Gas-Phase Reaction in a Trickle-Bed Reactor Operated at Low Liquid Flow Rates

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The catalytic hydrogenation of alpha-methylstyrene to cumene is studied in a laboratory trickle-bed reactor operated at low liquid flow rates. Under this condition, wetting is not complete, vaporization of the liquid phase may occur, and reaction could proceed via liquid-solid and gas-solid catalysis, which increase the hydrogenation rate significantly. To determine and quantify the effect of the gas-solid catalyzed reaction, we propose the use of post-packing sections of increasing lengths. The inert bed acts as an absorber of the gas-phase-produced cumene. The liquid and gas effluent were monitored. Experimental global rates determined from liquid cumene concentrations varied with the post-packing length. A simple one-dimensional model developed shows that theoretical and experimental results agree well.

Introduction

The behavior of trickle-bed reactors (TBR) operated at low liquid flow rates is extremely complex. Under this condition, wetting is not complete and regions of the catalytic bed might be bypassed by the flowing liquid reactant. The reaction rate over externally incomplete 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 gas phase or both liquid and gas phases. Some degree of partial wetting can be found in industrial units (Khadilkar et al., 1996).

If the reaction is exothermic and gas reactant limited (as in many hydrogenation reactions), vaporization of the liquid phase may occur and reaction between the gas-phase reactant, the vaporized liquid reactant, and the catalyst (gas-solid catalyzed reaction) could still proceed in the nonwetted regions. With no heat removal from the liquid phase, this might result in localized hot spot formation that can have a deleterious effect on reactor performance (Watson and Harold, 1993). Also, the vaporization phenomenon might result in higher reaction rates and temperatures. If controlled, rate and temperature increments may be exploited to achieve higher conversions, as in the periodic interruption experiments performed by Castellari and Haure (1995).

The occurrence under steady-state conditions of vaporization of the liquid phase is well documented. Sedriks and Kenney (1973) studied the reduction of crotonaldehyde over a Palladium catalyst and found that even when the extent of wetting was large, reaction taking place on the dry areas of the catalyst largely dominated the overall reaction rate.

Watson and Harold (1993) used a single catalytic pellet reactor to study dynamic multiphase reactor transport interactions. They measured pellet weight (liquid holdup) and center temperatures and developed a phenomenological mechanism of drying with exothermic reaction. Cini and Harold (1991) developed a new type of multiphase catalyst: the tubular supported ceramic membrane. The hydrogenation of alpha methyl styrene was selected as a model reaction. Apparent activation energy analysis revealed that for catalyst temperatures below 40°C, the rate is kinetically controlled and catalyst utilization nearly complete. A reduction in the activation energy above 40°C indicates the onset of transport controlled, gas-solid catalyzed reaction. Watson and Harold (1994) reported the existence of phase transition during the hydrogenation of cyclohexene, an exothermic multiphase reaction, using a single catalytic pellet reactor. Simultaneous measurements of the pellet temperature and weight were used to demonstrate the coexistence of gas-solid and liquid-solid catalyzed reaction.

Hessari and Bhatia (1996) also studied the hydrogenation of cyclohexene over a Pd single pellet catalyst. The authors reported the existence of multiple steady states and hysteresis effects obtained while cycling the hydrogen partial pres-

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sure. One important inference of this work is the important role played by the startup procedure: The vapor-filled steady state displaying a higher reaction rate and temperature rise may be attained when starting with a dry bed, while the predominantly liquid-filled steady state may arise with an initially wetted condition.

Ruzicka and Hanicka (1994) studied the hydrogenation of cyclohexene to cyclohexane in a model TBR in which three steady states were distinguished: a gaseous-phase reaction regime with externally, fully dry catalyst particle, a liquid-phase reaction mixture with a catalyst external surface totally covered with liquid reaction mixture, and, eventually, a mixed-phase reaction regime where part of the reactor was externally, completely wetted by the liquid reaction mixture and the other part was externally, completely dry.

Flow patterns in TBR operated at low liquid flow rates resemble the later behavior if the reaction is exothermic. Zones may exist in which the pellets are completely dry and the reaction proceeds on gas contacted catalyst surfaces. In the coolest zones, the pellets are likely to be completely filled with liquid and reaction occurs via liquid-solid catalysis, that is, between the dissolved gas reactant, the liquid reactant, and the catalyst.

Castellari and Haure (1995) studied the hydrogenation of AMS in a laboratory TBR and observed an interesting feature at the lowest flow rate considered (0.23 cm^3/s). After the initial three hours of the run, visual observation of the bed showed that the degree of wetting had diminished dramatically. At the same time, a rise in the temperature of about 12°C was recorded, and the reaction rate was increased up to a factor of 2. Rate and temperature enhancement were attributed to partial wetting effects.

The objective of this work is to measure and quantify the effect of the gas-solid catalyzed reaction in a laboratory TBR operated at low liquid flow rates. Hydrogenation of α-methylstyrene (AMS) into cumene over Pd/Al_2O_3 was used as a model reaction. Under certain circumstances, the experimental conversions found in the present study are higher than those reported previously (Herskowitz et al., 1979; Castellari and Haure, 1995) or predicted by models which only take into account the reduction of mass-transfer resistances. If the rate of generation of cumene in the gas phase is higher than the mass-transfer rate to the flowing liquid phase, cumene will build up in the gas phase. When a total condenser is used, the vaporized organics are recovered and recycled before being vented. However, in many cases, recovery is only partial. In any case, since analysis of the gas effluent is not performed, the use of a condenser probably masks the presence of a gas-phase reaction.

Table 1. Reactor Characteristics

Diameter	2.54 cm ID
Depth of pre-packing	12 cm
Type of pre-packing	Glass beads
Depth of catalytic bed	1.5 cm
Mass of catalyst	3.48 g
Depth of post-packing	5 cm (TBR1) 50 cm (TBR2)
Type of post-packing	Glass beads
Catalytic bed void fraction	0.48
Inert bed void fraction	0.48

Table 2. Catalyst Specifications

Palladium content (global)	0.5 wt. %
Active layer thickness	250 μm
Activation method	Reduction on hydrogen atmosphere
Particle size	2–3.2 mm
Support	γ alumina
Mean diameter	2.72 mm
Intraparticle porosity	0.60
BET surface area	70 m^2/g

In order to determine the presence and effect on reactor performance of the gas-phase reaction, we propose the use of post-packing sections of increasing lengths. To improve mass transfer between the phases, the length of the inert post-packing section was increased. The inert bed acted as an absorber of the gas-phase produced cumene. Liquid and gas effluent compositions were monitored. Experimental global rates determined from the liquid cumene concentrations varied with the post packing length.

A one-dimensional model was developed considering three different zones: Prepacking inert section in which H_2 is saturated with AMS; catalytic bed; and post packing inert section that acts as an absorber of the cumene produced in the gas phase.

Theoretical and experimental results are in agreement.

Experimental Procedure

The experimental setup and procedure were described previously (Castellari and Haure, 1995). Reactor data are summarized in Table 1. Catalyst properties and operating conditions are given in Tables 2 and 3, respectively. Gas and liquid effluent samples were withdrawn periodically and analyzed in a GC (Hewlett-Packard 5890 A) equipped with a PONA capillary column and a flame ionization detector. Low reproducibility of gas-phase values determined that only liquid samples were used to evaluate the rates, calculated following the Morita and Smith (1978) procedure for differential semi-batch reactors. Local bed temperatures were obtained by means of a thermocouple inserted axially in the middle of the catalytic bed and recorded continuously by a data acquisition device.

Results

Steady-state experiments started with the bed initially preflooded. Samples were withdrawn after 1 h of starting an experiment. Liquid cumene concentration was used to calculate global rates (reaction and mass transfer). Figures 1 and 2 show global rates against liquid flow rates for post packing lengths of 5 cm (TBR1) and 50 cm (TBR2), respectively. Obviously, the reaction rate is the same for both TBR configurations, but TBR2 results are higher due to enhanced mass transfer in the postpacking section. However, at high liquid rates, the

Table 3. Operating Conditions

Temperature	40°C
Pressure	1 atm
Gas flow rate	15 cm^3/s
Liquid flow rate	0.048–6 cm^3/s

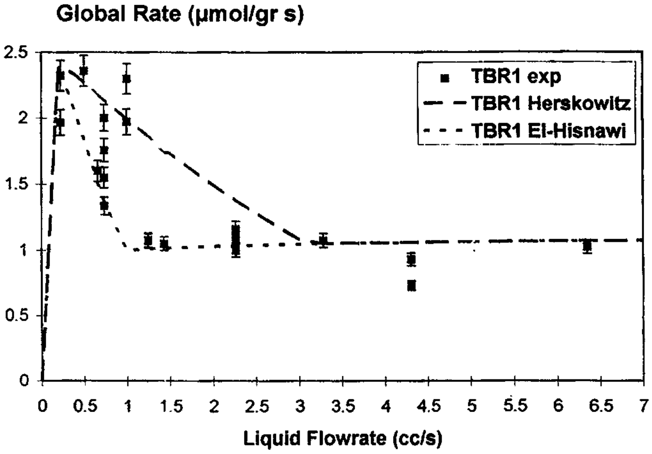

Figure 1. Global rates vs. liquid flow rate for TBR1 (short postpacking configuration).

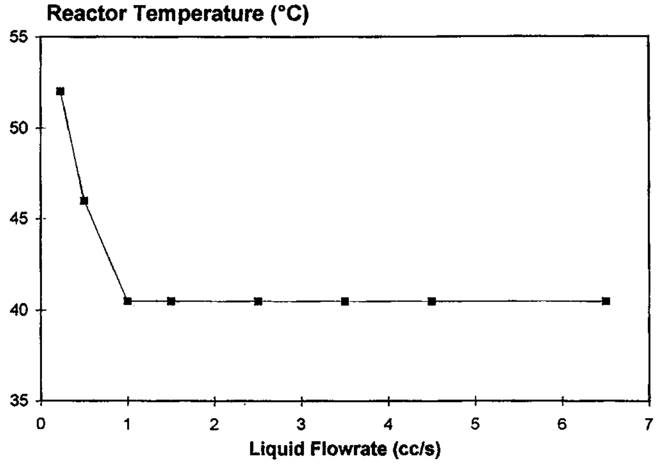

Figure 3. Reaction temperature vs. liquid flow rate.

difference is smaller. For liquid flow rates below 1.5 cm^3/s, visual observation of the bed indicated incomplete wetting of the catalyst. The system exhibited effectiveness enhancement. The maximum reaction rate occurs under incomplete wetting conditions. Similar results were found by others (Herskowitz et al., 1979; Funk et al., 1991; McManus et al., 1993).

At low liquid flow rates, bed temperature increases as shown in Figure 3 for TBR1. Similar results are found for TBR2. According to Watson and Harold (1993), under partial wetting conditions, the heat generated is not fully dissipated by the flowing liquid phase and this is responsible for the temperature increase. However, as indicated in Figures 1 and 2, global rate data evaluated from liquid cumene concentrations are higher for TBR2. Our explanation is that the rate of generation of cumene via gas-phase catalysis is higher than the mass-transfer rate to the flowing liquid phase for both reactors. In any case, cumene will concentrate in the gas phase. However, when the inert post packing section is longer (TBR2) mass transfer is enhanced and more cumene is transferred from the gas to the liquid phase. In TBR2, gas-phase cumene concentration approaches equilibrium. This is shown in Figures 4 and 5. Figure 4 presents deviations from equilibrium values for effluent gas and liquid samples withdrawn from TBR1 and TBR2. Better agreement is found for TBR2 data.

The equilibrium curves at different temperatures (40 and 50°C) were evaluated from Raoult's law as

$$Y_C = \frac{P_C \cdot X_C \cdot 100}{P_B(1 - X_C) + P_C X_C} \qquad (1)$$

where Y_C is the gas molar fraction of cumene free of hydrogen, and X_C is the liquid molar fraction of cumene free of hydrogen. P_C and P_B are vapor pressures of cumene and alpha methyl styrene. Vapor pressures at 40 and 50°C were calculated from Watson and Harold (1993). Concentrations are expressed in molar fractions free of hydrogen to compare with the experimental data. The effect of localized heating in the composition of the gas phase is addressed by considering the equilibrium at different temperatures. If localized heating occurs, then the partial pressure of cumene and AMS will exceed the values expected for 40°C. However, since the va-

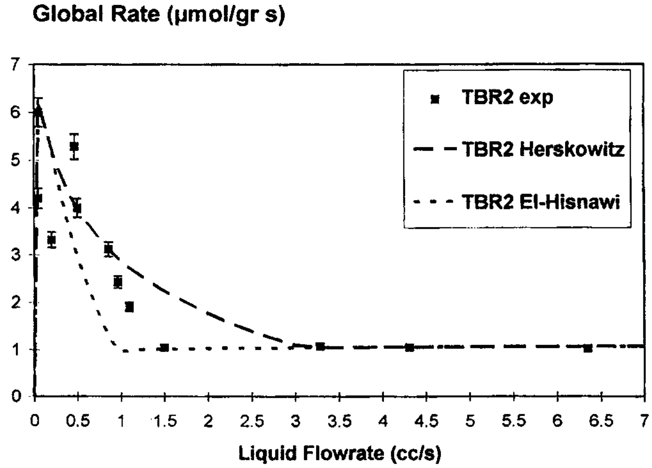

Figure 2. Global rates vs. liquid flow rate for TBR2 (long postpacking configuration).

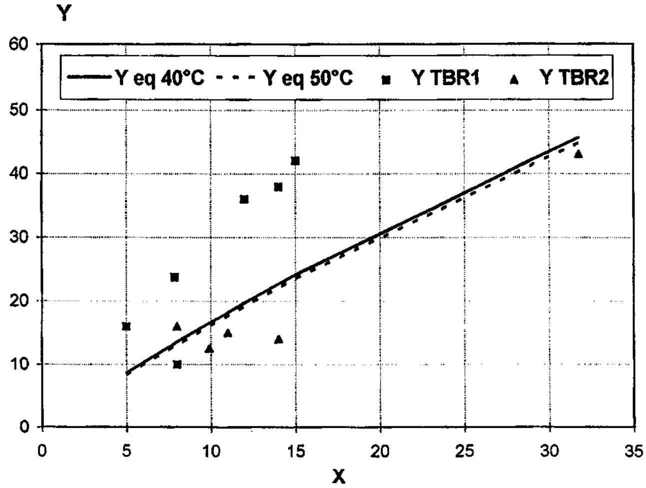

Figure 4. Gas vs. liquid cumene concentrations free of hydrogen.

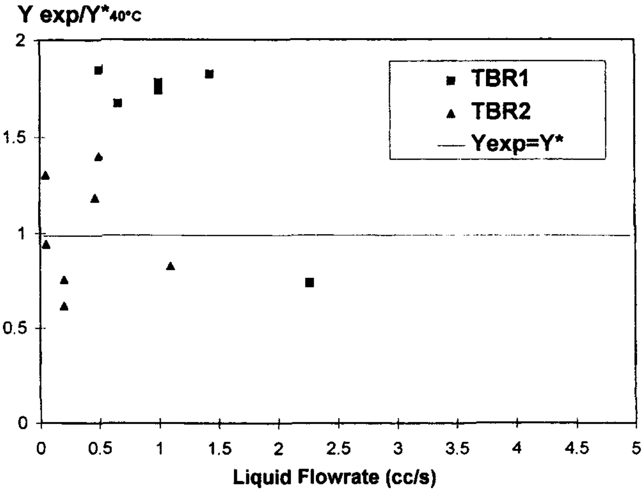

Figure 5. Dimensionless concentration vs. liquid flow rate.

por pressures of both components are of the same order of magnitude, the molar fraction of cumene free of hydrogen (Y_c) remains nearly constant. Furthermore, AMS partial pressure increases more with temperature than cumene's, so that the equilibrium curve for cumene at 50°C falls below that at 40°C. Experimental concentrations obtained with TBR1 are greater than the values predicted considering equilibrium: The above-equilibrium cumene gas phase mole fractions may be indicative of a gas-solid catalyzed reaction.

Figure 5 shows dimensionless concentrations (Y/Y^*40°C) values for both reactor configurations vs. liquid flow rates. Data for TBR2 are close to equilibrium. TBR1 presents deviations at low liquid flow rates, when partial wetting and gas-solid catalyzed reaction effects are important and cumene produced in the gas phase is not completely transferred to the liquid phase. For liquid flow rates above 1.5 mL/s, concentration values approach equilibrium: at high liquid flow rates, wetting is complete and reaction proceeds via liquid-solid catalyzed reaction.

Model Development

To describe the behavior presented in the previous sections, a one-dimensional model is developed. The model considers the irreversible reaction between the gas reactant (A) and a volatile liquid reactant (B) within a partially wetted, porous catalytic pellet. A fraction of the outer pellet surface is wetted by a liquid film consisting of the liquid reactant B and the dissolved gas A. The pellet is immersed in a gas atmosphere consisting of gas reactant A saturated with B. Liquid-solid and gas-solid catalytic reactions take place according to the following kinetics

$$A(g \rightarrow l) + B(l) \rightarrow \quad C(l) \quad r_w = k_w C_A$$

$$A(g) + B(g) \rightarrow \quad C(g) \quad r_n = k_n C_B$$

r_w and r_n are reaction rates in liquid-phase and gas-phase catalysis; C_A and C_B are concentrations in bulk liquid and gas phase. The overall reaction rate constant k_w was evaluated from steady-state experiments at high liquid flow rates ($k_w \eta$ = 0,4 cm^3/gr·s) (Castellari and Haure, 1995). The value of k_n (rate constant of reaction in nonwetted part) was not determined, since we assume that gas-solid mass-transfer resistance governs this step (Cini and Harold, 1991).

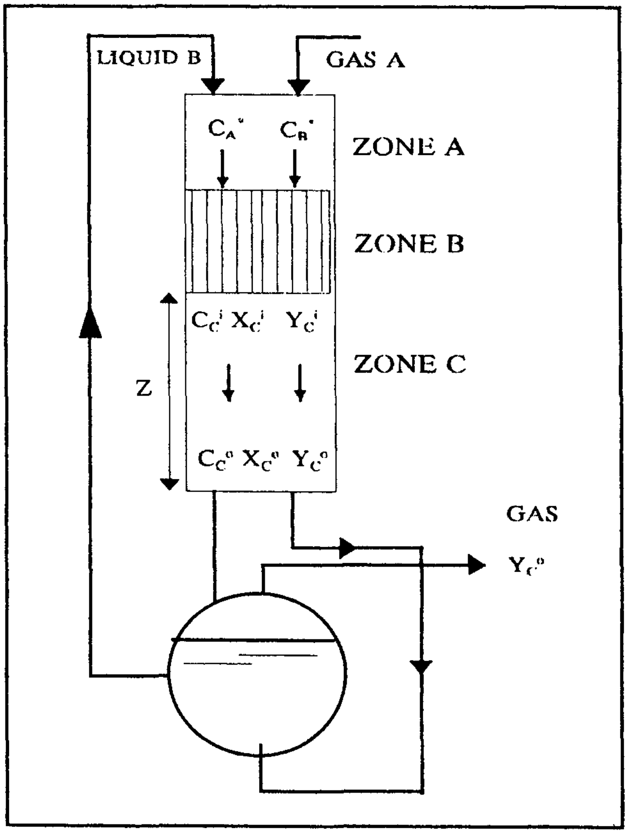

Figure 6. Simplified reactor.

Figure 6 shows a simplified reactor scheme. In zone A, the pre-packing section, the flowing H_2 is saturated with AMS (C_B^*). The liquid phase entering the reactor is pre-saturated with H_2 (C_A^*) in the absorber. The streams entering zone B (the catalytic bed) consist of H_2 saturated with AMS (C_B^*) and liquid AMS saturated with H_2 (C_A^*). At low liquid flow rates, reaction proceeds via liquid-solid catalysis (r_w) and gas-solid catalysis (r_n). The feed entering the post packing section (zone C) consists of H_2 with a concentration of cumene Y_c^i and liquid AMS with a concentration of cumene C_c^i or X_c^i (superscript i is the inlet). As Y_c^i is higher than the corresponding equilibrium value, cumene will transfer from the gas phase to the liquid effluent at a rate r_t. Mass transfer in zone C will proceed until equilibrium conditions. When equilibrium is reached that is, when zone C is long enough, Y_c^* is given by Eq. 1 with X_c^*. The values of X_c^* and Y_c^* can be obtained by GC analysis. (The asterisks are equilibrium). The governing equations are as follows:

Mass Balance for Liquid-Phase Cumene over the Equipment. Total liquid phase cumene is obtained considering the contribution of liquid-phase reaction rate and mass-transfer rate in the post-packing section. Global rate is defined as

$$\frac{1}{m_{\text{cat}}} \frac{dn_c}{dt} = r_w + r_t \tag{2}$$

where m_{cat} is the mass of catalyst, and n_c is the moles of cumene in the liquid phase.

Rate of Production of Cumene via Liquid-Solid Catalyzed Reaction in the Catalytic Bed. Reaction rate for a first-order kinetics (Ramachandran and Chaudari, 1983) is given by

$$r_w = f \frac{V_B}{m_{\text{cat}}} \frac{C_A^*}{\dfrac{1}{[K_L a_B]_A} + \dfrac{1}{k_s a_p} + \dfrac{1}{\omega (k\eta)_w}} \tag{3}$$

where f is the wetting efficiency, V_B is the volume of the catalytic bed (V is the total volume of liquid), $k_s\ a_p$ is the mass-transfer coefficient from liquid to solid for A. $\omega = V_B/m_{\text{cat}}$ and η_w is the catalyst effectiveness factor in wetted catalyst.

Rate of Production of Cumene via Gas-Solid Catalyzed Reaction in the Catalytic Bed. In absence of liquid phase resistance

$$r_n = (1-f) \frac{V_B}{m_{\text{cat}}} \frac{C_B^*}{\dfrac{1}{k_g a_p} + \dfrac{1}{(k\eta)_n}} \tag{4a}$$

where $k_g a_p$ is the mass-transfer coefficient from gas to solid gaseous B, and η_n is catalyst effectiveness factor in nonwetted catalyst.

For a transport controlled reaction (Cini and Harold, 1991)

$$r_n = (1-f) \frac{V_B}{m_{\text{cat}}} k_g a_p C_B^* \tag{4b}$$

Mass Transfer of Cumene in the Post Packing Section.

$$r_t = r_n \cdot (1 - e^{-\theta}) \tag{5a}$$

Equation 5 is obtained from solving the mass balance in zone C according to

$$\int_{C_{C,g}^{i}}^{C_{C,g}^{0}} \frac{dC_{c,g}}{\dfrac{C_c}{H} - C_{c,g}} = \int_0^{t_c} [K_L a_B]_C \cdot dt \tag{5b}$$

where H is the solubility coefficient.

Gas and liquid side external mass-transfer coefficients are evaluated by means of Goto and Smith (1975) correlations. A gas-solid mass-transfer coefficient was calculated according to Dwivedi and Upadhyay (1977). Wetting efficiencies were calculated using Herskowitz (1981) and El-Hisnawi (1982) correlations. The term $(k\eta)_w$ was evaluated by Castellari and Haure (1995) at 41°C. Steady-state experiments carried out at different temperatures (31 to 53°C) show that at high liquid flow rates, when liquid-solid catalyzed reaction governs, $k\eta$ remains approximately constant (Castellari and Haure, 1995). Equations 5a and 5b were also used to determine the depth in the postpacking section at which saturation occurs: A value close to 55 cm. Figure 1 also compares model and experimental results for TBR1. Wetting efficiencies were evaluated by Herskowitz (1981) (upper curve) and El-Hisnawi et al. (1982) (lower curve) correlations. Good agreement is found in both cases. When the post-packing section is longer, the concentration of cumene in the liquid phase at low liquid flow rates is higher, as shown in Figure 2 and indicated as TBR2 results. The model is a good approximation to predict experimental results and confirms the existence of gas-solid catalyzed reaction at low liquid flow rates. The appropriate length of the post-packing section or the use of a condenser is an important fact that should not be neglected when designing the experimental setup.

Conclusions

When a differential TBR is operated at low liquid flow rates wetting is incomplete. In the case of gas-limited, exothermic reaction and volatile liquid reactant rates and temperatures are higher than those predicted by the reduction of mass-transfer resistances only. Reaction rates are increased due to the reduction of mass-transfer resistances, temperature rise, and vaporization of the liquid reactant is followed by a gas-solid catalyzed reaction. Recovery of the vaporized product is enhanced if an inert post-packing section is added or a condenser is maintained at a temperature considerably below that of the catalyst used.

A simple 1-D model is developed to describe reaction between the liquid reactant, alpha methyl styrene, and the gas reactant (H_2) in the wetted areas or liquid-phase catalysis, and the gas-phase reaction in the nonwetted areas of a bed consisting of commercial Pd/Al_2O_3 catalytic pellets. The mass transfer in the post-packing section is also considered. Experimental and theoretical results are in agreement.

Efforts are currently under way to develop a criterion for the onset of vaporization followed by gas-solid catalyzed reaction.

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Notation

A = hydrogen
B = alpha methyl styrene
C_C = concentration of C in the bulk liquid
d_p = pellet diameter
$[K_L a_B]_A$ = overall mass-transfer coefficient from gas to liquid for A
$[K_l a_B]_C$ = overall mass-transfer coefficient from gas to liquid for C
Q_g = effective molar gas flux
t = time
t_c = contact time in the post packing section
Z = post-packing length
ϵ = post-packing void fraction
$\theta = [K_L a_B]_C \cdot C \cdot Z/Q_g$

Superscripts and Subscripts

o = outlet
A = gaseous reactant
B = volatile liquid reactant
C = product of reaction

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