more uniform Kan Liquid and Super modes. This can be attributed to the fact the highest velocity was associated with the high interaction regime for the LST liquid experiments, thereby producing an in-situ prewetting procedure.

Considering the films vs. rivulet concept, this result should indicate that stable film flow is only formed during the in-situ prewetting. According to conventional thinking, the lowered surface tension should have ensured film formation even at the lowest flow rates. The application of the films vs. rivulet concept is therefore once again not credible.

7. Conclusions and Recommendations

Large performance enhancements can be obtained by altering the prewetting procedure, even for systems with a low surface tension. The gas liquid mass transfer coefficient of the Kan Liquid and Super modes could be as much as 6 times greater than that of the Dry mode in the water system. For the low surface tension system, an even greater variation could be obtained, rendering gas liquid mass transfer up to 8 times greater for the Kan Liquid and Super modes than in the Dry mode. Through a thorough investigation of various types of transient upsets and manipulation strategies, it was confirmed that prewetting is indeed the only way by which drastic variation in hydrodynamic states may be obtained. None of the investigated upsets (hysteresis, periodic operation or surface tension doping) caused such severe changes in the liquid morphology that enabled it to compete with that caused by varying the prewetting mode.

Only two methods were identified by which the gap between the less uniform modes (Dry and Levec) and the more uniform modes (Kan Liquid and Super) could be bridged. The first method rests on the fact that Levec and Super modes are limiting cases of each other. By reducing the draining time of the Levec mode, the whole region between the high gas liquid mass transfer of the Super mode, and the lower gas liquid mass transfer of the Levec mode could be covered. The second method can be seen as an in-situ type of prewetting. Doping with a low surface tension liquid only resulted in substantial enhancement of the hydrodynamics if the high interaction regime was briefly accessed during the doping period. This occurrence may be seen as a form of prewetting. The Dry and Levec modes may therefore be enhanced to behave similar to the Kan Liquid and Super modes by doping with a low surface tension liquid if the doping velocity is in the high interaction regime for the specific low surface tension system.

Hysteresis was observed on all the modes. Though the hysteresis cycles did not drastically alter the predominant flow type, interesting trends were observed. The following hysteresis trends were observed for the hydrodynamic parameters in the liquid flow cycles:

- *Liquid Holdup:* Hysteresis behaviour was not observed on all of the prewetting modes. The Kan Liquid and Super modes did not exhibit hysteresis behaviour. The Dry, Levec and Kan Gas modes followed the trends mentioned in literature; the liquid holdup on the decreasing leg is higher than that of the increasing leg. A maximum increase of 86 % was obtained on the Dry mode of operation.
- *Pressure Drop:* All the prewetting modes exhibited pressure drop hysteresis, with the pressure drop higher on the decreasing leg than on the increasing leg. This agrees with the trends mentioned in literature for the Dry and Levec modes. A maximum increase of 44 % was obtained on the Levec mode of operation.
- *Gas Liquid Mass Transfer:* All the modes exhibited hysteretic behaviour. The Dry and Levec modes have higher gas liquid mass transfer on the decreasing leg than on the increasing leg. Kan Liquid, Kan Gas and Super modes had similar hysteresis, with the gas liquid mass transfer being higher on the increasing than in the decreasing leg. A maximum increase on 180% was obtained on the Dry mode of operation.

The following hysteresis trends were observed for the hydrodynamic parameters in the gas flow cycles:

- *Liquid Holdup:* The only mode that did not exhibit hysteresis was the Kan Gas mode. For the rest of the modes, the same type of hysteresis behaviour was observed; liquid holdup is higher on the decreasing leg than on the increasing leg, which agrees with the trend observed by Kan & Greenfield, 1978. A maximum increase of 24% was obtained on the Dry mode of operation.

- *Pressure Drop*: Not all of the modes exhibited hysteresis behaviour. Dry and Levec modes had a lower pressure drop on the increasing path than that of the decreasing path (agreeing with Wang *et al.*, 1995). For the Kan Liquid and Super modes, lower pressure drops were observed on the decreasing leg than on the increasing leg (similar to the results of Kan & Greenfield, 1978). The most significant decrease occurred on the Kan Liquid mode at 33%. The Kan Gas mode, showed no hysteretic behaviour.
- *Gas Liquid Mass Transfer*: Only the Kan Gas mode did not exhibit hysteretic behaviour for the gas liquid mass transfer. For all the other modes the hysteretic behaviour involved a higher gas liquid mass transfer on the decreasing leg than on the increasing leg (there was no literature to compare this result with). The greatest increase was obtained on the Dry mode, at 53%.

The influence of periodic operation on flow morphology did not behave as suspected. In fact, the suggestion of Lim *et al.*, 2004 that the catalyst will eventually be completely wet due to the periodically changing environment cannot be substantiated by these results. The transient operation may not necessarily modify the macroscopic gas liquid distribution within the bed, except for that which is caused primarily by the repetition of two or three cycles due to hysteresis. From the hysteresis investigation, a conclusion could be drawn that the film vs. rivulet concept simply does not serve to explain all of the observed trends.

One of the modes that specifically exhibit behaviour which proves the films vs. rivulet concept questionable, was the Kan Gas mode. Some of the interesting results obtained with this mode are:

- Gas liquid mass transfer on this mode decreased with an increase in liquid flow rate

- Relatively low pressure drops on this mode corresponded to relatively high liquid holdup
- It was the only mode that exhibited no hysteresis with gas flow variation, on any of the hydrodynamic parameters

In conclusion, the concept of films vs. rivulets simply does not provide adequate explanation of the observed results. What did become evident, is that the overall flow type can be categorized into that which is caused by an initial increase in liquid flow rate as opposed to that which is caused by an initial increase in gas flow rate. With the increasing gas flow, gas flow paths are literally blown open, orientating the liquid bridges, thereby reducing tortuosity. A decrease in liquid flow rate at this stage may possibly block some of the gas channels, thereby causing a rather large increase in liquid holdup and pressure drop, while at the same time reducing the available gas liquid mass transfer area. If the flow type is initially established by an increased liquid flow rate, the films and rivulet concept is more dominant. Here an increase in gas flow rate serves to spread the rivulets, or thinning of the films.

During the investigation of the different prewetting modes, the need for an investigation of the transition boundaries on different prewetting modes was recognized. It appeared as if a discontinuity was bound to exist in certain hydrodynamic parameters near the transition boundaries to the Kan Liquid mode (with an increase in liquid flow rate) and Kan Gas mode (with an increase in gas flow rate) on some of the modes investigated. The other explanation presented, claims that the transition boundaries appear at different flow rates on all the modes. This is substantiated in the constant liquid flow rate experiments with the low surface tension system. Here the high interaction regime was reached at the highest flow rates investigated, but only on the Super, Kan Liquid and Kan Gas modes. An investigation to determine the behaviour of each of the investigated parameters near the transition boundaries on all the modes is therefore recommended. Furthermore, it is recommended that non-intrusive visual techniques must be used to investigate the effect of the studied transient in-situ

upsets on the gas liquid distribution. This will improve the understanding of the flow morphology in trickle bed reactors on a micro scale. Lastly, it is recommended that this study be repeated with porous media as packing material.

8. References

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9. Appendices

Appendix 1: Quantifying the Gas-Liquid Mass Transfer Coefficient

(Goto and Smith, 1975)

To determine the volumetric gas-liquid mass transfer coefficient in the bed the mass transfer in the end regions need to be taken into account. The different concentrations and mass transfer coefficient, as defined by Goto and Smith (1975) are shown in figure A1.

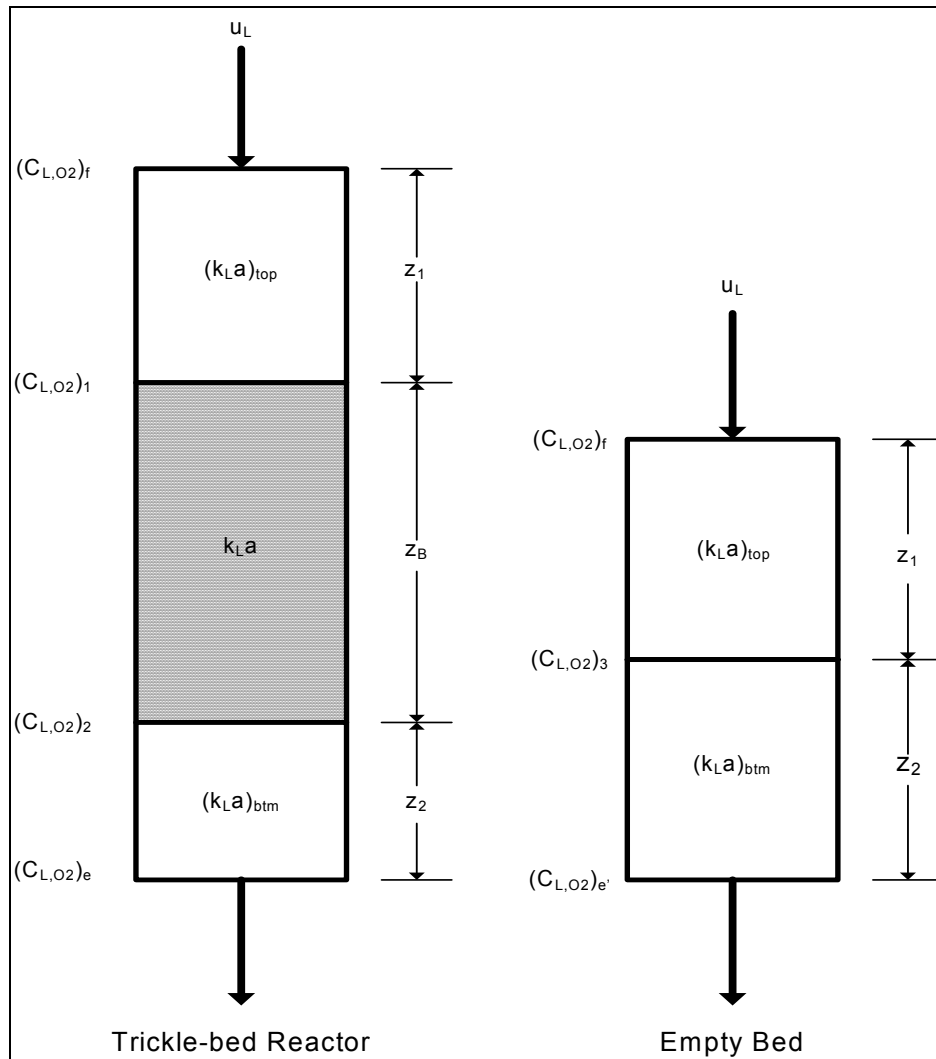


Figure A1: The modelling of end effects as shown by Goto and Smith (1975) If axial dispersion is neglected, the mass balance for oxygen in the two end regions and the bed itself, for desorption is:

$$U_L dC_{L,O_2} = -(k_L a)_{top} (C_{L,O_2} - 0) dZ \quad (A1)$$

$$U_L dC_{L,O_2} = -(k_L a) (C_{L,O_2} - 0) dZ \quad (A2)$$

$$U_L dC_{L,O_2} = -(k_L a)_{btm} (C_{L,O_2} - 0) dZ \quad (A3)$$

The resulting boundary conditions are:

At $Z = 0$

$$C_{L,O_2} = (C_{L,O_2})_f \quad (A4)$$

At $Z = Z_1$

$$C_{L,O_2} = (C_{L,O_2})_1 \quad (A5)$$

At $Z = Z_1 + Z_B$

$$C_{L,O_2} = (C_{L,O_2})_2 \quad (A6)$$

At $Z = Z_1 + Z_B + Z_2$

$$C_{L,O_2} = (C_{L,O_2})_e \quad (A7)$$

Solving equations (A1) to (A3) with the relevant boundary conditions leads to:

$$\int_{(C_{L,O_2})_f}^{(C_{L,O_2})_1} \frac{dC_{L,O_2}}{C_{L,O_2}} = \frac{-(k_L a)_{top}}{U_L} \int_0^{Z_1} dZ \quad (A8)$$



$$\ln(C_{L,O_2})_1 - \ln(C_{L,O_2})_f = -(k_L a)_{top} \frac{Z_1}{U_L} \quad (A9)$$

$$\ln \left[\frac{(C_{L,O_2})_1}{(C_{L,O_2})_f} \right] = -(k_L a)_{top} \frac{Z_1}{U_L} \quad (A10)$$

$$(C_{L,O_2})_1 = (C_{L,O_2})_f e^{- (k_L a)_{top} \frac{Z_1}{U_L}} \quad (A11)$$

Similarly,

$$\int_{(C_{L,O_2})_1}^{(C_{L,O_2})_2} \frac{dC_{L,O_2}}{C_{L,O_2}} = - \frac{(k_L a)}{U_L} \int_{Z_1}^{Z_1+Z_B} dZ \quad (A12)$$

leads to

$$(C_{L,O_2})_2 = (C_{L,O_2})_1 e^{- (k_L a) \frac{Z_B}{U_L}} \quad (A13)$$

and

$$\int_{(C_{L,O_2})_2}^{(C_{L,O_2})_e} \frac{dC_{L,O_2}}{C_{L,O_2}} = - \frac{(k_L a)_{btm}}{U_L} \int_{Z_1+Z_B}^{Z_1+Z_B+Z_2} dZ \quad (A14)$$

leads to

$$(C_{L,O_2})_e = (C_{L,O_2})_2 e^{- (k_L a)_{btm} \frac{Z_2}{U_L}} \quad (A15)$$

Substituting equation (A13) into equation (A15) leads to:

$$(C_{L,O_2})_e = (C_{L,O_2})_1 e^{- \left[k_L a \frac{Z_B}{U_L} + (k_L a)_{btm} \frac{Z_2}{U_L} \right]} \quad (A16)$$

Substituting equation (A11) into equation (A16) leads to:

$$(C_{L,O_2})_e = (C_{L,O_2})_f e^{-\left[k_L a \frac{Z_B}{U_L} + (k_L a)_{btm} \frac{Z_2}{U_L} + (k_L a)_{top} \frac{Z_1}{U_L} \right]} \quad (A17)$$

$(k_L a)_{btm}$ and $(k_L a)_{top}$ can be solved by performing the experiments in an empty bed.

$$\int_{(C_{L,O_2})_f}^{(C_{L,O_2})_3} \frac{dC_{L,O_2}}{C_{L,O_2}} = \frac{-(k_L a)_{top}}{U_L} \int_0^{Z_1} dZ \quad (A18)$$

$$(C_{L,O_2})_3 = (C_{L,O_2})_f e^{-(k_L a)_{top} \frac{Z_1}{U_L}} \quad (A19)$$

$$\int_{(C_{L,O_2})_3}^{(C_{L,O_2})_e} \frac{dC_{L,O_2}}{C_{L,O_2}} = \frac{-(k_L a)_{btm}}{U_L} \int_{Z_1}^{Z_1+Z_2} dZ \quad (A20)$$

$$(C_{L,O_2})_e = (C_{L,O_2})_3 e^{-(k_L a)_{btm} \frac{Z_2}{U_L}} \quad (A21)$$

Substituting equation (A19) into equation (A21) leads to:

$$(C_{L,O_2})_e = (C_{L,O_2})_f e^{-\left[(k_L a)_{btm} \frac{Z_2}{U_L} + (k_L a)_{top} \frac{Z_1}{U_L} \right]} \quad (A22)$$

From equations (A17) and (A22):

$$\frac{(k_L a)_{btm} \cdot Z_2}{U_L} = -\ln \left[\frac{(C_{L,O_2})_e}{(C_{L,O_2})_f} \right] - (k_L a) \frac{Z_B}{U_L} - (k_L a)_{top} \frac{Z_1}{U_L} \quad (A23)$$

$$\frac{(k_L a)_{btm} \cdot Z_2}{U_L} = -\ln \left[\frac{(C_{L,O_2})_e}{(C_{L,O_2})_f} \right] - (k_L a)_{top} \frac{Z_1}{U_L} \quad (A24)$$

Substituting equation (A23) into (A24) leads to:

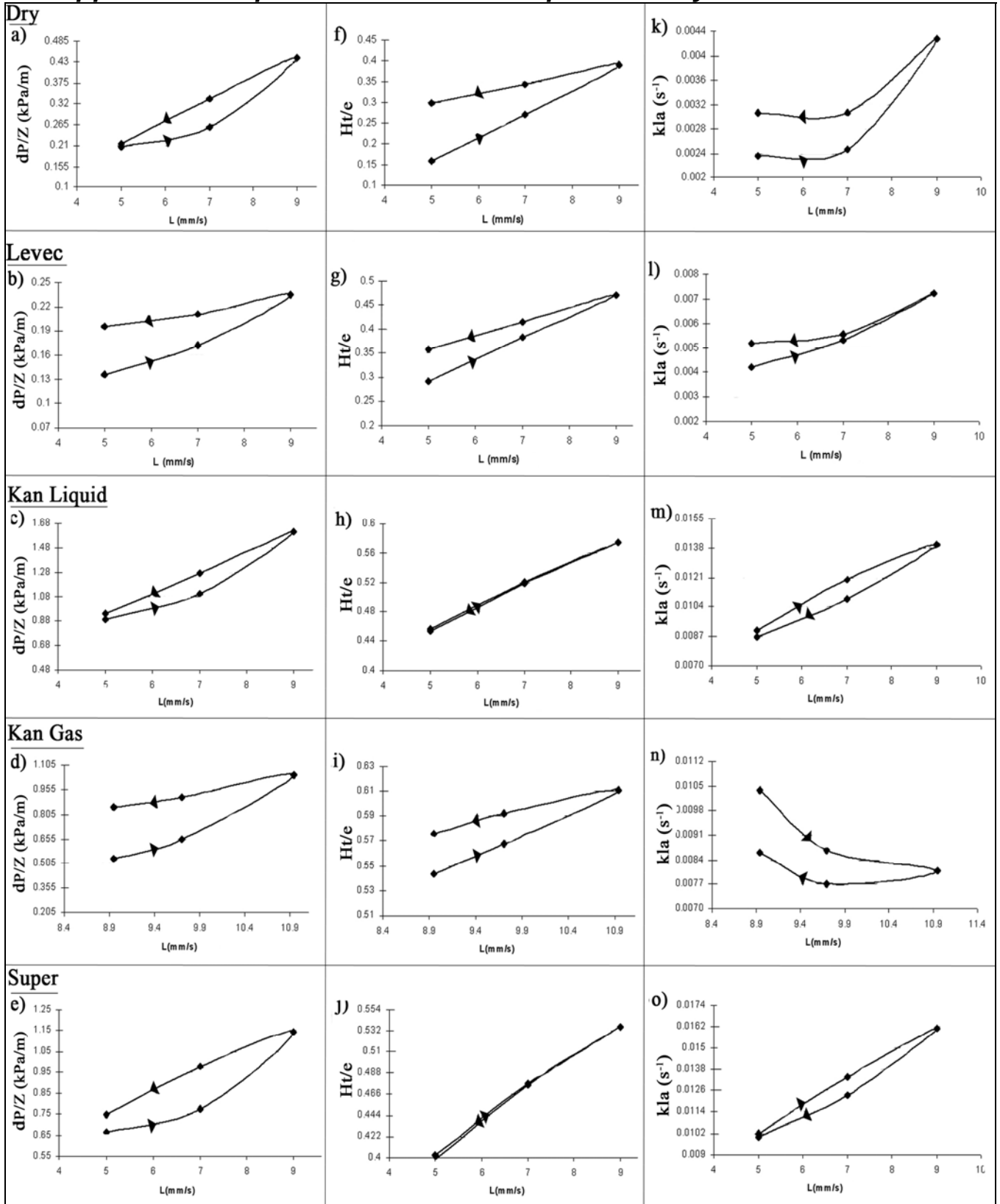
$$\ln \left[\frac{(C_{L,O_2})_e}{(C_{L,O_2})_f} \right] + (k_L a) \frac{Z_B}{U_L} + (k_L a)_{top} \frac{Z_1}{U_L} = \ln \left[\frac{(C_{L,O_2})_{e'}}{(C_{L,O_2})_{f'}} \right] + (k_L a)_{top} \frac{Z_1}{U_L} \quad (A25)$$

$$\ln(C_{L,O_2})_{e'} - \ln(C_{L,O_2})_{f'} + \ln(C_{L,O_2})_f - \ln(C_{L,O_2})_e = k_L a \frac{Z_B}{U_L} \quad (A26)$$

$$k_L a = \frac{U_L}{Z_B} \ln \left[\frac{(C_{L,O_2})_{e'} (C_{L,O_2})_f}{(C_{L,O_2})_e (C_{L,O_2})_{f'}} \right] \quad (A27)$$



Appendix 2: Experimental Data for Liquid Flow Cycles





Appendix 3: Experimental Data for Gas Flow Cycles

