Effect of Hydrodynamic Multiplicity on Trickle Bed Reactor Performance

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Multiple hydrodynamic states in trickle bed reactors have been the subject of numerous hydrodynamic investigations. The extent of variation in the hydrodynamic parameters (like holdup and pressure drop) is large and this variation can be expected to have a significant impact on the conversion in a reaction system. This study presents reaction data for α-methyl styrene hydrogenation in a trickle bed reactor over a range of conditions that include gas and liquid limitations. It is seen that liquid flow rate variation induced hysteresis has a large impact on the conversion. For gas-limited reactions, the upper branch of the pressure drop hysteresis loop has a higher conversion than the lower branch at the same linear fluid velocities and catalyst weight, while for liquid-limited reactions the lower branch has a higher conversion than the upper branch (the difference in productivity being up to 20%). These trends cannot be explained by differences in wetting efficiency. Instead, it is proposed that for this system the gas–liquid mass transfer rate is the limiting step in gas-limited reactions, while the liquid–solid mass transfer rate is the limiting step in liquid-limited reactions.
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Introduction

In cocurrent gas–liquid down-flow over a stationary packed bed as found in trickle bed reactors (TBR), the trickle flow regime is encountered at relatively low fluid fluxes. This regime is particularly important for down-scaled operations encountered in laboratory evaluations[1,2] and in industrial applications like hydroprocessing[3] and packed columns. In the trickle flow regime, the hydrodynamics is not uniquely determined by the operating conditions owing to the existence of multiple hydrodynamic states (MHS). This term refers to the fact that hydrodynamic parameters like pressure drop or liquid holdup can adopt different values (at the same operating conditions) depending on the flow history or prewetting procedures. This is often presented in the form of hysteresis loops, where the variation in a hydrodynamic parameter (such as pressure drop or liquid holdup) is shown as a function of the gas or liquid velocities.[4–6] It is seen that the pressure drop, for example, can vary by as much as several hundred percent at the same operating conditions as a result of the flow rate history. This is shown schematically in Figure 1 for the case of pressure drop as a function of liquid superficial velocity. Starting from point 1 on this figure, it is observed that if the liquid velocity is increased (to point 2) while keeping the gas velocity constant, the pressure drop increases as well. If the liquid velocity is now decreased back to the original value, the pressure drop is higher than what was originally obtained (point 3). If the liquid velocity

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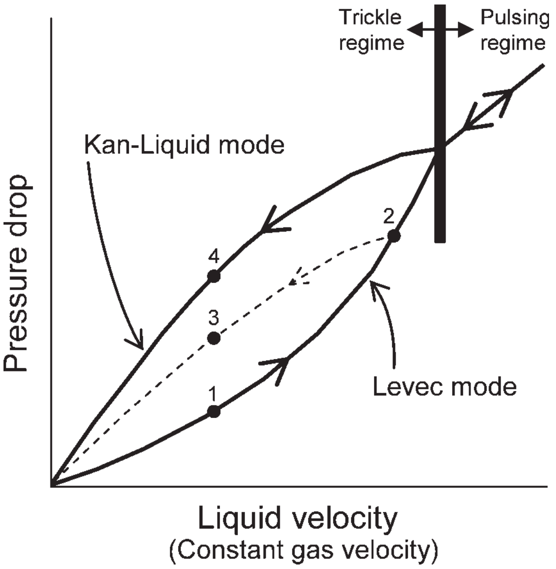

Figure 1. Schematic of pressure drop hysteresis showing the two modes employed in this study (based on Levec et al.; Christensen et al.; Wang et al.).

is increased until the pulsing boundary is reached, the pressure drop will return on the top branch (to point 4). Any value of pressure drop between points 1 and 4 can be obtained by suitably increasing and decreasing the liquid superficial velocity. The highest value of pressure drop for any given velocity is therefore attained on the top branch (which is called the Kan-Liquid mode after Kan and Greenfield[4]), while the lowest value is obtained on the bottom branch (which is called the Levec mode after Levec et al.[5]). These modes therefore represent the limits of pressure drop variation that can be obtained by liquid flow rate variation (provided that the bed had been prewetted). This strategy is, therefore, referred to as liquid flow rate variation induced hysteresis. It is possible to obtain similar loops by varying the gas velocity while keeping the liquid velocity constant (called gas flow rate variation induced hysteresis). There is also the possibility of performing multiple loops (as discussed in Maiti et al.[7]), or combinations of loops such as gas flow rate variation induced hysteresis followed by liquid flow rate variation induced hysteresis. Recognizing the multitude of possibilities, Loudon et al.[8] established approximate limiting cases of such loops by conscientiously defining a set of prewetting modes that form a conceptual basis by which hysteresis can be studied (a similar approach was followed by Wang et al.[9]). While the discussion has thus far used pressure drop as an example, it is important to note that similar loops exist for holdup, the gas–liquid volumetric mass transfer coefficient[8] and for wetting efficiency.[10] The terms hydrodynamic multiplicity and hysteresis therefore refer to variation in all the hydrodynamic parameters as a result of flow rate changes or prewetting methods. For liquid flow rate variation induced hysteresis in prewetted beds, the two limiting modes are those shown schematically in Figure 1. The lower branch (henceforth referred to as the Levec mode) is obtained by the following procedure (Levec et al.[5]):

- pre-flooding the bed, keeping it flooded until the catalyst is internally saturated
- draining it under gas flow until only the residual holdup remains
- commencing the liquid flow at the lowest operating velocity
- if a higher velocity is required, the liquid flow is increased accordingly, thereby advancing on the lower leg in Figure 1

The upper branch in this figure (henceforth referred to as the Kan-Liquid mode) is obtained by (Kan and Greenfield[4]):

- pre-flooding the bed (as before)
- establishing gas and liquid flow at the operating superficial velocities
- increasing the liquid velocity until the pulsing flow regime is prevalent
- decreasing the liquid velocity to the operating velocity, all at the desired gas velocity

It is imperative to note that there are several other limiting prewetting modes, such as those associated with gas flow rate variation induced hysteresis, or if the Levec mode is not given any time to drain before the gas and liquid are introduced at the operating velocities (called the Super mode[8]). However, indications are that the Super mode is comparable to the Kan-Liquid mode, while the effect of gas velocity changes is small compared with liquid velocity variation induced hysteresis.[8] For these reasons, the Levec and Kan-Liquid modes are used here to compare the performance of a TBR with two representative cases of hydrodynamic multiplicity. The extent of variation in the hydrodynamic parameters between these two modes is large and is summarized in Table 1. These large differences are likely to greatly influence a trickle bed reactor's performance. However, reaction studies generally do not take this effect into account (see for example, Wu et al.[12] and Rajashekharam et al.[13]) and there is no study that directly quantifies the impact of hydrodynamic multiplicity on reactor performance. Several authors[14–17] 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 because of 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).

Recently, Van Houwelingen et al.[11] 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.[18] 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

Table 1. Comparison Between Levec and Kan-Liquid Modes (Approximate)

Parameter	$\frac{[\text{Kan−Liquid Value}]}{[\textit{Levec Value}]}$		Reference	Conditions
Pressure drop	2–8		Loudon et al.[8]	3 mm Glass spheres, water, N_2 (ambient), u_L = 1–9 mm/s, u_G = 20–90 mm/s
Liquid holdup	1.4–1.7		Loudon et al.[8]	As above
	1.6		Van Houwelingen et al.[10]	2.5 mm Alumina spheres, water, air (ambient), u_L = 1.6, 5.4 mm/s, u_G = 20, 150 mm/s
Wetting efficiency	1.16–1.28		Van Houwelingen et al.[10]	As above
Gas–liquid mass transfer (volumetric)	1.1–2.4		Loudon et al.[8]	As above
Liquid–solid mass transfer	No data		–	–
	Levec	Kan-Liquid		
Maldistribution (percentage completely dry particles)	5–13*	0†	Van Houwelingen et al.[11]	2.5 mm Alumina spheres, water, air (ambient), u_L = 1.6, 5.4 mm/s, u_G = 20, 150 mm/s

*Represents the Levec mode in percentage.
†Represents the Kan-Liquid mode in percentage.

et al.[18] also showed the down flow mode to be superior to the upflow mode for gas-limited conditions, leading one to expect the Levec mode to outperform the Kan-Liquid mode in this case. For severely gas-limited reactions, Van Houwelingen et al.[10] 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).

Although a number of authors has speculated on the impact of MHS on reactor performance, reaction studies that address this issue are rare in literature. A recent review of MHS investigations[7] 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 study 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.[19] Additionally, 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.[18] 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:

$$\gamma = \frac{D_B C_{B,\text{feed}}}{b D_A C_A^*} \tag{1}$$

where D_B, liquid phase diffusivity of the liquid reagent (AMS); $C_{B,\text{feed}}$, 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.[20] Note that for gas-limited conditions ($\gamma > 1$) 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.[13] 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.,[21] Germain et al.,[22] and more recently Kirillov and Koptyug.[23] In these cases, it was shown how vaporization of the reaction mixture leads to complex thermal behavior, 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.[24] 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 prewetted bed outperforms a

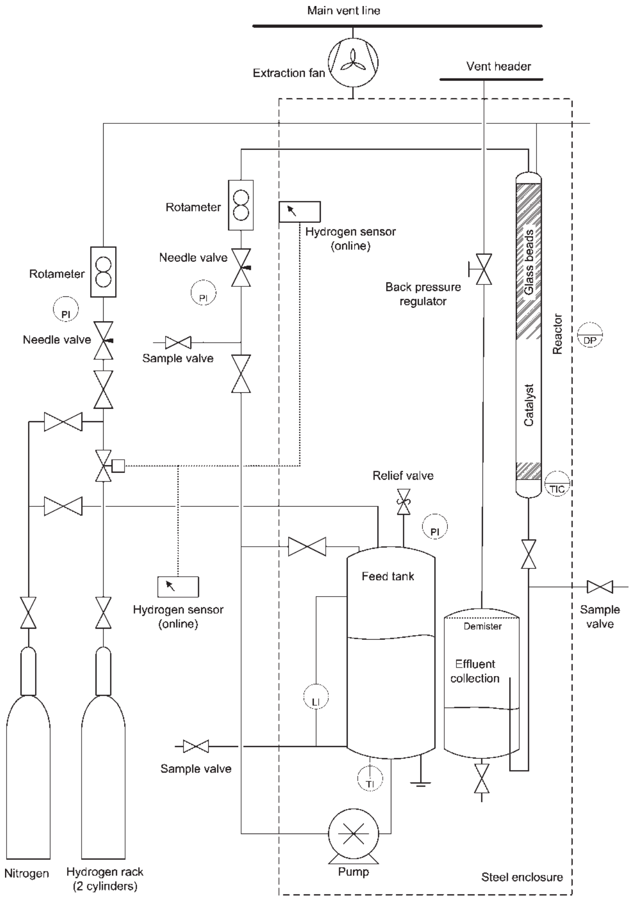

Figure 2. Schematic of hydrogenation reactor setup.

non-prewetted 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.

Table 1 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

The trickle bed reactor facility is shown schematically in Figure 2. The inner diameter of the reactor was 0.05 m. Prepurified hydrogen from a rack of two cylinders was fed into the reactor at a controlled flow rate. Liquid was charged into the feed tank which was subsequently pressurized with nitrogen. The liquid feed was made up of α-methyl styrene, AMS, (99%, Aldrich) in hexane (95%, Aldrich) as solvent with AMS concentrations from 1 to 9 v/v % (70 to 680 mol/m^3). The AMS concentration was determined by a Gas Chromatograph (Varian) that was precalibrated for a range of AMS concentrations between 7.7 and 680 mol/m^3. Analytical reproducibility was within ~2% on AMS concentration. The pressure difference between the feed tank and the reactor was kept at 340 kPa and was used to supply liquid into the reactor. The pump was used only to circulate the feed prior to operation to ensure a uniform feed concentration. Experiments were conducted for liquid velocities ranging from 1.4 to 4.4 mm/s (maximum liquid velocity used for pulsing prewetting was 9.4 mm/s) and the gas velocity was set at 3.4 mm/s at 790 kPa for all the runs (hydrogen is therefore in stoichiometric excess for all experiments except the most severely gas-limited condition—excess between 4 and 1100% depending on the liquid velocity and concentration). A differential pressure transducer (Validyne DP15-30) was used to measure the pressure drop over the entire reactor (i.e., catalyst bed, glass bead beds, the entrance and the exit). A thermocouple capable of registering intervals of 0.5°C is located at the exit of the bed. The liquid is funnelled at the bed exit by a metallic sieve and the thermocouple is placed in the liquid stream. The feed was always introduced at 19°C. The column itself is insulated with ceramic material to reduce heat losses to the environment. A heater was used to heat the catalyst for activation purposes, but was turned off during the reaction run. A bed of glass beads at the reactor entrance ensures that the liquid is saturated with hydrogen prior to it entering the catalyst bed. This was confirmed by estimating the hydrogen concentration in the liquid at the catalyst bed entrance by assuming plug flow of the liquid and a gas–liquid mass transfer rate characterized by a volumetric coefficient. Using either the Goto and Smith[25] or the Larachi et al.[26] correlation to estimate the coefficient, the concentration at the catalyst bed entrance was determined to be within 1% of the saturated concentration. The glass beads also serve as a distributor for the gas and liquid phases prior to it entering the catalyst bed. All experiments reported here were conducted at 790 kPa absolute pressure. Although it is possible to increase γ by operating at a lower pressure, there is indication that the intrinsic kinetics is dependent on the pressure,[27] which makes comparison between the gas- and liquid-limited runs difficult. At 800 kPa, the kinetics are usually taken to be dependent on both reactant concentrations.[27] An additional reason for operating at a single pressure for all the runs is the fact that it has not been established what the effect of different operating pressures is on the difference between the two prewetting modes. Operating at a single pressure for all the runs eliminates any hydrodynamic differences that might have occurred because of changes in the pressure. At this pressure, γ ranged between 0.48 and 4.6 for the different AMS concentrations. For each condition, liquid samples were taken at intervals of 5 min. Steady state was assumed once the pressure drop, temperature rise, and conversion had all stabilized. Steady state was usually achieved in about 10–15 min but sampling continued to 25 min in each case.

The catalyst bed height was either 337 mm or 148 mm depending on the degree of liquid limitation. That is, it was necessary to reduce the bed height of the cases where $\gamma < 2$ in order to keep the conversion in the measurable range (10–90%). For the shortest bed, the bed height was ~70 times the equivalent particle diameter (1.9 mm).

The catalyst was 1% Pd egg-shell on porous cylindrical alumina extrudate (Engelhard) with diameter 1.5 mm and length 4.3 ± 1.8 mm (equivalent diameter 1.9 mm, particle to column diameter ratio ~26). It was activated in situ at 120°C for 5 h with hydrogen flowing at the operating velocity. After activation, the catalyst activity decreases before it stabilizes (compare Wu et al.[12]). Consequently, it was necessary to operate the reactor for a prolonged period (~9 h) at a liquid velocity of 3.4 mm/s in the Kan-Liquid mode in order to reach stable operation. During this time, the activity was monitored by sampling the reactor effluent intermittently and calculating the conversion. After an initial decrease the conversion stabilized at ~6 h. As a final check, the conversion of a Kan-Liquid mode experiment at the end of the experimental program yielded approximately the same conversion as the initial stabilization run, thereby confirming that the catalyst was stable throughout the experimental program.

Additional experimental considerations were taken as follows:

- The absence of homogeneous side reactions was confirmed by operating the setup with only glass beads (no catalyst) loaded into the reactor. No reaction was detected. A polymerization inhibitor (*p-tert*-butylcatechol) present in the feed is likely to be responsible for the absence of oligomeric or polymeric activity.[28]
- At the reaction conditions, the vapor pressures of AMS, cumene, and hexane are well below 30 kPa.[29] Therefore, there is little expectation of liquid vaporization.
- The presence of hydrodynamic effects on the reaction rate was confirmed by performing two liquid-limited reaction experiments. In the first, 158 g of catalyst were loaded and the liquid superficial velocity was set to 2.7 mm/s (yielding a weight hourly space velocity of 0.12). The conversion was 44%. Another bed was then packed with 500 g of catalyst and the liquid velocity was set to 8.4 mm/s (again the weight hourly space velocity was 0.12). The conversion for this run was 81%. For a chemically controlled reaction rate, the conversion is a function of the space velocity and not the superficial velocity (as shown in Wu et al.[12]). These two experiments, therefore, show that hydrodynamic effects are present—the high superficial velocity in the second run facilitates transport to the catalyst and therefore yields a higher conversion.

Since hysteresis is involved, the exact operating procedure needs to be reported. The catalyst was saturated internally with feed by leaving the reactor flooded with feed overnight. Because of capillary action, the catalyst interior is expected to remain filled throughout the experiments. The bed was then drained with the gas flowing at the operating velocity for 15 min. The liquid was introduced at the lowest velocity and steady state was achieved. After the last steady state sample that had been taken, the liquid flow rate was increased to the next higher setting. This was repeated until the highest setting had been completed (i.e. the Levec mode). The liquid flow rate was then increased to 9.4 mm/s (pulsing flow) for 20 s and reduced to the 4.4 mm/s. After that operating condition had been completed, the liquid flow rate was reduced to the next lowest setting and so on until the Kan-Liquid mode had been completed. Several of the runs (five in each mode) were repeated in order to determine the reproducibility of results. These runs were conducted by establishing a Levec point (i.e., increasing the flow rate from zero to the operating velocity, e.g. 1.9 mm/s), then increasing the flow rate to 9.4 mm/s (pulsing) and then decreasing it directly back to 1.9 mm/s (i.e., the Kan-Liquid point). The repeat runs are shown on the figures in the results section. In most instances, the reproducibility was within a few percent. Although there were differences in a limited number of cases, the trends of which prewetting mode yielded higher conversions were never reversed.

Results and Discussion

Figures 3a–c and 4a,b 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 behavior of a gas-limited system. To keep conversions low enough to be properly measurable, the catalyst bed height was halved for the experiments depicted in Figures 3c and 4. The hydrogenation reaction is considered mildly exothermic ($-\Delta H = 110$ kJ/mol), and corresponding temperature rises in the reactor are shown in Figures 3d–f and 4c,d. 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). A representative plot of the measured pressure drop (Figure 5) in both modes show trends similar to those observed in literature, although the difference between the modes is only about 5–25% (probably because of the low gas velocity used here, as well as the end effects and the presence of the glass bead beds inside the reactor).

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 3), 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 4), 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:[30]

$$P = \frac{XC_{\mathrm{B,feed}}Q_{\mathrm{L}}}{W_{\mathrm{Pd}}} \tag{2a}$$

$$P_{\mathrm{difference}} = \frac{P_{\mathrm{Kan-L}} - P_{\mathrm{Levec}}}{P_{\mathrm{Levec}}} \times 100\% \tag{2b}$$

For gas-limited conditions ($\gamma = 4.6$ and 2.5), the productivity is roughly 10–15% higher in the Kan-Liquid mode. For liquid-limited conditions ($\gamma = 0.48$), the productivity is 2–20% higher in the Levec mode (14% on average). It seems as though the modes are equally productive when $\gamma = 1$. The productivity difference between modes is shown in Figure 6 as a function of γ or $1/\gamma$ (a γ value of 2 for the gas-limited

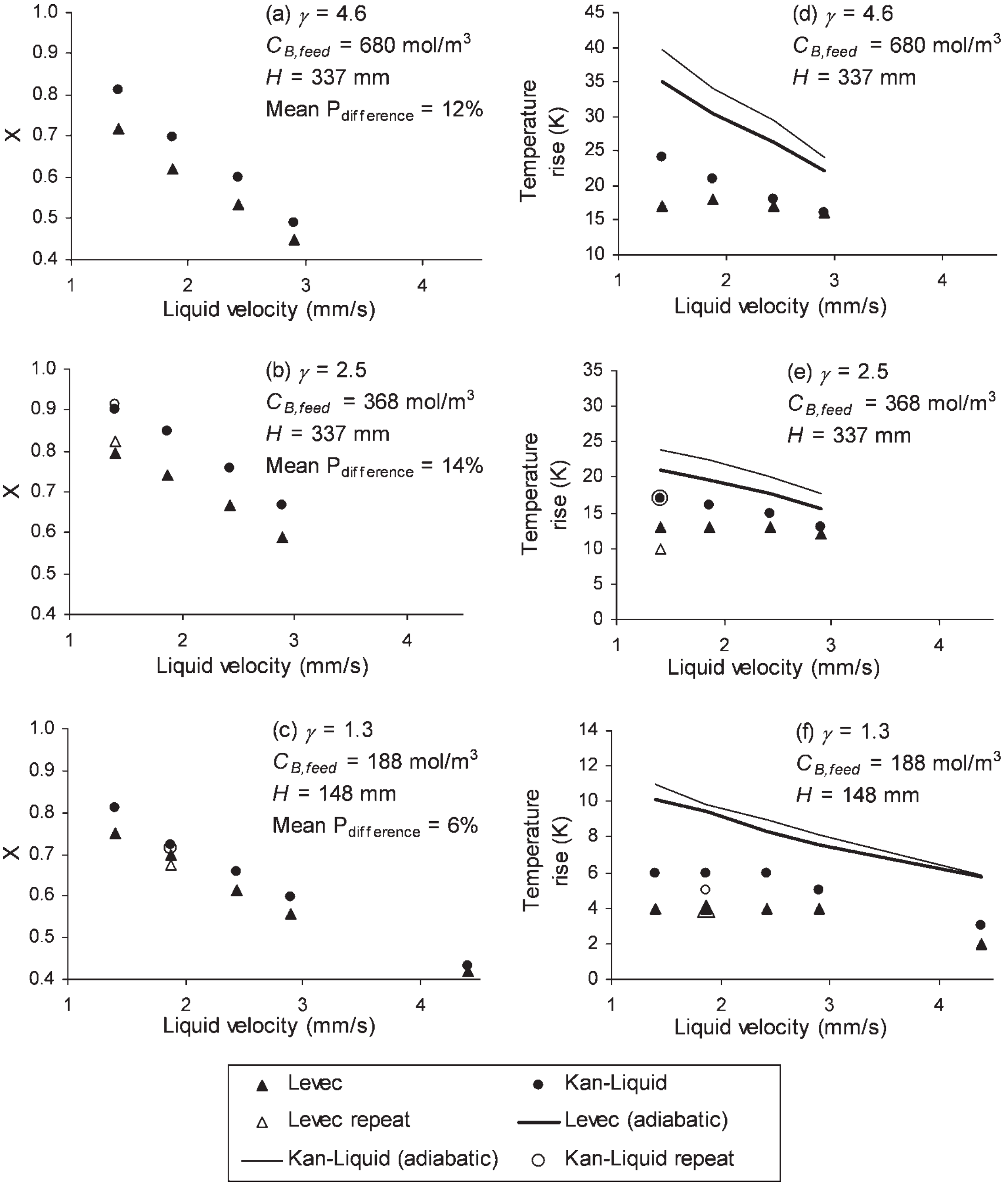

Figure 3. Gas-limited results.

(a) Conversion and (d) corresponding temperature rise for $\gamma = 4.6$. (b) Conversion and (e) corresponding temperature rise for $\gamma = 2.5$. (c) Conversion and (f) corresponding temperature rise for $\gamma = 1.3$. Bed heights for (a–b) and (d–e) are 337 mm. Bed height for (c–f) is 148 mm.

condition corresponds to a $1/\gamma$ 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 prewetting 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 behavior. To start, a comparison between the gas-limited exothermic reaction data of Rajashekharam et al.[13] and the gas-limited condition (Figure 3) reveals a fundamental dissimilarity in the thermal behavior. 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 nonadiabatic 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 with the increasing liquid velocity leg, Levec). The hysteresis was therefore attributed to the fact that the bed was warmer

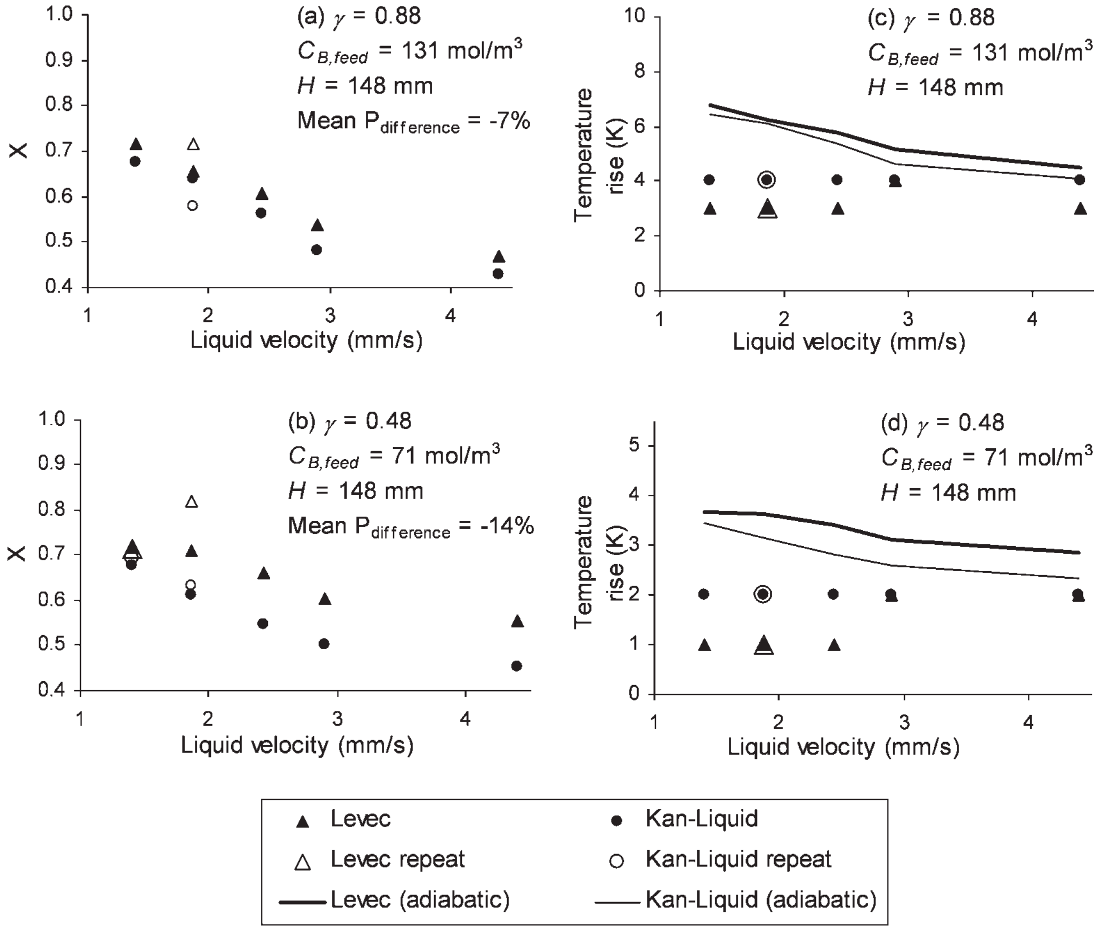

Figure 4. Liquid-limited results.

(a) Conversion and (b) corresponding temperature rise for γ = 0.88. (b) Conversion and (d) corresponding temperature rise for γ = 0.48. All bed heights equal to 148 mm.

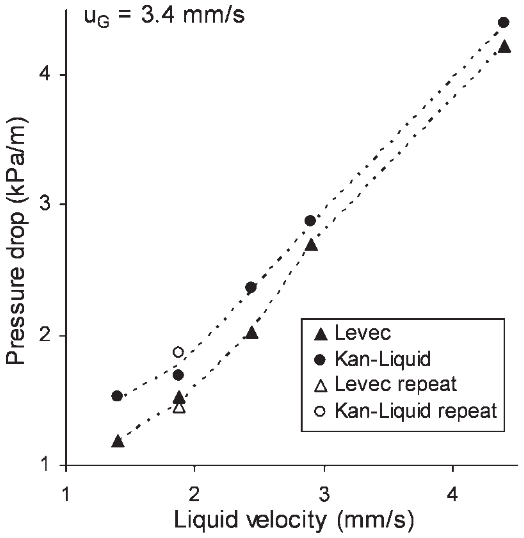

Figure 5. Representative pressure drop vs. superficial liquid velocity plot.

Dotted lines are added for interpretation.

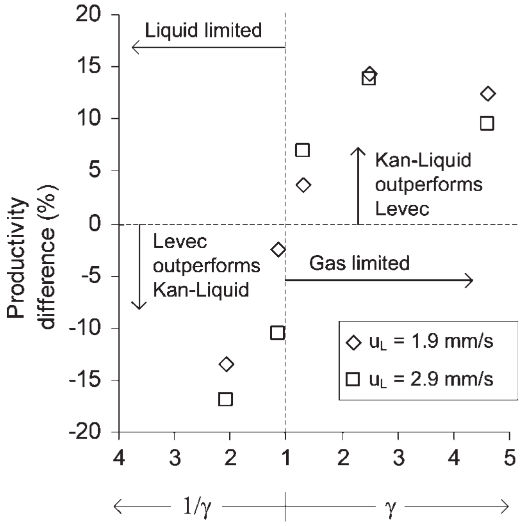

Figure 6. The difference in productivity between the two hydrodynamic modes as a function of the extent of gas or liquid limitation.

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 3e 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 behavior. Instead, the higher conversion because of hydrodynamic effects in turn resulted in a higher bed temperature. This interpretation is further supported by the liquid-limited data (Figure 4), 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 prewetting procedure), it is likely that the wetting efficiency is close to 1.[31] The focus should therefore be on the gas–liquid and liquid–solid mass transfer steps for hydrogen, and $(k_{\mathrm{LS}}a_{\mathrm{LS}})_A$ is typically an order of magnitude larger than $k_{\mathrm{GL}}a_{\mathrm{GL}}$ (compare for example the data of Tan and Smith[32] to that of Goto and Smith[25]). 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 $k_{\mathrm{LS}}a_{\mathrm{LS}}$ because of hydrodynamic multiplicity are therefore insignificant compared with changes in $k_{\mathrm{GL}}a_{\mathrm{GL}}$. 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 behavior 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 1). The present results are in agreement with the work of Ravindra et al.[24] 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 3) despite the expectation of a lower average wetting efficiency (Table 1). 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 needs 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}.[33] Also, the mass transfer area (a_{LS}) is 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:

$$\frac{[k_{\mathrm{LS}}a_{\mathrm{LS}}]_{\mathrm{Levec}}}{[k_{\mathrm{LS}}a_{\mathrm{LS}}]_{\mathrm{Kan-L}}} = \left(\frac{[\varepsilon_{\mathrm{L}}]_{\mathrm{Kan-L}}}{[\varepsilon_{\mathrm{L}}]_{\mathrm{Levec}}}\right)^{\frac{1}{2}} \left(\frac{[f]_{\mathrm{Levec}}}{[f]_{\mathrm{Kan-L}}}\right) \tag{3}$$

In Eq. 3, the power of 0.5 is predicted by film theory and was confirmed over a wide range of operating conditions.[17] Evaluation of Eq. 3 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[31] (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.[9] 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 1). 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 4). A proper evaluation of the effect of prewetting 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.

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 behavior 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 optimizing the hydrodynamic conditions in the reactor by exploiting the multiplicity behavior in order to suit specific reaction conditions. In more general terms, this study reemphasizes the need for a more complete and preferably fundamentally sound understanding of trickle bed hydrodynamics based on experimental investigations.

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Notation

a = specific interfacial area (m^2/m^3)
C = concentration in the liquid phase (mol/m^3)
d = equivalent particle diameter (m)
D = diffusivity (m^2/s)
f = wetting efficiency (−)
g = gravitational acceleration constant (m/s^2)
Ga = Galileo number, $Ga = \frac{d^3 g \rho^2}{\mu^2}$
ΔH = heat of reaction (kJ/mol)
k = mass transfer coefficient (m/s)
P = productivity (mol/kg s)
Q = volumetric flow rate (m^3/s)
Re = Reynolds number, $Re = \frac{u \rho d}{\mu (1-\varepsilon)}$
Sc = Schmidt number, $Sc = \frac{\mu}{\rho D}$
u = superficial velocity (m/s)
W_{Pd} = mass of Pd (kg)
X = conversion
γ = limitation indicator
ε = bed porosity
ε_{p} = particle porosity
ε_{L} = liquid holdup
μ = viscosity (Pa s)
ρ = density (kg/m^3)

Subscripts

A = gas phase reagent (hydrogen)
B = liquid phase reagent (AMS)
G = gas
i = phase (either A or B)
L = liquid

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