Chapter 8. Impact of Multiplicity on Reactor Performance[5]

Previous chapters have focussed on generating hydrodynamic multiplicity data and on explaining the observed trends by means of a fundamental interpretation based on the pore-scale structure of the bed. This chapter now considers the implications that hydrodynamic multiplicity has on the performance of a trickle bed reactor. This chapter does not form part of the main strategic outline of this work, but is presented as interesting additional evidence of the importance of the multiplicity phenomenon.

8.1 Multiplicity in an Industrial Reactor

This section provides the first (published) evidence that hydrodynamic multiplicity is encountered in industry. Returning to Figure 4, note that the state can be changed from the Levec mode (point A) to a mode in-between Kan-Liquid and Levec (point E) by performing a liquid flow rate variation induced hysteresis loop. Also, getting back from E to A is achieved by shutting off the liquid flow rate, allowing the bed to drain and then re-introducing the liquid flow rate. In an industrial setting, pressure drop and gas and liquid flow rates are usually recorded. Examining this data for a period of 2 years (2004-2005) for a hydroprocessing trickle bed reactor at a large petrochemical plant in South Africa, it was found that it is common for the liquid flow rate to be increased and decreased incrementally over periods of days (all at approximately constant gas flow rate). It is equally common for the liquid flow rate to be shut-off (during a trip for example) and re-established. More specifically, we are looking for the following

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[5] The work reported in this section was completed at the Chemical Reaction Engineering Laboratory (CREL) at Washington University in St Louis, USA. It has been accepted for publication in AIChE Journal (2007) and the second section is written in paper format.

sequence of events: the flow rate was increased up to $u_{L,max}$, then decreased down to $u_{L,1}$, then interrupted ($u_L = 0$) and then re-established at $u_{L,1}$. This is shown schematically in Figure 73a. The corresponding hysteresis loop is shown in Figure 73b. Note that hysteresis is present when $\Delta P_A < \Delta P_B$, and that ΔP_A is the pressure drop in the Levec mode but ΔP_B is not necessarily the pressure drop in the Kan-Liquid mode (since $u_{L,max} < u_{L,pulse}$). Figure 74 is the actual industrial data for cases that correspond to Figure 73a (experimental conditions are listed in Table 18). Note that the bed was not re-packed during this period and that there was no appreciable fouling that could account for the observed trends.

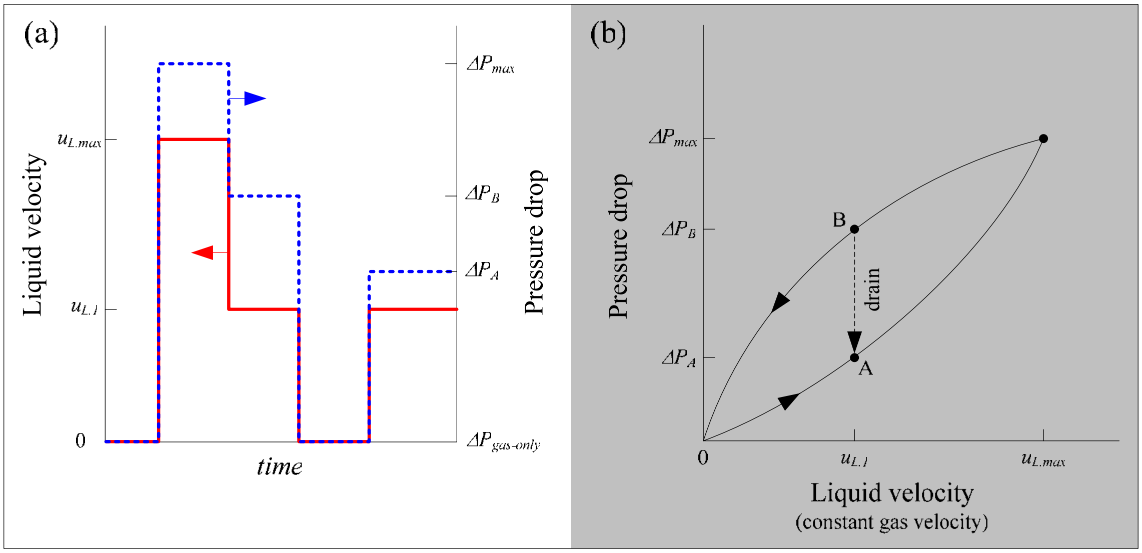

Figure 73. Schematics of the method of investigating hysteresis in an industrial reactor. (a) Liquid velocity (red) and pressure drop (blue) against time for the cases of interest, (b) The equivalent pressure drop hysteresis loop.

This figure establishes that pressure drop hydrodynamic multiplicity occurs in an industrial hydroprocessing reactor. Unfortunately, other information (for example conversion/selectivity) that can be used to establish the effect that multiplicity has on the reactor performance is not available. In fact, Figure 74 provides a motivation for investigating both the nature of hydrodynamic multiplicity and its potential impact on reactor performance.

Table 18. Experimental conditions in industrial reactor

Liquid	Petrochemical
Gas	Hydrogen
Liquid density	620 kg/m^3
Surface tension	0.015 kg/s^2
Particle size	3 mm extrudate
Column diameter	1.8 m
Bed length	7.8 m
Pressure	4 MPa (gauge)
Temperature	571 K

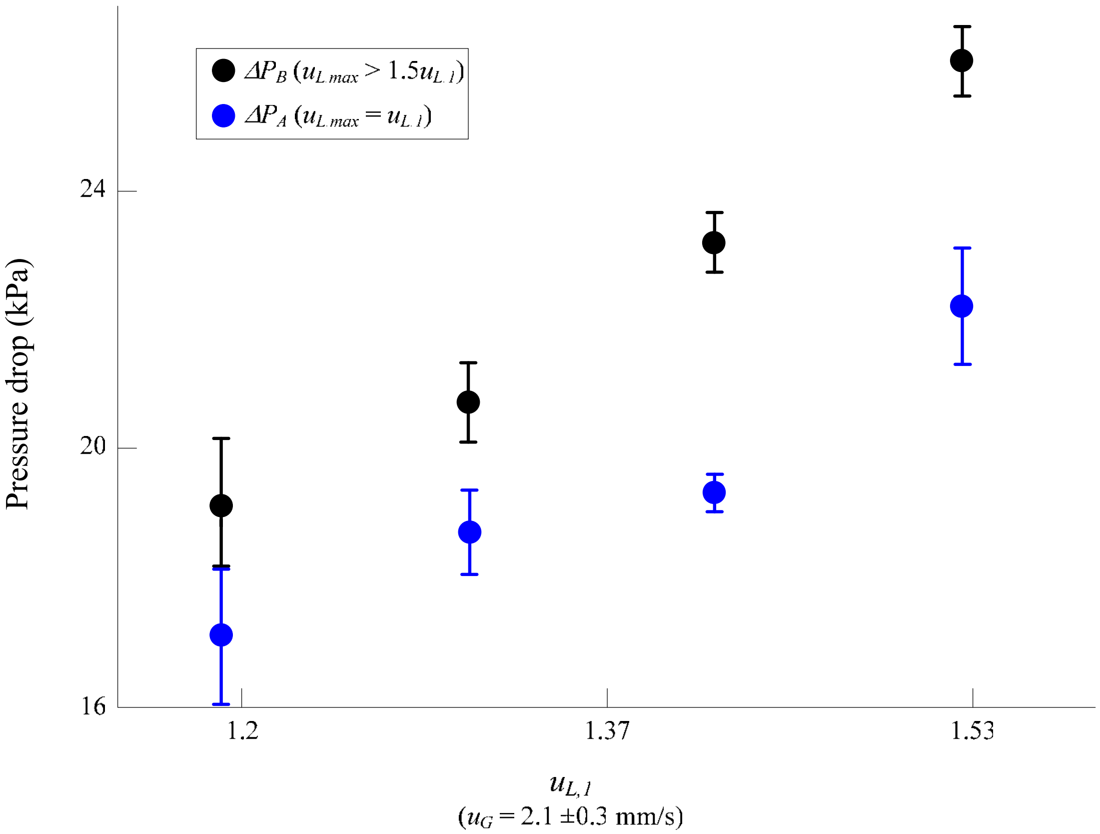

Figure 74. Pressure drop hysteresis in an industrial reactor. Error bars indicate relative standard deviations of the pressure drop signal over a period of approximately 2 days. The difference between the upper and lower legs is 8-20%.

8.2 Expectations of Impact on Reactor Performance

On the basis of the observed behaviour (Chapters 2 and 4 to 6), the expected impact on the reactor performance can be formulated. There are (in general) three reagent phases (solid, gas and liquid) of which the solid is fixed and in the form of porous catalyst particles. Consider therefore, the rate processes of the gas and liquid phase reagents and the impact that hydrodynamic multiplicity has on each. If mass transfer is treated by applying the boundary layer concept, the concentration profiles of the reagents can be sketched qualitatively as shown in Figure 75 (adapted from Mills & Dudukovic, 1980), where the liquid phase reagent has been assumed to be non-volatile (as will be the case in the next section). Note that for illustrative purposes these figures are drawn assuming that both gas and liquid phase reagents are limiting the overall reaction rate. Gas phase reagents undergo the following rate processes (as numbered in Figure 75):

1) Gas-side gas-liquid mass transfer
2) Liquid-side gas-liquid mass transfer
3) Liquid-solid mass transfer
4) Internal diffusion
5) Reaction
6) Gas-solid mass transfer (directly to the dry surface)

Non-volatile liquids are subject to the following steps:

1) Liquid-solid mass transfer
2) Internal diffusion
3) Reaction

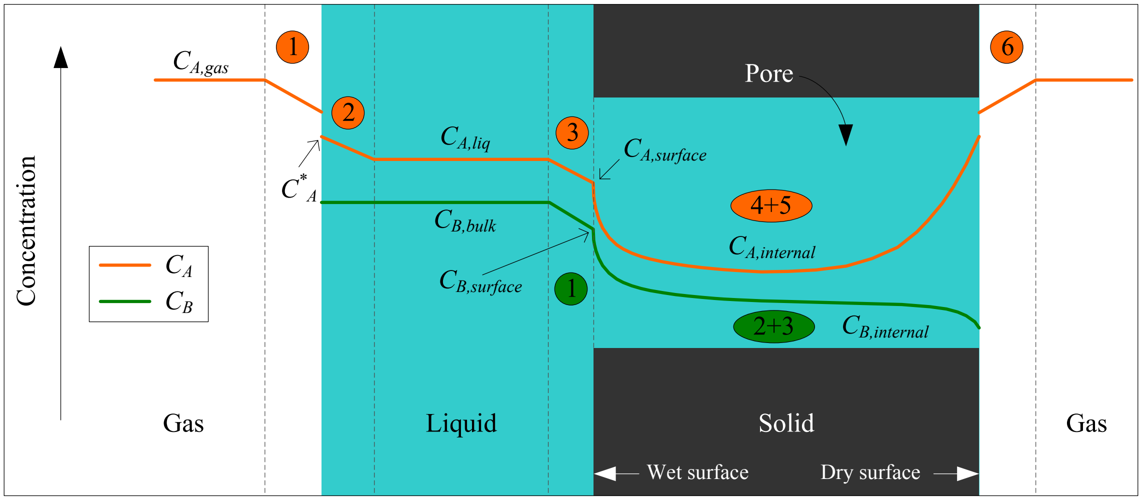

Figure 75. Concentration profiles and rate processes for gas phase reagents and non-volatile liquid phase reagents (based on Mills & Dudukovic, 1980).

If the overall rate is limited by the *chemical reaction kinetics (steps 5 and 3 for gas and liquid respectively)*, the sole effect of hydrodynamic multiplicity is that the liquid is maldistributed in some modes (Levec) but not in others (Kan-Liquid/Super). This means that a fraction of the bed may not be contacted (renewed) at all by the liquid phase reagent and that there will be no reaction in these particles. We have recently shown how such a fraction will influence the overall effectiveness factor (Van Houwelingen et al., 2007), and will not delve into the detail here. If the overall rate is inhibited by *internal mass transfer (steps 4 and 2 for gas and liquid respectively)*, the hydrodynamic multiplicity impacts the overall performance by changing the wetting efficiency (since wetting efficiency directly impacts the boundary condition at the particle surface). If it is also liquid limited, higher wetting efficiency leads to higher particle effectiveness factors according to the model proposed by Dudukovic (1977), and it is therefore concluded that the Kan-Liquid mode would outperform the Levec mode for such a case. If instead, it is gas limited, the additional dry areas in the Levec mode would facilitate the gas supply to the interior of the catalyst (step 6 in the figure) and result in a comparatively higher particle effectiveness factor in the Levec mode. If the *external liquid-solid mass transfer step (steps 3 and 1)* is limiting (for either the gas or liquid limited conditions), the multiplicity impacts both the mass transfer area (wetting efficiency) and the value of the mass transfer coefficient itself (though the average interstitial liquid velocity which is related to the holdup). The next section examines these effects in detail. If it is a gas limited reaction and the *external gas-liquid mass transfer (gas step 1)* is limiting the rate, one would expect the Kan-Liquid mode to outperform the Levec mode, since the former has a much higher volumetric gas-liquid mass transfer coefficient (see Chapter 4). Of course, this effect would be offset by increased gas supply through the dry surface *(step 6)* in the Levec mode (where the wetting is lower). Liquid limited reactions where volatile liquid phase reagents are present would likely also benefit from the lower wetting in the Levec mode, although there is of course less area for direct liquid-solid mass transfer. In the general case, it is necessary to consider all these steps for any reaction and it is informative to write the species balance for the liquid and gas phase reagents in the bulk liquid and solid at the phase interfaces:

$$-u_L \frac{dC_B}{dz} = k_{LS} a_{LS} \left(C_B - C_{B,surface} \right) \tag{33}$$

$$-u_L \frac{dC_A}{dz} = -k_{GL} a_{GL} \left(C_A^* - C_A \right) + k_{LS} a_{LS} \left(C_A - C_{A,surface} \right) \tag{34}$$

$$D_{A,eff} \left(\frac{\partial C_{A,internal}}{\partial r} \right)_{r=R} = \begin{cases} k_{LS} a_{LS} \left(C_A - C_{A,wet\ surface} \right) & \text{on wetted surface} \\ k_{GS} a_{GS} \left(C_A^* - C_{A,\ dry\ surface} \right) & \text{on dry surface} \end{cases} \tag{35}$$

$$D_{B,eff} \left(\frac{\partial C_{B,internal}}{\partial r} \right)_{r=R} = \begin{cases} k_{LS} a_{LS} \left(C_B - C_{B,wet\ surface} \right) & \text{on wetted surface} \\ 0 & \text{on dry surface} \end{cases} \tag{36}$$

The third and fourth equations are the boundary conditions for the solution of the internal concentration profile of each reagent and can in the symmetric case (e.g. fully wetted) be solved for a particle effectiveness factor. Different assumptions can be applied to simplify the calculation of such effectiveness factors. For liquid limited reactions, the

Dudukovic (1977) model alluded to previously was applied and it was shown that the maldistribution effect is the major impact of multiplicity (Van Houwelingen et al., 2007). For gas limited reactions, the catalyst is treated as separate zones (wet and dry, see for example Rajashekharam et al., 1998). However, it is in the mass transfer steps shown in the equations above that the effect of multiplicity is particularly obvious since the mass transfer coefficients (and areas) are directly impacted (although there are no mass transfer correlations that accommodate hydrodynamic multiplicity and we are therefore restricted to qualitative evaluations). The next section explores these effects experimentally and is intended as a proof-of-concept study. The concept explored here is how multiplicity impacts reactor performance and whether or not this effect can be used to make an appreciable impact on that performance.

8.3 Experimental Case Study: Alpha-Methyl Styrene Hydrogenation

8.3.1 Introduction

In this section, the impact of hydrodynamic multiplicity on trickle bed reactor performance is investigated experimentally and then rationalized in terms of the body of knowledge regarding multiplicity that has been built up in the previous chapters. The Kan-Liquid and Levec modes are compared as two extremes of hydrodynamic multiplicity in pre-wetted beds (since by now the importance of the pre-wetting step is well established). Also, indications are that the Super mode is comparable to the Kan-Liquid mode, while the effect of gas velocity changes is small compared to liquid velocity variation induced hysteresis (as shown in Chapters 4 and 6). The extent of variation in the hydrodynamic parameters between these two modes is large and is again summarized in Table 19 for the reader’s convenience. These large differences are likely to greatly influence a trickle bed reactor’s performance.

Table 19. Comparison between Levec and Kan-Liquid modes (approximate)

Parameter	**Extent***		**Reference**	**Conditions**
Pressure drop	2 – 8		Loudon et al. (2006)	3 mm glass spheres, water, N_2 (ambient), u_L = 1-9 mm/s, u_G = 2-9 cm/s
Liquid holdup	1.4 – 1.7		Loudon et al. (2006)	As above
	1.6		Van Houwelingen et al. (2006)	2.5 mm alumina spheres, water, air (ambient), u_L = 1.6, 5.4 mm/s, u_G = 2, 15 cm/s
Wetting efficiency	1.16 – 1.28		Van Houwelingen et al. (2006)	As above
Gas-liquid mass transfer (volumetric)	1.1 – 2.4		Loudon et al. (2006)	As above
Liquid-solid mass transfer	No data		-	-
	Levec	**Kan-Liquid**		
Maldistribution (percentage completely dry particles)	5 – 13%	0%	Van Houwelingen et al. (2007)	2.5 mm alumina spheres, water, air (ambient), u_L = 1.6, 5.4 mm/s, u_G = 2, 15 cm/s

* Extent according to equation 1: Kan-Liquid value divided by Levec value

However, reaction studies generally do not take this effect into account (see for example Wu et al., 1996, and Rajashekharam et al., 1998) and there is no study that directly quantifies the impact of hydrodynamic multiplicity on reactor performance in pre-wetted beds. Several authors (Nemec & Levec, 2005, Bartelmus & Janecki, 2003, Nigam et al., 2002, Lakota et al., 2002) confined their hydrodynamic investigations to the Kan-Liquid mode of operation because this mode exhibits the highest pressure drop and therefore the highest degree of gas-liquid interaction. On this basis, it is assumed that a trickle bed reactor will always perform better in this mode. Hydrodynamic multiplicity has also been neglected in reaction studies due to other arguments, particularly that the impact of hysteresis will not be large because reactions are usually run at higher pressures (increased gas-liquid interaction) with low surface tension liquids and porous particles (i.e. particles with high wettability). These issues were addressed in Chapter 4.

Recently, Van Houwelingen et al. (2007) showed that based on particle wetting efficiency distributions, the Kan-Liquid mode (higher wetting) is expected to outperform the Levec mode (lower wetting) for liquid limited reactions, especially in the case of little internal diffusional resistance (small adjusted Thiele moduli). This is due to liquid maldistribution that leads to the existence, in the Levec mode, of particles that are not contacted by the flowing liquid and therefore do not contribute to the reaction. Khadilkar et al. (1996) showed that an upflow (fully wetted) reactor outperforms a downflow (partially wetted) reactor for liquid limited conditions. This also leads one to expect the Kan-Liquid mode to outperform the Levec mode for liquid limited reactions. Khadilkar et al. (1996) also showed the downflow mode to be superior to the upflow mode for gas limited conditions and attributed this to the state of partial wetting that exists in the downflow mode. This leads one to expect the Levec mode to outperform the Kan-Liquid mode in this case. For severely gas limited reactions, Van Houwelingen et al. (2006) also expected the Levec mode to outperform the Kan-Liquid mode. This is because the lower wetting efficiency (more gas-solid area) in the Levec mode allows greater access for the gas phase to the particle interior through the gas-solid surface area (although it is also likely to be more prone to liquid diffusional limitations due to the presence of particles with very low wetting efficiencies, Beaudry et al., 1987).

Although a number of authors have speculated on the impact of multiple hydrodynamic states (MHS) on reactor performance, reaction studies that address this issue are rare in literature. A recent review of MHS investigations (Maiti et al., 2006) indicate that authors have generally concerned themselves only with qualifying the effect of hysteresis on pressure drop, holdup and wetting efficiency (mostly at low pressure using air and water as fluids). It is apparent that reaction data is necessary to:

- determine the extent of the impact that hydrodynamic multiplicity has on reactor performance, and

- provide quantitative knowledge on which a conceptual foundation for the understanding of the impact of multiplicity can be built (i.e. to verify or refute the expectations of reactor performance based on hydrodynamic concerns).

This section addresses these issues by comparing reaction data for the Levec and Kan-Liquid modes for the hydrogenation of α-methylstyrene (AMS) over porous Pd/alumina extrudate. This reaction is commonly used as a model reaction for pyrolysis gasoline hydrogenation (Nijhuis et al., 2003). Additionally, as discussed in section 8.1, hydrodynamic multiplicity is not expected to impact the performance when it is limited by the chemical reaction kinetics and AMS hydrogenation in a TBR is a mass-transfer limited reaction. Moreover, the reaction can be run as liquid- or gas-limited by changing the operating conditions (Khadilkar et al., 1996). At low AMS concentration and high pressure the reaction is limited by the rate of transfer of the liquid reagent (AMS) to the catalyst. Conversely, at high AMS concentration and low pressure, the reaction is limited by the rate of transfer of hydrogen. This is expressed as a ratio of effective diffusivities and feed concentrations:

$$\gamma = \frac{D_B C_{B,feed}}{b D_A C_A^*} \tag{37}$$

where

D_B = Liquid phase diffusivity of the liquid reagent (AMS)

$C_{B,feed}$ = Liquid reagent concentration in the feed

b = Stoichiometric coefficient (equal to 1)

D_A = Liquid phase diffusivity of the gaseous reagent

C_A^* = saturated hydrogen concentration in the liquid

Using this criterion, the reaction is liquid limited when $\gamma << 1$ and gas limited when $\gamma >> 1$. If γ is bigger than 1 but close to 1, it is possible that some liquid internal diffusion limitations exits for parts of the catalyst particle that is poorly wetted (Beaudry et al., 1987). Note that for gas-limited conditions (γ>1) where the gas phase is continuously supplied (as in a trickle bed reactor), the depletion of the liquid phase reagent actually reduces γ down the length of the bed and it is possible to enter into the liquid limited regime.

Some instances of MHS in a TBR with chemical reaction are discussed in literature. Rajashekharam et al. (1998) showed how the conversion in a denitrogenation reaction is higher in a decreasing liquid flow rate mode (possibly Kan-Liquid) than in an increasing liquid flow rate mode (Levec). They attributed the difference to the temperature history in the bed. Similar temperature effects were observed by Hanika et al. (1981), Germain et al. (1974) and more recently Kirillov & Koptyug (2005). In these cases, it was shown how vaporization of the reaction mixture leads to complex thermal behaviour, including hot spot formation and temperature induced hysteresis. These studies do not explicitly consider the hydrodynamic effects that accompany changes in flow rates.

Ravindra et al. (1997b) studied the liquid phase oxidation of sulphur dioxide to sulphuric acid over activated carbon. In this case, the gas phase reagents are oxygen and SO_2 and the liquid phase reagent is water (which is also the solvent). The reaction is conducted at atmospheric pressure and room temperature. For these conditions, the reaction is severely gas-limited ($\gamma \approx 10^7$). The authors report that a pre-wetted bed outperforms a non-pre-wetted bed for a range of liquid velocities from 1 to 7 mm/s. The authors attribute the difference in performance between these modes to the different flow morphologies and mixing characteristics in the two modes of operation. It is likely that the severe maldistribution associated with the Non-pre-wetted mode also played a role in their results.

Table 19 suggests that hydrodynamic multiplicity may greatly influence the performance of a TBR. Therefore, this study focuses exclusively on the impact of hydrodynamic multiplicity (of all the hydrodynamic parameters) although due consideration is given to temperature effects.

Experimental details including the setup, analytics, operating procedures and experimental precautions are reported in Appendix A.

8.3.2 Results and Discussion

Figure 76a to Figure 76c and Figure 77a and Figure 77b show the conversion as a function of liquid velocity for $\gamma > 1$ and $\gamma < 1$ respectively (i.e. gas limited and liquid limited respectively). For the gas limited data ($\gamma > 1$), a complicating factor is the fact that γ decreases down the length of the catalyst bed as the liquid reagent is depleted. This effect is more severe for values of γ near 1 for low velocities where the conversion is high. In these cases the γ value at the exit of the bed can be below 1 and there are two regimes in the bed: the first being gas-limited and the second liquid-limited. However, for the case of large entrance γ and high velocities, the exit γ is still above 1. It is specifically these conditions that are used to evaluate the functional behaviour of a gas limited system. In order to keep conversions low enough to be properly measurable, the catalyst bed height was halved for the experiments depicted in Figure 76c and Figure 77. The hydrogenation reaction is considered mildly exothermic ($-\Delta H$ = 110 kJ/mol), and corresponding temperature rises in the reactor are shown in Figure 76d to Figure 76f and Figure 77c and Figure 77d. Also shown on these figures are the adiabatic temperature rises calculated from the measured conversions assuming constant specific heat capacities (liquid specific heat capacity of 190 kJ/kmol.K and gas specific heat capacity of 29 kJ/kmol.K) and thermal equilibration between the gas and the liquid. As indicated, there were significant heat losses to the environment for the conditions where high AMS feed concentrations were used (gas limited conditions).

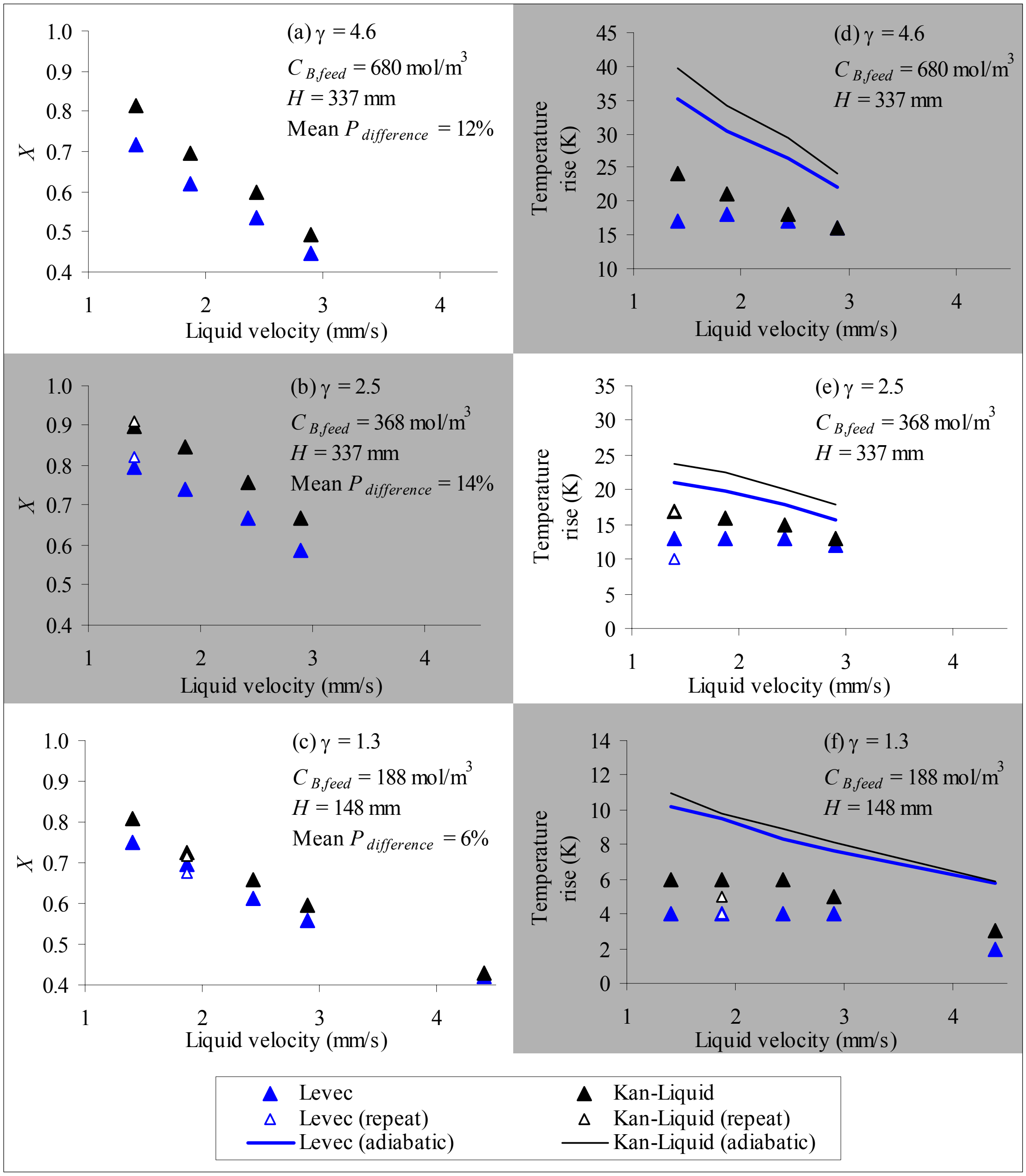

Figure 76. Conversion and temperature rise for gas limited conditions

A representative plot of the measured pressure drop (Figure 78) in both modes show trends similar to those observed in literature, although the difference between the modes is only about 5-25% (probably due to the low gas velocity used here, as well as the end effects and the presence of the glass bead beds inside the reactor).

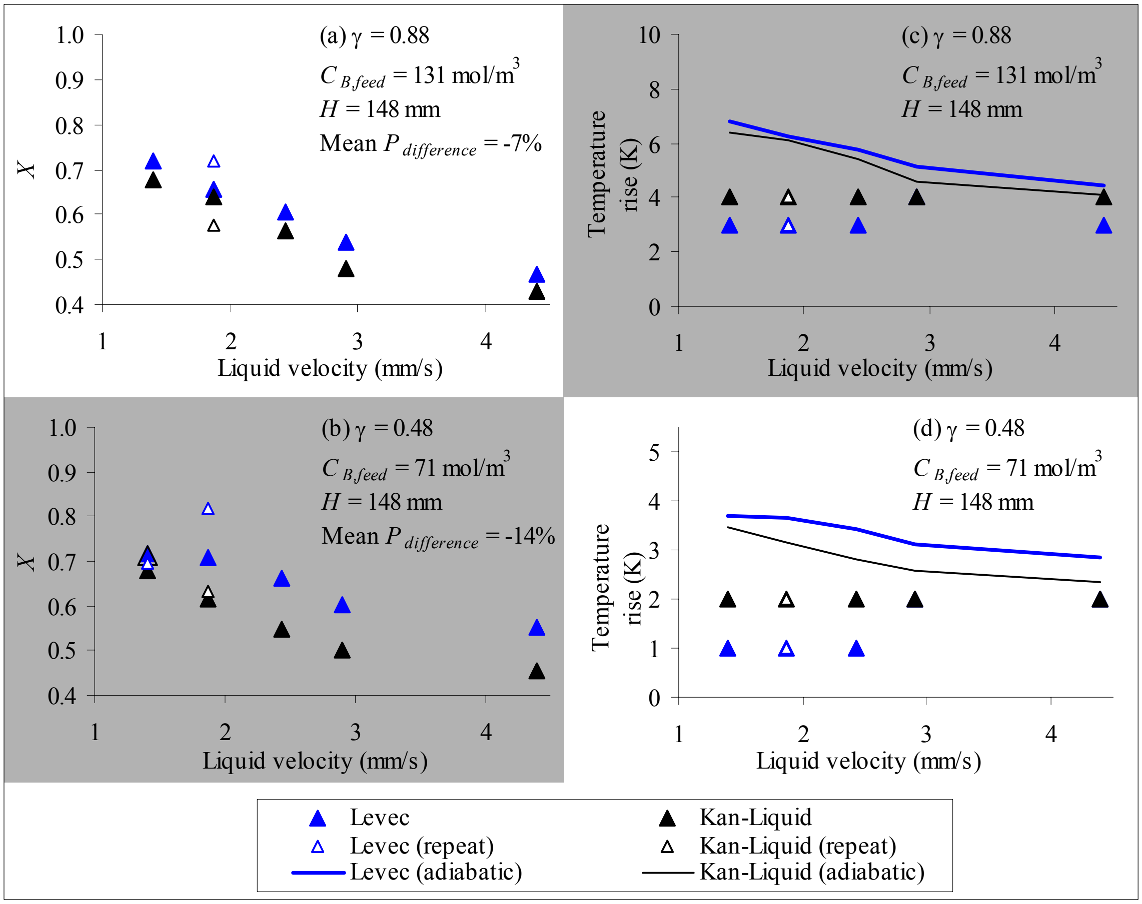

Figure 77. Conversion and temperature rise for liquid limited conditions

The results indicate clearly that a significant change in reactor performance occurs as a result of flow multiplicity. Moreover, higher conversions are not always achieved in one particular mode. For gas limited reactions (large γ, Figure 76), the Kan-Liquid mode outperforms the Levec mode. As the liquid feed concentration (and γ) is reduced the difference between the modes becomes smaller (as both gas and liquid limitations become important). When $\gamma < 1$ (liquid limitations, Figure 77), the Levec mode outperforms the Kan-Liquid mode (and apparently increasingly so as γ is reduced further). The difference in performance is considerable. A measure of this difference can be gained from defining the productivity and the productivity difference between modes respectively as (Levenspiel, 1998):

$$P = \frac{XC_{B,feed}Q_L}{W_{Pd}} \tag{38a}$$

$$P_{difference} = \frac{P_{Kan-L} - P_{Levec}}{P_{Levec}} \times 100\% \tag{38b}$$

For gas limited conditions (γ = 4.6 and 2.5), the productivity is roughly 10-15% higher in the Kan-Liquid mode. For liquid limited conditions (γ = 0.48), the productivity is 2-20% higher in the Levec mode (14% on average). It seems as though the modes are equally productive when γ = 1. The productivity difference between modes is shown in Figure 79 as a function of γ or 1/γ (a γ value of 2 for the gas-limited condition corresponds to a 1/γ value of 2 for the liquid-limited condition). The coupling between reactor performance and hydrodynamics is intricate. It is desirable to reconcile the conversion data with the hydrodynamics of the different pre-wetting modes. Because of the unavailability of quantitative kinetic and hydrodynamic data for this system and conditions, the discussion is restricted to a qualitative rationalization of the observed behaviour.

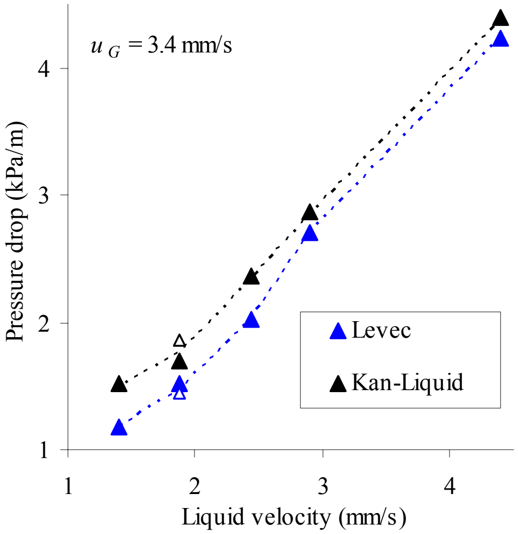

Figure 78. Representative pressure drop plot

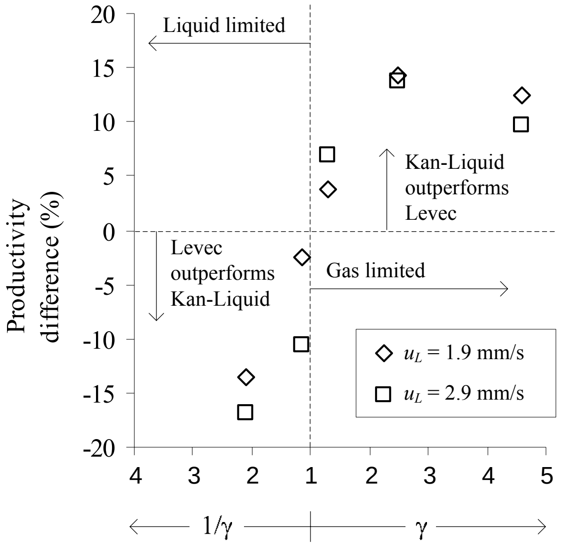

Figure 79. Productivity difference as a function of the degree of gas or liquid limitation

To start, a comparison between the gas-limited exothermic reaction data of Rajashekharam et al. (1998) and the gas limited condition (Figure 76) reveals a fundamental dissimilarity in the thermal behaviour. In their work, an initial *increase* in the liquid velocity (presumably in the Levec mode) resulted in an *increase* in the temperature. This happens despite a decrease in the overall conversion, and therefore is likely to be attributed to non-adiabatic effects (e.g. the heating of the reactor by the heaters mounted on the reactor wall). A subsequent decrease in the liquid velocity (the return leg, Kan-Liquid) then yielded a higher conversion of the feed reagent at a higher temperature (compared to the increasing liquid velocity leg, Levec). The hysteresis was therefore attributed to the fact that the bed was warmer on the decreasing liquid velocity leg (Kan-Liquid mode) which led to a higher conversion. In this study, the steady state temperature slightly *decreased* as the liquid flow rate was *increased* on the Levec mode (see Figure 76e for example). This corresponds to a lower AMS conversion. The lowest temperature in the bed was reached during pulsing flow. Upon returning to lower velocities (Kan-Liquid mode), the temperature was higher than it was before. The temperature history in the bed cannot therefore account for the hysteretic behaviour. Instead, the higher conversion due to hydrodynamic effects in turn resulted in a higher bed temperature. This interpretation is further supported by the liquid limited data (Figure 77), where almost no temperature variation occurred as a result of flow rate changes but a considerable difference in conversion is observed. From these observations it is evident that the multiplicity in conversion is caused by a hydrodynamic effect and not a temperature history effect. It is therefore imperative to determine the nature of these hydrodynamic multiplicity effects on the reactor performance.

Considering that the reaction is mass transfer limited and that the active metal is deposited on the support in an egg-shell configuration (i.e. on the outer shell of each particle), external mass transfer is expected to play the most important role. Insofar as the gas limited case is concerned, note that the gas phase reactant (A) can be supplied to the catalyst particle either through the liquid or directly to the dry surface. However, for the conditions in this study (small, porous particles, a low surface tension liquid and the presence of a particle pre-wetting procedure), it is likely that the wetting efficiency is close to 1 (Al-Dahhan & Dudukovic, 1995). The focus should therefore be on the gas-liquid and liquid-solid mass transfer steps for hydrogen, and $(k_{LS}a_{LS})_A$ is typically an order of magnitude larger than $k_{GL}a_{GL}$ (compare for example the data of Tan & Smith (1982) to that of Goto & Smith, 1975). This means that the total gas-liquid-solid mass transfer coefficient is approximately equal to the gas-liquid mass transfer coefficient (i.e. all of the resistance is in the gas-liquid mass transfer step). Changes in $k_{LS}a_{LS}$ due to hydrodynamic multiplicity are therefore insignificant compared to changes in $k_{GL}a_{GL}$. Based on this analysis, it is anticipated that, for the present system (gas limited conditions), gas-liquid mass transfer is the controlling rate. This conclusion accords with the observed behaviour of the reactor in that it is known that the volumetric gas-liquid mass transfer rate is appreciably larger in the Kan-Liquid mode (Table 19). The present results are in agreement with the work of Ravindra et al. (1997b) who found a higher reaction rate in the hydrodynamic mode with a higher wetting efficiency (but also a higher volumetric gas-liquid mass transfer coefficient).

The liquid limited case presents an interesting phenomenon in that the Levec mode has a higher conversion than the Kan-Liquid mode (Figure 77) despite the expectation of a lower average wetting efficiency (Table 19). Having established that this is not a temperature effect, the interplay between wetting efficiency and holdup and how they affect the volumetric liquid-solid mass transfer coefficient need to be clarified. Unfortunately, mass transfer coefficient correlations are generally inaccurate and also does not account for hydrodynamic multiplicity. For these reasons, the present discussion is limited to a qualitative rationalization of the observed trends. Note that a smaller holdup corresponds to a larger interstitial velocity, which corresponds to an increased k_{LS} (Lakota & Levec, 1990). Also, the mass transfer area (a_{LS}) is obviously proportional to the wetting efficiency (f). For the two modes, all other parameters in typical mass transfer correlations (like superficial velocities and the bed properties) are equal, so that is possible to estimate the ratio of volumetric mass transfer coefficients in the two modes:

$$\frac{\left[k_{LS}a_{LS}\right]_{Levec}}{\left[k_{LS}a_{LS}\right]_{Kan-L}} = \left(\frac{\left[\varepsilon_L\right]_{Kan-L}}{\left[\varepsilon_L\right]_{Levec}}\right)^{\frac{1}{2}}\left(\frac{\left[f\right]_{Levec}}{\left[f\right]_{Kan-L}}\right) \tag{39}$$

In equation 39 the power of 0.5 is predicted by film theory and was confirmed over a wide range of operating conditions (Lakota et al., 2002). Evaluation of equation 39 requires estimates of the ratios of holdup and wetting efficiency in the two modes. For the present conditions, the use of small particles and a low surface tension liquid is expected to yield high wetting efficiency (Al-Dahhan & Dudukovic, 1995) (especially at high liquid velocity), meaning that the wetting efficiency ratio can be expected to be close to 1 (because wetting nears 1 for both cases). The ratio of liquid-solid mass transfer coefficients in the two modes is therefore roughly proportional to the square root of the inverse ratio of holdup. Wang et al. (1995) showed that smaller particles have more severe holdup hysteresis and one can therefore expect the holdup ratio to be larger than that reported for the 3 mm spheres (Table 19). Since the holdup in the Levec mode is lower than that in the Kan-Liquid mode, the Levec coefficient exceeds the Kan-Liquid coefficient. This then serves as a possible explanation for the higher conversion that was achieved for the Levec mode in the liquid limited reaction experiments (Figure 77). A proper evaluation of the effect of pre-wetting on mass transfer limited reactions therefore has to take into account both the difference in interstitial velocity (holdup) and the difference in mass transfer area (wetting efficiency). Note that in this case, the depletion of the liquid reagent serves to make the conditions more liquid limited as conversion increases down the length of the reactor.

8.3.3 Reaction Case Study Conclusions

The effect of hydrodynamic multiplicity on a mass transfer limited reaction was shown to be significant when either gas or liquid limitations are dominant. The observed trends are counter-intuitive when evaluated from a partial wetting perspective: the Kan-Liquid mode outperforms the Levec mode for gas limited conditions, while the Levec mode outperforms the Kan-Liquid mode for liquid limited conditions. However, the reaction data can be rationalized qualitatively when it is considered that the wetting for the conditions in this study is likely to be nearly complete. In such a case, hydrodynamic multiplicity impacts the applicable mass transfer coefficients directly in a manner consistent with the available literature and the observed behaviour of the reactor. It is likely that the effects described in this study (mass transfer rates) are applicable to a range of conditions similar to those employed, while the full range of effects probably warrant consideration in the general case. These should include stagnancy, the effect of gas flow, maldistribution, localized hot spot formation, particle scale phenomena (in particular the use of uniformly impregnated particles) and the use of different particle sizes, particle geometries and operating conditions. However, there is limited data available on these issues as researchers have generally not considered hydrodynamic multiplicity apart from specifying operating in the Kan-Liquid mode. This study introduces the idea of optimising the hydrodynamic conditions in the reactor by exploiting the multiplicity behaviour in order to suit specific reaction conditions.

8.4 Conclusions

This chapter discussed the industrial implications of hydrodynamic multiplicity. First, experimental evidence of the existence of pressure drop multiplicity was presented, but unfortunately the implications for the reactor performance were not clear. To illustrate that hydrodynamic multiplicity directly impacts the performance of a trickle bed reactor, an experimental case study was completed in a pilot scale hydrogenation reactor. The results indicate that for the conditions examined, hydrodynamic multiplicity greatly affects the conversion. Moreover, different modes yield optimal performance depending on the system conditions. These results again emphasize the importance of properly understanding hydrodynamic multiplicity.

Chapter 9. Conclusions

As a whole, this work advanced the understanding of trickle flow to the extent of comprehending the role that capillary phenomena play in establishing diverse hydrodynamic states under different operating conditions. This is accomplished as illustrated in Figure 1. First, a conceptual framework was introduced by which hydrodynamic multiplicity can be studied successfully. This framework was then applied to the existing multiplicity data and some deficiencies were identified. Additional experimental insights were generated both at the traditional bed scale and at the more informative pore scale. These experimental investigations included extending the scope of the data (to include bed characteristics, operating conditions and procedures that have not been investigated before), as well as advancing existing visualization techniques through novel applications and improved processing strategies.

The major conclusions of this study are as follows:

- *Hydrodynamic multiplicity significantly impacts all the hydrodynamic parameters* investigated.
- The *limiting cases framework* proves to be both applicable to and useful for the study of hydrodynamic multiplicity.
- A proposed *capillary gate mechanism* is capable of providing qualitative rationalizations of all of the experimentally observed *characteristic trends* (that embodies the behaviour of the flow in the various hydrodynamic states).
- It is further established experimentally that *hydrodynamic multiplicity directly impacts trickle bed reactor performance*, and that different hydrodynamic modes are preferable depending on the reaction specifics.

It is recommended that:

- The development of a *fully predictive hydrodynamic multiplicity model* be pursued. The model should be based (at least in part) on the experimental and theoretical insights provided in this work.
- The impact of hydrodynamic multiplicity on trickle flow performance be studied in depth, in particular for industrially important conditions (for example, systems with multiple reactions or systems limited by chemical kinetics, internal mass transfer, external mass transfer or combinations thereof).

In conclusion, this work has emphasized the importance of hydrodynamic multiplicity, has shown experimentally that its effects are far reaching and potentially advantageous, and that it can be understood in relatively simple terms if capillary effects are appropriately included in a pore-level description of trickle flow.