

Comparison of Upflow and Downflow Two-Phase Flow Packed-Bed Reactors with and without Fines: Experimental Observations

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This study compares the performance of laboratory trickle-bed and upflow reactors over a range of operating conditions, using the hydrogenation of α -methylstyrene to cumene in hexane solvent over 2.5% Pd on alumina extrudate catalyst as a test reaction. It is shown that the trickle bed performs better than the upflow reactor at low pressures when the reaction is gas limited, due to ready access of the gas to the incompletely externally wetted catalyst, while the upflow reactor performs better at high pressures when the liquid reactant limitation controls the rate, due to the completely wetted catalyst. Comparison of the two reactors at different pressures, liquid reactant feed concentrations, and gas flow rates is presented, and differences in performance are explained based on the observed shift from gas limitation to liquid limitation. Experiments in beds diluted with fines yield identical performances in both upflow and downflow modes of operation under both gas- and liquid-limited conditions, corroborating the fact that hydrodynamics and kinetics can be decoupled by using fines. It is also shown that the advantage of upflow or downflow depends on whether liquid or gas reactant is rate limiting and that a single criterion for identifying the limiting reactant can explain most of the data reported in the literature on these two modes of operation.

Introduction

Trickle-bed reactors are packed beds of catalyst over which liquid and gas reactants flow cocurrently downward, whereas in packed bubble columns the two phases are in upflow. Trickle-bed reactors, due to the wide range of operating conditions that they can accommodate, are used extensively in industrial practice, both at high pressures (e.g., hydroprocessing, etc.) and at normal pressures (e.g., bioremediation, etc.). In laboratory-scale trickle beds, packed with the commercially used catalyst shapes and sizes, the reactor to catalyst particle diameter ratio is undesirably low, and low liquid velocity is frequently used in order to match the liquid hourly space velocity (LHSV) of the commercial unit. These conditions give rise to wall effects, axial dispersion, maldistribution, and incomplete external catalyst wetting which are not observed to the same extent in commercial reactors. Hence, in laboratory reactors, an accurate estimate of catalyst wetting efficiency is essential to determine their performance (Duduković and Mills, 1986; Beaudry et al., 1987). The reaction rate over externally incompletely wetted packing can be greater or smaller than the rate observed over completely wetted packing. This depends on whether the limiting reactant is present only in the liquid phase or in both gas and liquid phases. For instance, if the reaction is liquid limited and the limiting reactant is nonvolatile, such as occurs in many hydrogenation processes, then a decrease in the catalyst–liquid contacting efficiency reduces the surface available for mass transfer between the liquid and catalyst, causing a decrease in the observed reaction rate. However, if the reaction is gas limited (and/or the reactant is in the gas phase as in the case of the volatile liquid reactant), the gaseous reactant can easily access the catalyst pores from the externally dry areas and consequently, a higher reaction rate is observed with a decreased level of external catalyst wetting (Duduković and Mills, 1986; Beaudry et al., 1987). The above analysis is based on the assumption that particles in trickle beds are always

internally wetted, which has been confirmed for all but extremely exothermic processes that generate vapors. Kim and Kim (1981) present the criterion that allows one to estimate when an internal pore dryout can occur. This is not the case in the studies presented here. Thus, the difficulties of using trickle-bed reactors in laboratory-scale investigation for scale-up and scale-down are mainly caused by the interactions between the gas, the liquid, and the solid–catalyst phases, all of these interactions being strongly dependent on the reacting system used. Hence, upflow reactors are often used in laboratory-scale studies for testing catalysts and alternative feedstocks for commercial trickle-bed processes, since in them complete catalyst wetting is ensured and better heat transfer (due to a continuous liquid phase) and higher overall liquid–solid mass-transfer coefficients can be achieved. However, as will be shown in the present study and as the diversity of literature results discussed herein indicate, the relative merit and the performance of upflow and trickle bed is dependent on the reaction system used. Upflow, as a test reactor, may not portray the trickle-bed reactor performance for scale-up and scale-down for each and every reaction and operating condition. It is, therefore, important to investigate the comparative performance of both reactors in order to address the following important questions: (a) When will upflow outperform downflow and vice versa? (b) When can upflow be used to produce accurate scale-up data for trickle-bed operation?

No systematic study has been reported which compares the performance of downflow and upflow operation over a wide range of operating conditions, particularly reactor pressure. The few studies that are available in the open literature do not relate the observed performance to the type of reaction system used (gas-limited or liquid-limited), nor do they conclusively elucidate which is the preferred reactor for scale-up and scale-down. Goto and Mabuchi (1984) concluded that, for atmospheric pressure oxidation of ethanol in the presence of carbonate, downflow is superior at low gas and

liquid velocities but upflow should be chosen for high gas and liquid velocities. Beaudry et al. (1986) and Mills et al. (1984) studied atmospheric pressure hydrogenation of α -methylstyrene at high concentrations and observed the downflow performance to be better than upflow except at very high conversion. Mazzarino et al. (1989) observed higher rates in upflow than in downflow for ethanol oxidation and attributed the observed phenomenon to better effective wetting in upflow, without considering the type of reaction system (gas or liquid limited). Liquid holdup measurements at elevated pressures, using water/glycol as the liquid phase with H_2 , N_2 , Ar, or CO_2 as the gas phase, by Larachi et al. (1991) indicate that liquid saturation is much greater in upflow than in downward flow at all the pressures studied (up to 5.1 MPa). Lara Marquez et al. (1992) studied the effect of pressure on upflow and downflow using chemical absorption and concluded that the interfacial area and the liquid-side mass-transfer coefficient increase with pressure in both cases. Goto et al. (1993) observed that downflow is better than upflow at atmospheric pressure (for hydration of olefins) and noted that the observed rates in downflow were independent of gas velocity, while those in upflow were slightly dependent on it. Thus, it is obvious that there is no clear guidance as to which reactor will perform better for a given reaction system. An extensive study of the effect of operating conditions is necessary to understand the interplay of factors in the particular reacting system in order to explain why these reactors perform differently and whether upflow can be used for scale-up in each case. We provide the rationale behind the literature results and their conclusions in the Results and Discussion section. This gives us the rules by which to a priori judge whether an upflow or downflow reactor is to be preferred for laboratory testing.

Another alternative for scale-up and scale-down studies that is practiced in industry is the use of trickle-bed reactors diluted with fines (which are inert particles, an order of magnitude smaller compared to the catalyst pellets). The lack of liquid spreading due to the use of low liquid velocities in laboratory reactors is compensated by fines which provide additional solids contact points over which liquid films flow. This improves liquid spreading and helps achieve the same liquid-solid contacting in laboratory reactors as obtained in industrial units at higher liquid superficial velocities. Fines decouple the hydrodynamics and the kinetics and provide an estimate of the true catalyst performance of the industrial reactor by improving wetting and catalyst utilization in a laboratory-scale unit at space velocities identical to those in industrial reactors. The diluted-bed studies reported in the open literature investigated the performance of downflow only but did not compare it with upflow performance (without or with fines), nor did they incorporate the impact of the reaction system (Van Klinken and Van Dongen, 1980; Carruthers and DeCamillo, 1988; Sei, 1991; Germain, 1988; Al-Dahhan, 1993). It is noteworthy to mention that the use of fines in upflow reactors would eliminate the possibility of channeling.

In this study, we investigate the comparative performance of laboratory trickle-bed and upflow reactors, without and with fines, and the dependence on the reaction system used, over a wide range of operating conditions covering both gas- and liquid-limited reactions. For this purpose, hydrogenation of α -methylsty-

Table 1. Catalyst and Reactor Properties

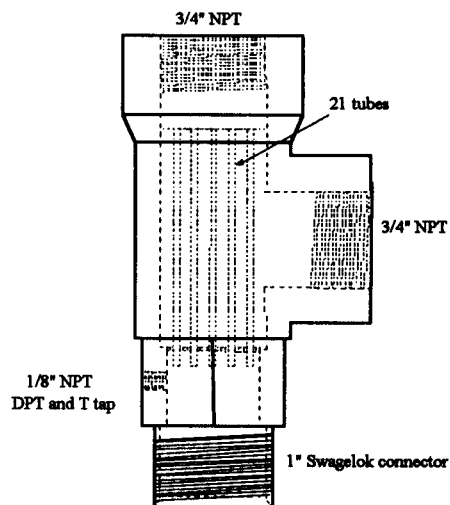
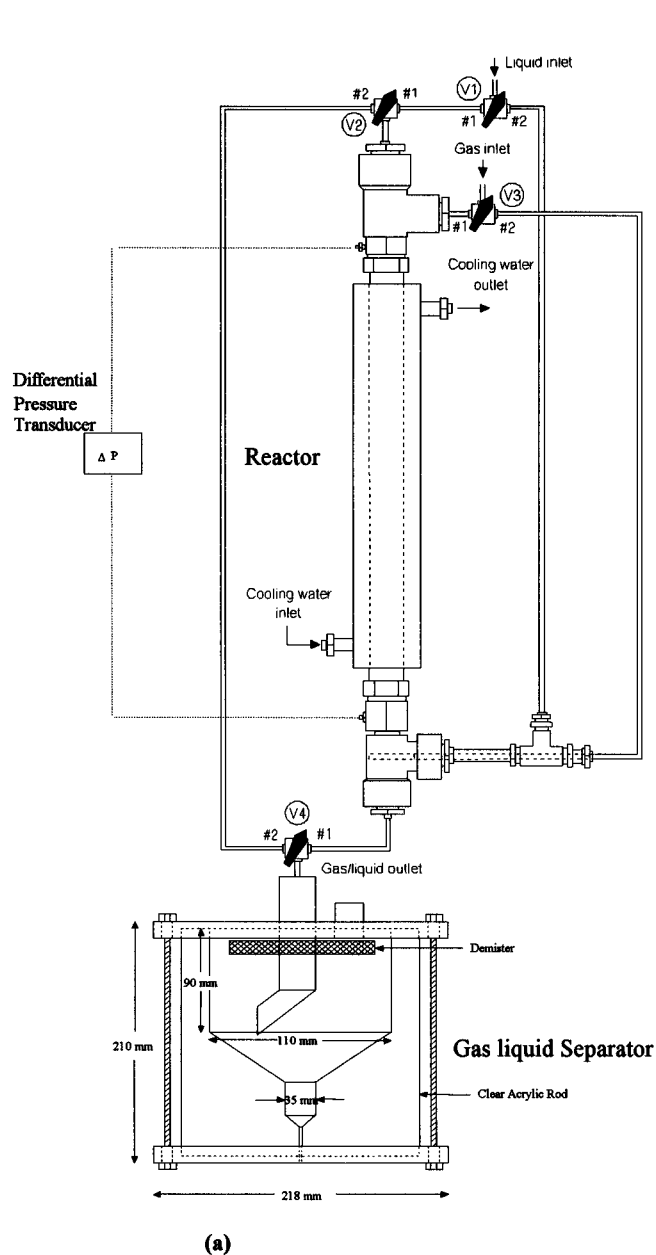
| Catalyst Properties | |
|-------------------------------------------|--------------------|
| active metal | 2.5% Pd |
| catalyst support | alumina |
| packing shape | cylinder |
| packing dimensions (cm) | 0.13×0.56 |
| surface area (m^2/g) | 184 |
| total pore volume (cm^3/g) | 0.481 |
| pellet density ρ_p (g/cm^3) | 1.222 |
| true pellet density ρ_t (g/cm^3) | 2.965 |
| pellet porosity ϵ_p | 0.5878 |
| Reactor Properties | |
| total length (cm) | 50 |
| catalyst length (cm) | 27.5 |
| diameter (cm) | 2.2 |
| Fines | |
| material | silicon carbide |
| diameter (cm) | 0.02 |

rene to cumene in hexane solvent over 2.5% Pd on alumina $1/16$ in. extrudate catalyst is utilized as a test reaction.

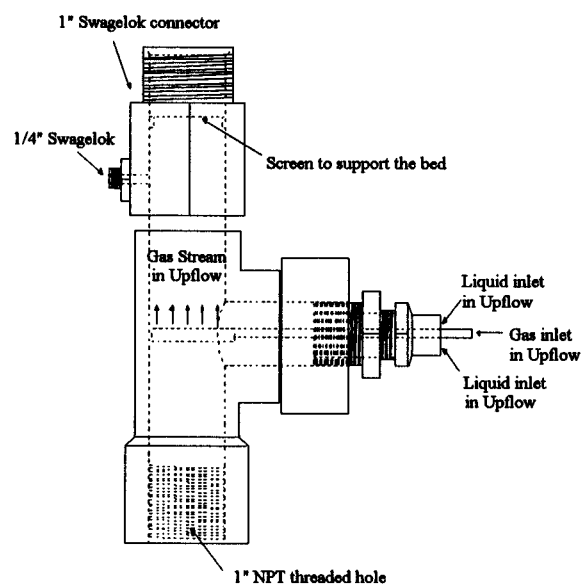
Experimental Work

The high-pressure packed-bed reactor facility used in this study has been described in detail elsewhere (Al-Dahhan, 1993; Al-Dahhan et al., 1995). The main components of this facility are the reactor section, the gas-liquid distributor (for trickle-bed operation), the gas distributor (for upflow operation), and the gas-liquid separator as shown in Figure 1. The same bed of catalyst is used (once it is activated and packed) for both modes of operation. For trickle-bed reactor operation, all the valves are set to position #1, while for upflow operation all the valves are set to position #2 (Figure 1). The upflow distributor was tested using a clear acrylic reactor to ensure that no channeling of gas occurs during upflow operation. Since all the experiments were done with a prewetted bed (i.e., completely flooded bed) and a uniform distributor, it is very unlikely that any pellets were not contacted by liquid and remained internally dry. As mentioned earlier, in the absence of a strongly exothermic vapor-generating reaction, the pellets remain completely internally wetted.

Catalyst (2.5% Pd on alumina extrudate (properties as listed in Table 1)) supplied by Engelhard was packed to a height of 27.5 cm, with glass beads (3 mm diameter) packed on both sides to a total reactor length of 50 cm. α -Methylstyrene (Eastman Kodak) in hexane (ACS grade, 99.9% purity) was used as the liquid phase delivered to the reactor by a precalibrated high-pressure pump. Pure hydrogen (prepurified, analytical grade) bubbled through a hexane saturator (to prevent evaporation of hexane in the reactor) was used as the gas phase. The jacketed reactor was kept isothermal readily due to a dilute liquid reactant in the feed (at a room temperature of 24 °C the maximum temperature rise is 2 °C). At these conditions very little loss of liquid can occur due to volatilization. The liquid reactant can, therefore, be considered nonvolatile. Liquid samples were drawn from the gas-liquid separator after steady state was reached at each liquid flow rate (about 20–25 min, after which no further change in the exit concentration of α -methylstyrene was observed). The samples were analyzed on a gas chromatograph (Gow Mac Series 550, with thermal conductivity detector), from which the conversion of α -methylstyrene was



(b) Downflow Distributor



(c) Upflow Distributor

Figure 1. (a) Reactor and gas-liquid separator. (b and c) Downflow and upflow distributors.

determined. Pressure drop across the bed was measured using a differential pressure transducer as shown in Figure 1. Experiments were conducted at a fixed gas flow rate by varying the liquid flow rate for each mode of operation. The stability of the catalyst over the duration of the experiments was verified by taking intermittent samples at identical operating conditions. The reproducibility of the data was observed to be within 3%. The range of operating conditions investigated in this study is presented in Table 2.

Upon completion of the entire set of experiments with the above-described catalyst bed, the catalyst was discharged and repacked with fines (silicon carbide, 0.02 cm particles) using a reproducible packing procedure developed in our laboratory by Al-Dahhan et al. (1995). Runs as those described above were also conducted with fines to study the effect of fines on the performance of downflow and upflow modes of operation.

Prior to the above-mentioned experimentation, stirred basket reactor tests were performed to establish a

reproducible catalyst activation procedure and to test the stability of the catalyst before undertaking the packed-bed reactor studies. Preheating in an inert (nitrogen) atmosphere to 140 °C followed by activation with hydrogen at reaction temperature (~24 °C) yielded consistent activity for over 40 h of operation (after an initial 9 h of stabilization runs). Figure 2 shows the plot of activity with time for the reaction conducted in the basket reactor.

Results and Discussion

Theoretical Background. The performance of upflow and downflow reactors depends upon the type of reaction, i.e., whether gas (reactant) limited or liquid (reactant) limited. A simple and usable criterion for establishing gas or liquid limitation is needed. In order to obtain such a criterion for the complex processes involved, a step by step comparison of the different transport processes contributing to the observed rate,

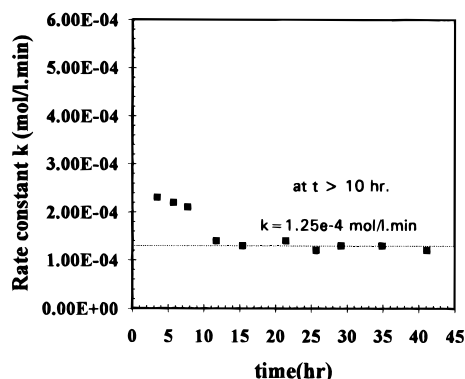


Figure 2. Basket reactor catalyst stability test.

Table 2. Range of Operating Conditions

| | |
|------------------------------------------------|-------------------------------------------------------------------------------------|
| temperature | 24 °C |
| pressure | 30–200 psig (3–15 atm) |
| concentration of α-methylstyrene | 3.1–7.8% (v/v) (230–600 mol/m ³) |
| superficial gas velocity (mass velocity) | 3.8–14.4 cm/s (3.3 × 10 ⁻³ –12.8 × 10 ⁻³ kg/m ² s) |
| superficial liquid velocity (mass velocity) | 0.09–0.5 cm/s (0.63–3.85 kg/m ² s) |

as illustrated below, is required. For a typical reaction $A(g) + bB(l, \text{nonvolatile}) = \text{products}(l)$, the limiting step can be identified by first comparing the estimated rates of mass transfer with the observed reaction rates. The estimated volumetric mass-transfer coefficients for the system under study can be evaluated from appropriate correlations in the literature (e.g., $(ka)_{GL}$ from Fukushima and Kusaka (1977) and k_{LS} from Tan and Smith (1982)). The comparison of these with the experimentally observed rates, $(r_A)_{obs}$ as per inequality (1), where C_A^* is the gas solubility at the conditions of interest, confirms that external gas reactant mass transfer does not limit the rate, if inequality (1) is satisfied. This was

$$\begin{aligned} (ka)_{GL} &\gg (r_A)_{obs}/C_A^* \\ k_{LS}a_{LS} &\gg (r_A)_{obs}/C_A^* \end{aligned} \quad (1)$$

the case in the present study.

The observed rate in the above criterion is the mean rate for the reactor evaluated from the mass balance on the system. For systems where the conversion space–time relationship is highly nonlinear, criterion (1) should be applied at the exit of the reactor also. The limiting reactant can then be identified by further comparing the effective diffusivity terms with the observed rate. This can be achieved by evaluation of the Weisz modulus ($\phi_{We} = (r_A)_{obs}(V_p/S_x)^2/(D_e C)$, where $D_e C$ is the smaller of the two, $D_{eB}C_{Bi}/b$ or $D_{eA}C_A^*$) (which

for our reaction system yielded $\phi_{We} > 1$ (see Table 3)). In order to identify the limiting reactant in the case of $\phi_{We} > 1$, the diffusional fluxes of the two reactants should be compared, whereas, for $\phi_{We} < 1$, it is the liquid reactant concentration and the gas reactant dissolved concentration that counts. Thus, the limiting reactant can be identified by evaluation of the $D_e C$ terms and examining the ratio of this product (effective diffusivities and concentration) of both reacting species in the range of operating conditions of interest (Doraiswamy and Sharma, 1984). This ratio ($\gamma = (D_{eB}C_{Bi})/b(D_{eA}C_A^*)$) is indicative of the relative availability of the species at the reaction site. Thus, a value of $\gamma \gg 1$ would imply a gaseous reactant limitation, while $\gamma \ll 1$ indicates liquid reactant limitation for the conditions mentioned above. This criterion is relied on for analyzing our results as well as the literature data.

The limiting reactant in a gas-limited reaction can enter the porous particles through both the actively and inactively wetted surfaces, but it enters at different rates (Mills and Duduković, 1980). Accordingly, for a gas-limited reaction, the trickle-bed reactor is expected to perform better due to its partially wetted catalyst, over which gas reactant has an easy access to the particles, than the upflow reactor, in which the only access of the gaseous reactant to the catalyst is through the liquid film engulfing the catalyst. In a liquid-limited reaction, a nonvolatile liquid reactant can only enter the catalyst particle through its actively wetted surface, leaving the inactively wetted areas unutilized. Liquid-limited conditions for a nonvolatile liquid reactant, therefore, result in a better performance in upflow, where particles are completely surrounded by liquid, than in downflow, where particles may be only partially wetted.

The literature data confirm the above assertion and the use of the proposed criterion for identifying the limiting reactant (values of ϕ_{We} and γ are listed in Table 3). The experimental data of Goto and Mabuchi (1984) have γ values in the range of 300 (approximate estimate using reported concentration and molecular diffusivities), which indicates a clear gas-limited behavior, and so their observation that downflow performs better than upflow at low liquid and gas velocities is a forgone conclusion. Beaudry et al. (1987) operated under γ values ranging between 20 and 100, and again downflow outperformed upflow, except at very high conversion when γ was lower than 3 and liquid reactant limitations occur, as explained by Beaudry et al. (1986), in which case upflow tends to perform close to downflow. The range of γ values ($\gamma = 0.5$ –17) encountered by Mazzarino et al. (1989) shows both liquid- and gas-limited regimes. At one set of conditions ($\gamma = 0.5$) liquid

Table 3. Identification of the Limiting Reactant for Literature and Present Data^a

| | rate(obs) (mol/m ³ s) | V_p/S_x (m) | C_A^* (mol/m ³) | C_{Bi} | D_{eB}/D_{eA} | Weisz modulus (ϕ_{We}) | γ | limiting reactant |
|------------------|-------------------------------------|-----------------------|----------------------------------|-----------------------|-----------------|----------------------------------|----------|----------------------|
| Goto (1984) | 1.50×10^{-2} | 9.50×10^{-4} | 0.977 | 6.00×10^{-2} | 0.51 | 39.5 | 314 | gas |
| Beaudry (1987) | 1.7 | 3.24×10^{-4} | 3.76 | 1.71×10^{-3} | 0.20 | 21.0 | 92 | gas |
| Mazzarino (1989) | | | | | | | | |
| extreme I* | 5.0×10^{-4} | 5.58×10^{-4} | 0.55 | 0.55 | 0.51 | 1.52 | 0.51 | liquid |
| extreme II* | 3.0×10^{-2} | 5.58×10^{-4} | 1.66 | 55.31 | 0.51 | 15.3 | 17 | gas |
| Goto (1993) | 1.0×10^{-2} | 1.3×10^{-4} | 12.0 | 5.5×10^{-4} | 2.2 | 0.04 | 10300 | gas |
| this study | | | | | | | | |
| extreme I** | 1.4 | 2.91×10^{-4} | 14.0 | 520 | 0.23 | 107.7 | 8.8 | gas |
| extreme II** | 1.1 | 2.91×10^{-4} | 63.0 | 2.37×10^{-2} | 0.23 | 21.4 | 0.87 | liquid |

^a Extreme I*: low liquid reactant feed concentration, atmospheric pressure. Extreme II*: high liquid reactant feed concentration, atmospheric pressure. Extreme I**: high liquid reactant feed concentration, low pressure. Extreme II**: low liquid reactant feed concentration, high pressure.

limitation is indicated based on our criterion and the fact that upflow outperforms downflow can be anticipated. However, Mazzarino et al. (1989) report that upflow performs better than downflow even at $\gamma = 17$, which should be a gas-limited reaction. It may be noted that their experiments on downflow (Tukac et al., 1986) and upflow (Mazzarino et al., 1989), while using presumably the same catalyst, were not performed at the same time. Our experience with active metals on alumina catalyst (Mazzarino et al. used Pt on alumina) is that exactly the same state of catalyst activity is very difficult to reproduce after repeated regeneration. This sheds some doubt on whether the two sets of data can be compared. In addition, at the temperature used, ethanol will not behave as a nonvolatile reactant and does not satisfy the conditions of our hypothesis. Goto et al. (1993) report downflow performance superior to upflow for their reaction system, for which estimates of γ yield values of over 8000, which is why any short circuiting of the gas via the dry areas yields higher gas-transfer rates to particles and hence higher conversion in downflow.

In the present study, γ values range from 0.7 to 10 and individual results can be explained on the basis of this ratio. However, it must be noted here that exact evaluation of effective diffusivities, and, hence, γ , requires effectiveness factor data which were not available for the literature cases, and approximate values based on molecular diffusivity ratios have been used to obtain reasonable estimates. The estimates for D_{eB} and D_{eA} for the present study are based on the basket reactor tests and are accurate enough to give fairly precise estimates of γ .

Comparison of the Performance of Trickle-Bed and Upflow Reactors without Fines. Comparison of the two reactors is achieved by studying the conversion at identical volumetric nominal space times (defined as reactor length/superficial liquid velocity) and identical reactant feed concentration. This is the proper scale-up variable (space time = $3600/\text{LHSV}$), when the beds for upflow and downflow are identically packed (i.e., bed voidage = constant) and the reaction rate is based per unit volume of the catalyst. At low pressure (30 psig) and high feed concentration of α -methylstyrene ($C_{Bi} = 7.8\% \text{ v/v}$), the reaction is gas limited ($\gamma = 8.8$). In this case downflow performs better than the upflow reactor as shown in Figure 3a. This is due to the nature of the hydrogenation reactions which are typically hydrogen (gas reactant) limited at low pressure (at or just above atmospheric) and high α -methylstyrene concentrations (Beaudry et al., 1987). It is obvious that this is due to low hydrogen solubility at these pressures. In downflow mode of operation, the catalyst particles are not fully wetted at the liquid flow rates used (Figure 4 shows contacting efficiency calculated using the correlation of Al-Dahhan and Duduković (1995)). This facilitates the access of the gas reactant to the pores of the catalyst on the externally dry parts and reduces the extent of gas limitation compared to fully wetted pellets in the upflow reactor. The result is a higher conversion in downflow than in the upflow mode of operation. In the case of upflow, since the catalyst is almost completely wetted, the access of gaseous reactant to the catalyst site is limited to that through liquid film only. This provides an additional resistance for the gaseous reactant (especially at high space time, i.e., low liquid flow rate) and results in conversion lower than that obtained in downflow. This effect is more prominent

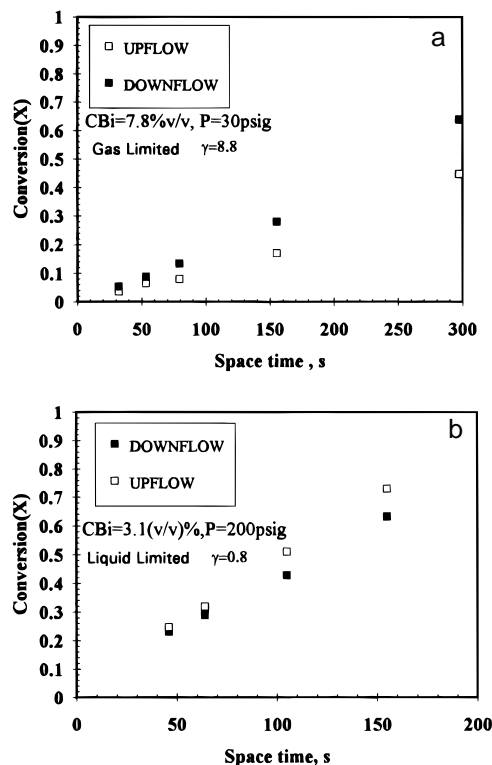


Figure 3. (a) Trickle-bed and upflow performance at $C_{Bi} = 7.8\% \text{ (v/v)}$ and $U_g = 4.4 \text{ cm/s}$ at 30 psig. (b) Comparison of downflow and upflow performance at $C_{Bi} = 3.1\% \text{ (v/v)}$ at 200 psig.

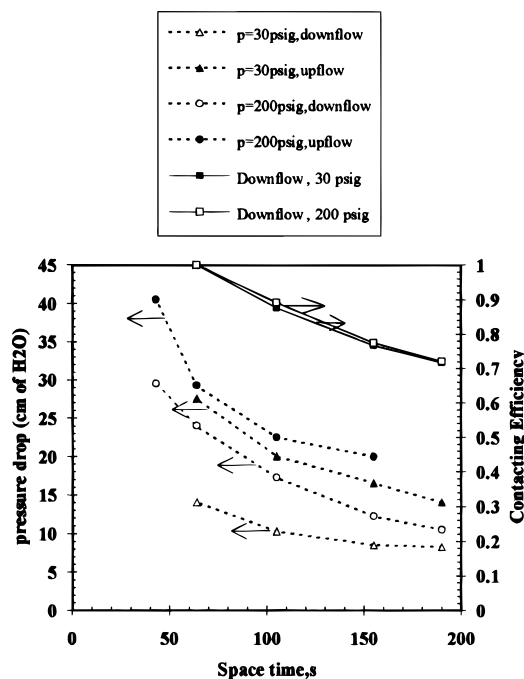


Figure 4. Pressure drop in downflow and upflow reactors and contacting efficiency for downflow reactor at 30 and 200 psig.

at higher liquid reactant feed concentrations, due to the larger extent of gas limitation at such conditions (higher γ values). As liquid mass velocity increases (space time decreases), the downflow performance approaches that of upflow, due to a catalyst wetting efficiency approaching that of upflow (contacting efficiency approaches 1 as seen in Figure 4).

As the reactor pressure increases and the feed concentration of α -methylstyrene decreases, the value of γ decreases and the reaction approaches liquid limited

behavior as postulated earlier. This is reflected in a complete reversal in performance at higher pressures and at low α -methylstyrene concentration (Figure 3b), where the performance of upflow becomes better than downflow. This is because under these conditions the catalyst in downflow is still partially wetted (since at the operating gas velocities and gas densities (hydrogen), high pressure only slightly improves wetting in downflow (Figure 4 based on Al-Dahhan and Duduković, 1995), while catalyst is fully wetted in upflow. In a liquid-limited reaction, the conversion will be governed by the degree of catalyst wetting, and since upflow has higher wetting (100%) than downflow, it will outperform downflow. As the liquid mass velocity increases and the contacting efficiency of downflow approaches 100%, the performance of the two reactors approaches each other, as evident in Figure 3b at low space times. Thus, as pressure is increased from 30 to 200 psig and the feed concentration of α -methylstyrene is decreased from 7.8 to 3.1% (v/v), the reaction is transformed from a gas-limited ($\gamma = 8.8$) to a liquid-limited regime ($\gamma = 0.8$). The criterion (γ) is dependent on two factors (apart from the diffusivity ratio), pressure (hydrogen solubility) and feed concentration of the liquid reactant (α -methylstyrene). Further insight into the gas and liquid limitation can be obtained by investigating these two contributions individually for the set of operating conditions examined.

(a) Effect of Reactor Pressure on Individual Mode of Operation. As the reactor pressure increases, the performance of both upflow and downflow improves due to an increase in the gas solubility, which both helps the rate of transport to the wetted catalyst (in both modes) and improves the driving force for gas to catalyst mass transfer to the inactively wetted catalyst in the downflow mode. At low feed concentration of the liquid reactant (α -methylstyrene (3.1% v/v)) and at high pressure (> 100 psig), the reaction becomes liquid reactant limited (or liquid reactant affected), as can be seen from parts a and b of Figure 5, where no further enhancement is observed when pressure is increased from 100 to 200 psig (where γ drops from 1.5 at 100 psig to 0.8 at 200 psig). This means that any further increase in the reactor pressure, and hence liquid phase hydrogen concentration, will have a minimal effect since hydrogen is not the limiting reactant anymore.

To confirm the above observation, the reaction was studied at a higher feed concentration of α -methylstyrene (4.8% v/v) in order to determine whether gas-limited behavior is observed at higher γ values. The performance indeed improves when pressure is increased from 100 to 200 psig (Figure 6), implying that the reaction is not completely liquid limited at this feed concentration at 100 psig operating pressure ($\gamma = 2.44$). It becomes liquid limited at pressures above 200 psig ($\gamma = 1.3$) at this feed concentration, whereas it is liquid limited at lower α -methylstyrene concentration (3.1% v/v) even at lower pressures as noted previously in parts a and b of Figure 5. Both upflow and downflow conversion increases with increasing pressure, primarily due to an increase in the solubility of the gaseous reactant as the pressure increases. A significant improvement in performance (conversion) occurs when pressure is changed from 30 to 100 psig as compared to the change in conversion when pressure changes from 100 to 200 psig. This confirms that the effect of pressure diminishes when liquid limitation is approached (as γ approaches 1.0 from above (Figure 6)).

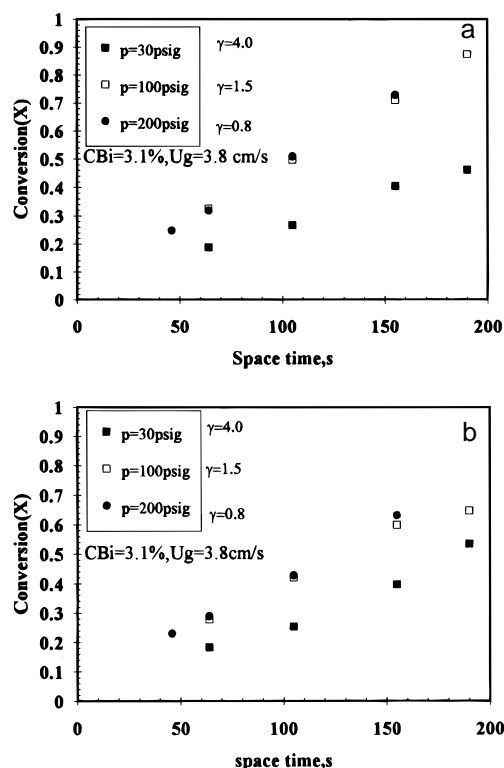


Figure 5. (a) Effect of pressure at low α -methylstyrene feed concentration on upflow reactor performance. (b) Effect of pressure at low α -methylstyrene feed concentration (3.1% v/v) on downflow performance.

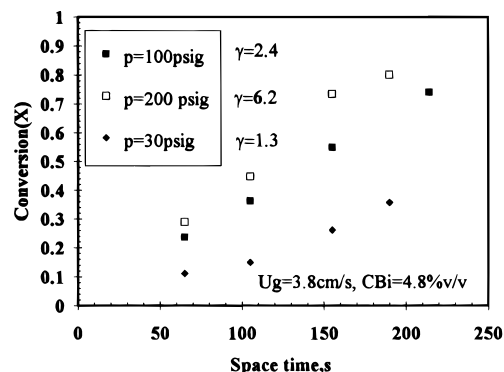


Figure 6. Effect of pressure at higher α -methylstyrene feed concentration on downflow performance.

Experimental pressure drop measurements were also made for both modes of operation during the reaction runs. The data obtained (shown in Figure 4) indicate higher pressure drops for upflow at both ends of the pressure range covered (30 and 200 psig) than for downflow, which is in agreement with expectation and the pressure drop data reported in the literature. The higher downflow performance (conversion) at 30 psig, despite lower pressure drop, confirms that poor contacting does yield better conversion due to reaction being gas limited, which seems contrary to the notion that higher transport always involves higher pressure drop (which is observed to be true here in the case of liquid-limited reaction at 200 psig).

(b) Effect of Feed Concentration of α -Methylstyrene on Individual Mode of Operation. Atmospheric pressure hydrogenation of α -methylstyrene has been known to be a zeroth-order reaction with respect to α -methylstyrene and first-order with respect to hydrogen (Beaudry et al., 1986). Our observations confirm that, at 30 psig as well as at 100 psig, the

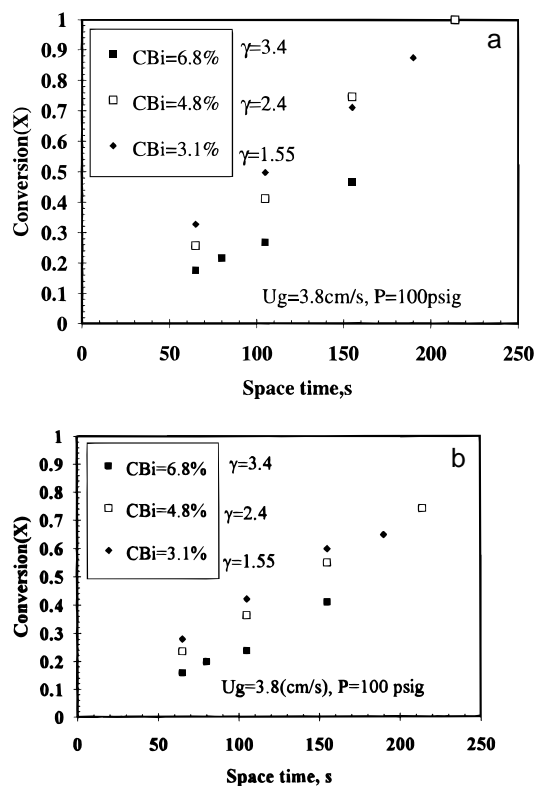


Figure 7. (a) Effect of α -methylstyrene feed concentration at 100 psig on Upflow Performance. (b) Effect of α -methylstyrene feed concentration at 100 psig on downflow performance.

reaction is zero-order with respect to α -methylstyrene as shown in parts a and b of Figure 7 for upflow and downflow, respectively. An inverse proportionality of conversion with liquid reactant feed concentration (typical of zero-order behavior) is observed especially at higher liquid flow rates (lower space times). At lower liquid flow rates, at 100 psig the zero-order dependence appears to vanish and a first-order dependence (due to α -methylstyrene transport or intrinsic rate limitations), i.e., conversion independent of feed concentration, is observed. This shift in feed concentration dependence is confirmed by data at higher pressure (200 psig; Figure 8a,b). When liquid limitation is observed, there is no effect of feed concentration on the conversion in either mode of operation, as can be seen in parts a and b of Figure 8. This is a consequence of the liquid (reactant) transport or intrinsic rate limitation which shows up as a first-order dependence, making conversion independent of feed concentration.

The effect of gas velocity on reactor performance was also examined for both upflow and downflow reactors. A significant effect was not observed in the range of the gas velocities studied (3.8–14.4 cm/s, i.e., gas Reynolds number in the range of 6–25) on either downflow or upflow performances at all the concentrations tested. This is in agreement with the observations of Goto et al. (1993).

Comparison of the Performance of Trickle-Bed and Upflow Reactors with Fines. Fines (nonporous inert particles, order of magnitude smaller than catalyst pellets packed only in the voids of the catalyst) are used to investigate the performance of the two modes of operation using the same reaction in an attempt to demonstrate the decoupling of hydrodynamic and kinetic effects. A way to establish this decoupling is to use the upflow and downflow modes, which are intrinsically hydrodynamically different (as discussed earlier),

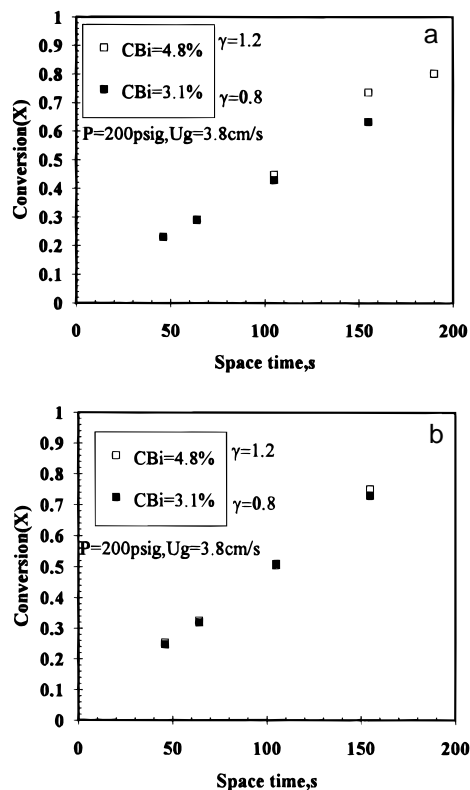


Figure 8. (a) Effect of α -methylstyrene feed concentration at 200 psig on downflow performance. (b) Effect of α -methylstyrene feed concentration at 200 psig on upflow performance.

and assess whether fines can indeed yield the “true” kinetic behavior (more properly called “apparent” rates on catalyst pellets of interest, i.e., rates unmasked by external transport resistances and hydrodynamic effects). The two extreme cases discussed before, i.e., gas limitation (downflow performance better than upflow, Figure 3a) and liquid limitation (upflow performance better than downflow, Figure 3b), are now conducted in the presence of fines. Parts a and b of Figure 9 show the performance of both reactors when the bed is diluted with fines. It can be seen by comparing Figure 9a with Figure 3a and Figure 9b with Figure 3b that fines have eliminated the disparities between the two modes of operation even in the extreme cases of reactant limitation. This is primarily due to the fact that fines improve liquid spreading considerably and achieve comparable (and almost complete) wetting in both modes of operation. It must be noted that Figures 3a and 9a, or Figures 3b and 9b, could not be directly superimposed due to slightly different catalyst activity obtained after repacking the bed with fines and catalyst and reactivating it. Nevertheless, fines have successfully decoupled the hydrodynamics and apparent kinetics, and the data with fines reflect the kinetics in the packed bed under “ideal” liquid distribution conditions. It can be observed in Figure 9a that, at low liquid flow rate and low pressure (gas limited reaction), a trickle bed with fines still performs slightly better than upflow with fines, which indicates that the degree of wetting is still not complete in downflow, resulting in some direct exposure of the internally wetted but externally dry catalyst to the gas. This may be due to the fact that, at low liquid flow rate even with fines, the catalyst is not completely externally wetted (Al-Dahhan and Duduković, 1995). At high pressure (liquid-limited reaction) Figure 9b reveals identical performances of both reactors where complete wetting is achieved in both modes.

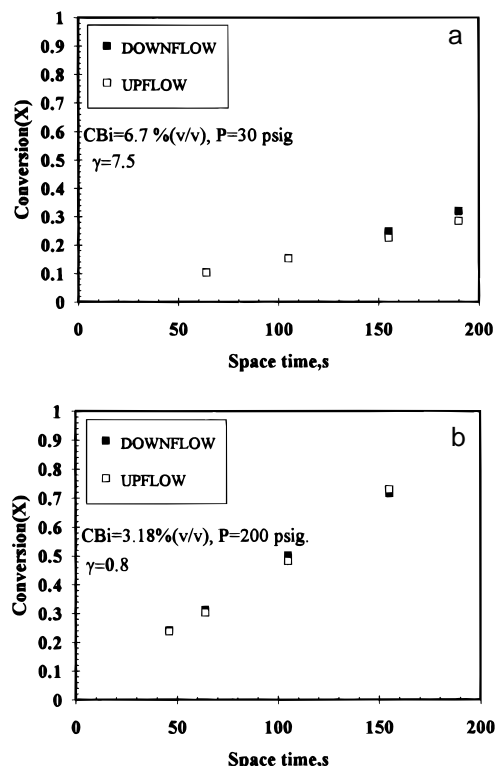


Figure 9. (a) Effect of fines on low-pressure downflow versus upflow performance. (b) Effect of fines on high-pressure downflow versus upflow performance.

Since we studied the impact of the two factors, pressure and feed concentration on the performance without fines, the same study was conducted for the bed diluted with fines.

(a) Effect of Pressure in the Diluted Bed on Individual Mode of Operation. The effect of pressure on the performance of both modes of operation in beds with fines is illustrated in parts a and b of Figure 10. At higher pressure the performance of both upflow and downflow is better than that at low pressure. This observation, and the reasoning behind it, is also consistent with the data obtained without fines.

(b) Effect of Feed Concentration in the Diluted Bed on Individual Mode of Operation. At 30 psig, the conversion is higher at lower feed concentration of α -methylstyrene (lower two curves for downflow (Figure 10a) and upflow (Figure 10b). At higher reactor pressure, there is no effect of feed concentration (upper two curves, Figure 10a,b). This was also observed for the reactors without fines and explained on the basis of liquid limitation in the previous section. The fact that it is observed with fines confirms the feed concentration dependence (of performance) in the case of gas- and liquid-limited reactions.

Conclusions

Performance (conversion) comparison of downflow and upflow modes of operation of laboratory packed-bed reactors over a range of identical feed and pressure conditions yields two conclusions. Gas-limited conditions imply better downflow performance (due to easier access of the gas to the partially externally wetted catalyst areas in downflow), while liquid-limited conditions result in better upflow performance over downflow. Conversion is seen to improve with pressure in the gas-limited domain and remains fairly constant once liquid limitation sets in. Zero-order behavior with respect to

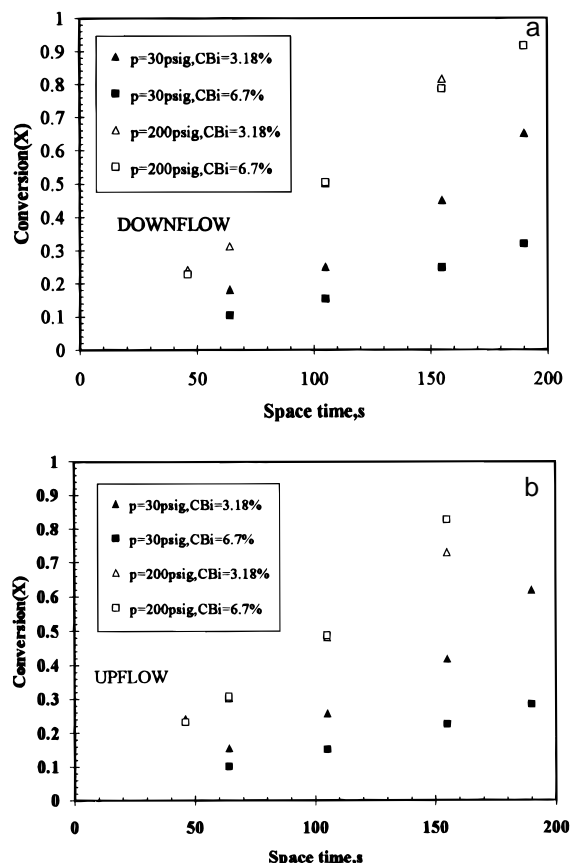


Figure 10. (a) Effect of α -methylstyrene feed concentration at different pressures on performance of downflow with fines. (b) Effect of α -methylstyrene feed concentration at different pressures on performance of upflow with fines.

liquid reactant feed concentration is exhibited at the gas-limited end, and first-order behavior with respect to the liquid reactant (either transport or kinetic) at the liquid-limited end. Gas velocity has no significant effect on the performance of either mode of operation in the range of velocities examined.

Studies of the downflow and upflow mode of operation in a bed diluted with fines under identical conditions show that fines do indeed neutralize the differences between the two modes of operation for both gas- and liquid-limited conditions and successfully decouple hydrodynamics (flow pattern and wetting) and apparent kinetics. This implies that the performance of the diluted bed is not dependent on the reactant limitation and flow mode used. This conclusion is important in establishing the use of fines in laboratory-scale reactors as an effective and viable scale-up tool possibly to be preferred to upflow reactors. While one can argue that upflow reactors also provide rates on completely wetted particles and, hence, to some extent decouple the kinetics and hydrodynamics, they do so only at the expense of increased liquid holdup which can alter the relative amount of homogeneous and heterogeneous reactions occurring in more complex systems and should be avoided. In addition, upflow can lead to more dispersion and flow non-idealities than encountered in beds with fines. Finally, holdup and flow regimes in diluted beds are closer to those in trickle beds than in upflow.

Further understanding and quantitative comparison of the performance with and without fines, under upflow and downflow conditions, requires detailed modeling which is currently under investigation.

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Nomenclature

C_A^* = concentration of gaseous reactant in liquid phase (mol/m³)
 C_{Bi} = concentration of liquid reactant in liquid phase (mol/m³)
 D_{eA} = effective diffusivity of gaseous reactant in the catalyst (m²/s)
 D_{eB} = effective diffusivity of liquid reactant in the catalyst (m²/s)
 D_{mA} = molecular diffusivity of gaseous reactant in the catalyst (m²/s)
 D_{mB} = molecular diffusivity of liquid reactant in the catalyst (m²/s)
 $(ka)_{GL}$ = volumetric gas-liquid mass-transfer coefficient (1/s)
 $k_{LS}a_{LS}$ = volumetric liquid-solid mass-transfer coefficient (1/s)
 P = reactor pressure (psig)
 $(r_A)_{obs}$ = observed rate of reaction (mol/m³)
 S_x = catalyst external surface area (m²)
 V_p = catalyst pellet volume (m³)
 U_g = gas velocity (m/s)
 $\gamma = (D_{eB}C_{Bi})/b(D_{eA}C_A^*) \sim (D_{mB}C_B)/b(D_{mA}C_A^*)$
 ϕ_{We} = Weisz modulus, $(r_A)_{obs}(V_p/S_x)^2/(D_e C)$

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