Experimental Study of the Periodic Operation of a Trickle-Bed Reactor

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Trickle-bed reactors are a commonly used type of three-phase catalytic reactors in which liquid and gas phases flow concurrently through a bed of catalyst particles. They are usually operated in the trickling regime. A common feature of most trickle-bed reactors is the complexity of the gas-liquid flow and that, in most cases, the overall reaction rate is governed by mass-transfer resistances. Gaseous species must dissolve into and then pass through the liquid phase to reach the catalyst particles. Mass-transfer resistances between the phases affect the conversion and the overall reaction rate. However, the liquid phase is essential to the system and cannot be completely eliminated.

According to the recent literature, many attempts have been made to overcome this drawback by means of reducing the mass-transfer resistances. This can be accomplished using other reactor configurations (segregated flow reactors) or by means of cycling of the liquid phase. Segregated flow reactors basically consist of a tubular supported catalytic membrane. The liquid and gas streams are separated as they flow through the membrane (Hatziantoniou and Andersson, 1984; De Vos et al., 1986; Cini and Harold, 1991; Young and Cussler, 1987; Hatziantoniou et al., 1986; Carlsson et al., 1983). In all the cases the solution to overcome the mass-transfer resistance limitations is suggested by means of using another reactor, not a trickle-bed reactor.

In the case of cycling, an inlet variable (that is, the liquid-flow rate) is periodically changed between two given levels. When the liquid flow is cut off, the bed partially drains. This thins out or eliminates the liquid film surrounding the particles with a decrease in the transport resistance for the gaseous species. This mode of operation could be viewed as a way of segregating, at least partially, liquid and gas phases.

Periodic operation of a trickle-bed reactor was studied by Haure et al. (1989). The reaction system under consideration was the sulfur dioxide oxidation over carbon catalyst. In this case, the reactants were present in the gas phase only. The sulfur trioxide formed was removed by the liquid flow (water). The liquid flow was turned on and off and an increase in the oxidation rate of about 30 to 40% was found within a range of cycle periods from 2 to 80 min. Under this condition, wetting plays an important role in the behavior of the reactor. The influence of cycling results from the interplay of mass-transfer and heat effects.

Multiphase reaction-transport interactions at the single catalytic pellet level were studied by Funk et al. (1991) and Watson and Harold (1993, 1994). Their approach provides valuable information about local unsteady behavior within the fixed-bed multiphase reactor and gives insight into catalyst performance during periodic operation.

The objective of this article is to compare the performance of a laboratory trickle-bed reactor operated in the cycling and conventional modes for a reaction system which is volatile-reactant-limited mass-transfer controlled, and where reactants are present in both phases. The hydrogenation of alpha methyl styrene (AMS) to cumene over Pd/alumina catalyst was selected as test reaction since it is representative of a large number of commercially important reactions that follows the above restrictions.

Experimental Details

The hydrogenation of AMS to cumene over a Pd/alumina catalyst was selected as a test reaction. Kinetics have been extensively studied by others (Babcock et al., 1957; Satterfield et al., 1969; Harold and Ng, 1987). Compared to other multiphase reactions, the reaction rate is rather fast under mild conditions, and cumene is the only measurable product at low temperature. The reaction is mildly exothermic ($-\Delta H = 109$ KJ/mol). Several studies demonstrate that the liquid phase/catalytic reaction is mass-transport-limited with respect to sparingly soluble hydrogen (in AMS and cumene) under typical laboratory conditions. (Babcock et al., 1957; Satterfield et al., 1969; Morita and Smith, 1978; Herskowitz et al., 1979; Turek and Lange, 1981; Cini and Harold, 1991).

The AMS (Aldrich Chemical Co.) had a purity of 99%. The polymerization inhibitor *p*-tert-butyl-catechol was eliminated by soaking the AMS in alumina beads for 12 h before use. Rectified hydrogen of a purity of at least 99,99% was used. The catalyst pellets used were of a form often employed commercially, where the active metal is deposited in a relatively thin shell on the outside of the pellet. The support

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Table 1. 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
Mean Diameter	2.72 mm
Particle Porosity	0.60
BET Surface Area	70 m^2/g

Table 2. Properties of the Bed

Bed Dimensions	25.4 mm ID × 15 mm
Catalyst Mass	3.48 g
Bed Porosity	0.48
Type of Prepacking	Glass Beads
Depth of Prepacking	120 mm

is porous throughout. Properties of the catalyst are given in Table 1. Catalyst was reduced prior to its utilization. The reaction was carried out in a batch-recycle system. The experimental apparatus is similar to that described by others (Morita and Smith, 1978; Herzkowtiz et al., 1979), as shown in Figure 1. The liquid phase was pumped from a reservoir where it was saturated with hydrogen to the reactor, flowed concurrently with the gas phase and then was separated from the gas and returned to the reservoir. The gas containing small amounts of liquid was cooled in a vertical gas condenser. The condensate flowed back into the absorber and the remaining gas was discharged. In all the experiments, a constant gas flow of 900 mL/min was used. The AMS was fed to the reactor by a variable speed peristaltic pump (Cole Parmer model 7554-20). The reservoir and fed pipes were immersed in a water bath at 41°C. A glass jacketed reactor of 2.54 cm ID was packed with glass and catalyst spheres of similar size supported by a screen. A sheathed thermocouple was inserted axially in the middle of the catalytic bed. Continuous data were monitored by a recorded (Omnigraphic 3000). Bed properties are presented in Table 2. A three way on-off solenoid valve (Jefferson model 365) activated by timers was used to generate liquid variations in the cycling experiments. Samples were taken at the outlet of the reactor and analyzed in a Hewlett-Packard GC (model 5890-A) equipped with a PONA capillary column. The operating procedure and analysis of data are given in detail by Castellari (1993).

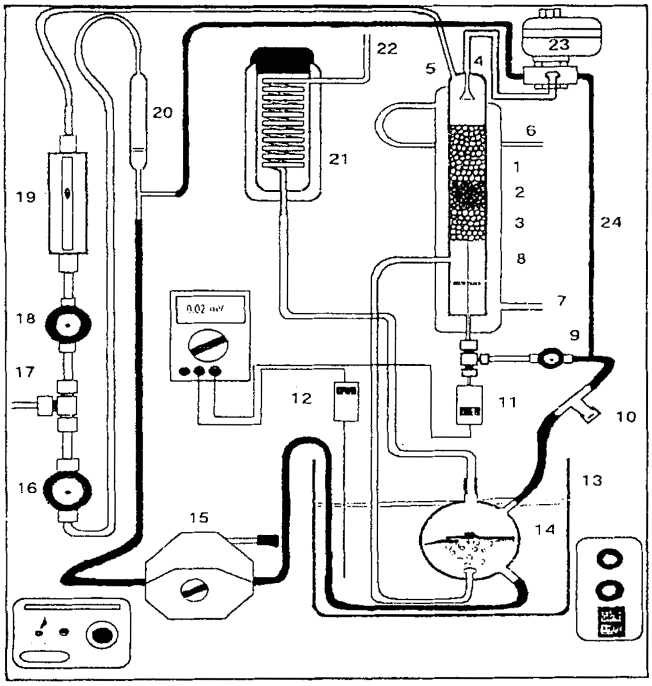

Figure 1. Experimental Setup.

(1) Prepacking; (2) catalyst bed; (3) post packing; (4) liquid distributor; (5) hydrogen inlet; (6, 7) heating water; (8) gas-liquid separator; (9) needle valve; (10) sampling; (11) bed thermocouple; (12) reference thermocouple; (13) constant temperature bath; (14) absorber; (15) peristaltic pump; (16) needle valve; (17) hydrogen inlet; (18) needle value; (19) rotameter; (20) liquid flow stabilizer; (21) condenser; (22) gas exit (to the fume hood); (23) three-way solenoid valve; (24) AMS by-pass.

Steady-State Experiments

Steady-state experiments were conducted over a range of different liquid-flow rates. The experiments were performed at 41°C, 1 atm and constant hydrogen flow rate of 900 mL/min. The AMS was saturated with hydrogen at 41°C. The startup and operational procedure are similar to those described by Morita and Smith (1978). The same catalyst load was used in all the experiments. No catalyst deactivation was observed and the experiments were quite reproducible. Prior to each run, the bed was preflooded with AMS. In all the experiments the concentration of cumene was constant in all parts of the apparatus. During one run the total liquid volume changed by 1%. Due to the low conversions achieved (per pass and per run), hydrogen and AMS concentrations can also be considered constant. Under these conditions, the overall reaction rate can be calculated from the batch-recycle equation (Morita and Smith, 1978).

Small samples of liquid were withdrawn and analyzed using GC after enough time passed for the steady-state concentration profiles to be established. In most of the liquid-flow rates studied, samples were taken after one hour from starting up a run and at intervals of 30 min. Plots of the measured cumene concentrations against time were linear indicating a constant rate.

Figure 2 shows the dependence of the reaction rate on the liquid flow rate. The solid line indicates an approximate fit. The results can be explained in terms of differences in the external mass transport fluxes (Herskowitz et al., 1979; Funk et al., 1991). At high liquid-flow rates, the particles are completely covered by liquid. The rate is limited by the external supply rate of the volatile reactant (hydrogen). As the liquid-flow rate is decreased to a point in which incomplete wetting becomes important, the volatile reactant reaches the catalyst surface through the non-wetted part. Since the supply rate of the gaseous reactant increases, the overall rate also increases. This phenomenon is called "effectiveness enhancement by partial wetting" (Harold and Ng, 1987).

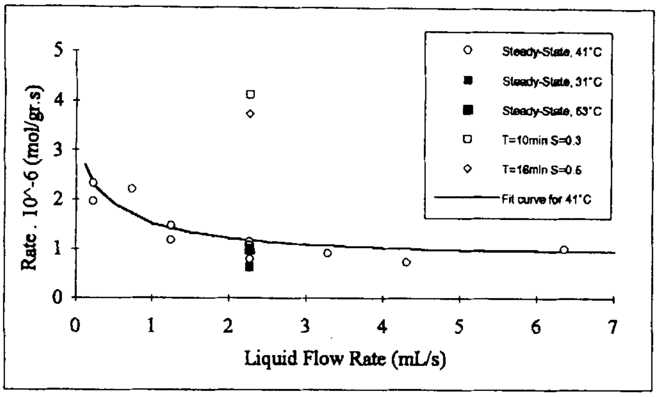

Figure 2. Dependence of the reaction rate on the liquid-flow rate (steady-state experiments).

An interesting feature was observed at the lowest liquid-flow rate studied (0.23 mL/s). After initial three hours of the run, visual observation of the bed showed that the degree of wetting had diminished dramatically. The catalyst had a "grayish" appearance, indicating dryness of the surface. Probably the liquid receded some distance from the surface into the porous. At the same time, a rise in the temperature of about 12°C was recorded. Figure 3 shows the concentration of cumene against time. It can be clearly seen that there are two different slopes, hence two reaction rates. We must emphasize that this behavior was not observed for the high-flow rates runs in which steady-state was reached after one hour.

Harold (1988) showed that for an exothermic reaction, the heat of reaction can cause vaporization of the liquid. Under that condition, the reaction could take place between gases over a dry catalyst or between liquid and dissolved hydrogen. The low rate (9.6×10^{-7} mol/g·s) obtained during the first hours of operation can be explained due to mass-transfer control in the liquid film surrounding the particles. As the reaction proceeded, the heat generated was poorly dissipated by the low liquid-flow rate. This heat of reaction could cause vaporization of the AMS. The high rate (2×10^{-6} mol/g·s) observed after approximately three hours of operation could be attributed to a gas-phase reaction over an externally dried catalyst plus a reaction between liquid and dissolved hydrogen gas in the zones irrigated by AMS.

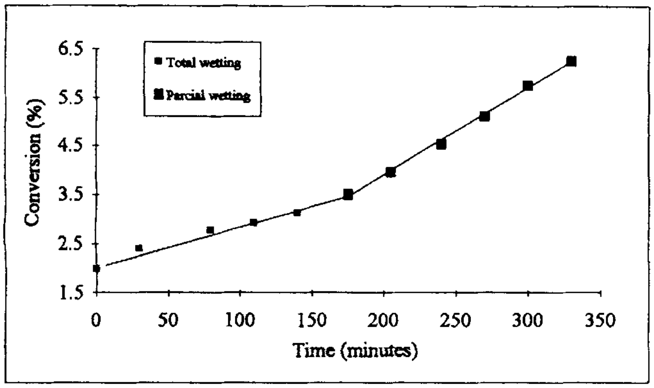

Figure 3. Cumene conversion against time.

Experiment performed at low liquid-flow rate (0.23 ml/s).

At the lowest flow rate studied, we did not observe the depletion effect pointed out by Harold and Ng (1978). It is important to point out that at low liquid-flow rates, steady state is achieved after several hours from the beginning of the operation and the operation is not isothermal.

Cycling Experiments

The variable cycled in all the experiments presented here was the liquid-flow rate. Since only a few seconds are needed to drain the bed and the shortest cycle period studied lasted ten minutes, then the on-off operation can be considered as square-wave cycling. The average liquid flow rate (ν_L) was 2.27 mL/s in all the experiments presented here. A constant flow of pure hydrogen of 900 mL/min passed through the reactor during the entire on-off cycle.

Experiments were arranged randomly, alternating steady state and cycling runs having short and long periods. No deactivation of the catalyst was observed. Reproducibility was good (15%). Liquid samples were taken a minute before ending each "wet cycle." Changes in the cumene concentration with time were used to evaluate the reaction rate according to

$$r_{\text{PERIOD}}=\frac{V_{\text{TOT}}\cdot C_{\text{AMS,O}}}{M_{\text{CAT}}}\left(\frac{\Delta X_{\text{cumene}}}{T}\right)_{\text{PERIOD}} \tag{1}$$

Rates obtained under different cycling conditions are shown in Figure 2. It can be seen that cycling increases the reaction rate up to a factor of 4.

Figure 4a shows the temperature profiles for split (S) 0.5, period (T) 40 min. That is, the reactor was exposed to the hydrogen flow for 20 min (T_1) and then it was flushed with AMS (saturated with hydrogen) and hydrogen (gas) for another 20 min (T_2). During the wet cycles, the bed can be considered isothermal (41°C). When the liquid flow was halted, temperature increased sharply, with a maximum value of about 80°C, reached after 7–8 min. Then, the temperature decreased. Following each flush, the bed is restored to isothermally.

Temperature profiles obtained at different cycling conditions exhibit the same trends. Figure 4b shows the results for

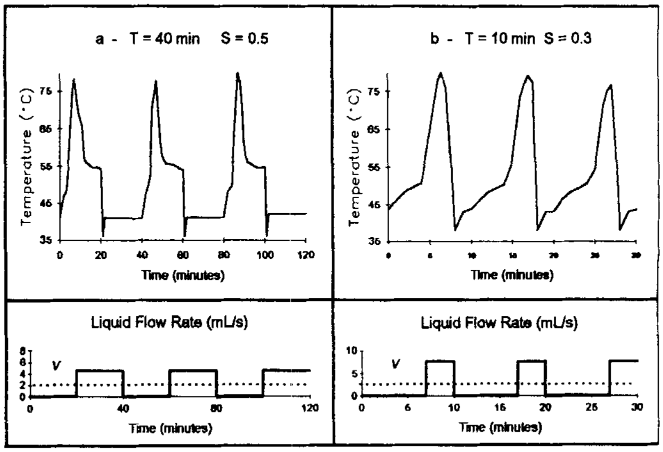

Figure 4. Temperature profiles during periodic operation.

split 0.3, period of 10 min. Once the liquid flow is cut off, temperature increases up to a maximum of about 75°C (at approximately 7 min). Then, flushing of the bed restores the initial temperature (42°C).

Under periodic operation, the reactor operates at average temperatures of about 53°C; 12°C higher than the steady-state temperatures. The reaction rate enhancement observed cannot be explained taking into account only the higher average reaction temperatures: steady-state experiments performed at constant temperatures of 31, 41 and 53°C (see Figure 2) show no significant variation of the reaction rate.

Figure 5 shows a temperature profile for a typical cycle period of 40 min, split 0.5. During the flushing cycle (zone A), the bed is isothermal. The heat generated during reaction is dissipated by the high AMS flow (4.5 mL/min). Temperature is constant at 41°C.

When the liquid flow is cut off, the bed partially drains (zone B). The reaction proceeds between the holdup and the flowing hydrogen. Gas reactant must dissolve and then pass through the liquid film surrounding the particles. The heat generated by the exothermic reaction could not be effectively removed by the gas flow. As a consequence, temperature and reaction rate increase. Under these conditions, vaporization of the AMS may occur. The abrupt temperature (reaction rate) increase observed after approximately four minutes of exposure to the gas phase only could be attributed to the gas-phase reaction over a dry catalyst. This represents a change in the reaction mechanism from a mass-transfer limited reaction to a gas-phase reaction, with different activation energies (Cini and Harold, 1991).

Drying out of the bed was observed after minutes of exposure to the gas phase. After the maximum is reached, temperature decreases sharply (zone C). Our explanation is that, in absence of any liquid flow, depletion of the AMS reduces the overall reaction rate and allows to cool down the reaction zone by convection.

Similar trends were discussed by Watson and Harold (1993) in experiments with a prefilled pellet exposed to a pure hydrogen flow. Their results demonstrated that without the heat removal of the flowing liquid, and with the direct contact of stagnant liquid and flowing gas, drying of the catalyst results. However, if sufficient time elapses that a fraction of catalyst becomes exposed to the gas, a much more rapid gas-phase catalytic reaction occurs with an accompanying temperature excursion. The authors proposed a sequence of steps to explain the associated dynamics of drying with reaction. Funk et al. (1991) reported that in transient experiments of hydrogenation of AMS when a pellet prefilled with AMS was exposed to pure hydrogen, a temperature rise of nearly 100°C was observed, and the pellet dried out in minutes. Thermal effects in the periodic operation of a trickle-bed reactor were also observed by Haure et al. (1989, 1990). Mean temperatures in cycling were a few degrees higher than bed temperatures at steady state.

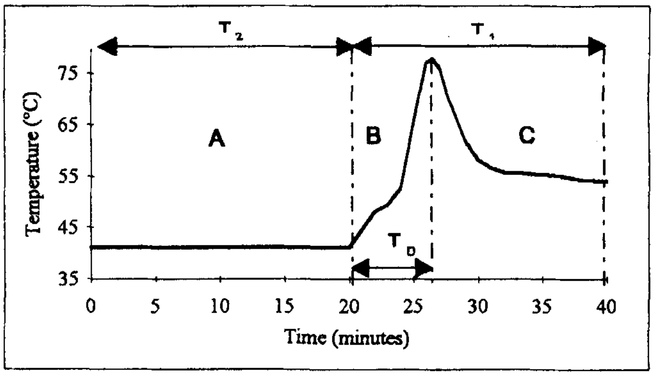

Figure 5. Typical temperature profile during one cycle.

Rates obtained under cycling were normalized with respect to the corresponding steady-state rate at the mean liquid flow rate, as shown in Figure 6. These normalized rates are plotted against cycle periods for splits 0.5 and 0.3. Cycling can increase the reaction rate up to a factor of 4. The normalized rates presents a maximum with the cycle period. According to our results, for a split of 0.3 the maximum is obtained for a cycle period of 10 min; while for a split of 0.5 the maximum is reached at 16 min.

To explain this results, we would refer to the temperature profiles described in Figure 5. For a constant split (S) there is an optimum (T_{OPTIMUM}) in which the reaction rate is at its highest value. In the case of reactants present in both phases, the optimum period is the one in which the time of exposure to the gas reactant only (T_1) equals the depletion time of the less volatile reactant (T_D), or

$$T = T_1 + T_2 \tag{2}$$

if

$$T_1 = T_D \Rightarrow T_{\mathrm{OPT}} - T_2 = T_D \tag{3}$$

$$\frac{T_{\mathrm{OPT}} - T_2}{T_{\mathrm{OPT}}} = \frac{T_D}{T_{\mathrm{OPT}}} \Rightarrow \tag{4}$$

$$1 - S = \frac{T_D}{T_{\mathrm{OPT}}} \tag{5}$$

$$T_{\mathrm{OPT}} = \frac{T_D}{1 - S} \tag{6}$$

A comparison of predicted (Eq. 6) and experimental optimum periods is given in Table 3. The depletion time of the

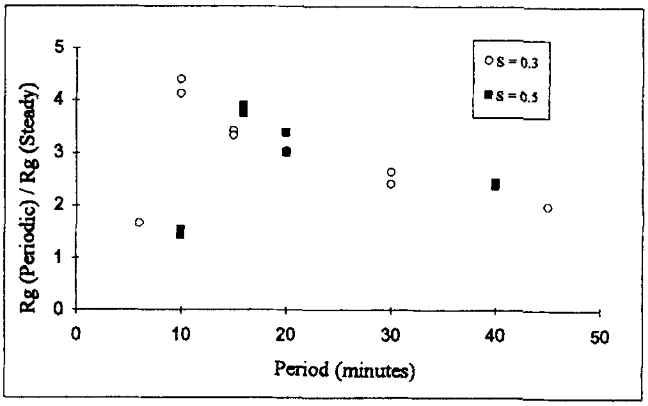

Figure 6. Normalized reaction rates against cycle periods.

Table 3. Comparison Between Predicted and Experimental Optimum Periods

Split	Predicted Period	Experimental Period
0.3	10.71 min	10 min
0.5	15 min	16 min

less volatile reactant (T_D) was obtained from the temperature profiles. It could also be calculated from evaluated liquid holdups and reaction and evaporation rate expressions for zone B in Figure 4. Experimental and theoretical values are in good agreement.

Conclusions

In this study, we have demonstrated that cycling of the liquid phase improves substantially the performance of a trickle-bed reactor for the case of reactants present in both phases. The principle of rate enhancement by partial wetting is also demonstrated.

Improvement is due to the reduction of mass-transfer resistances, the formation of controlled hot spots that results in higher catalyst temperatures and the appearance of gas-phase reaction over a dry catalyst.

As pointed out, depletion of the liquid may have a deleterious effect on cycling performance but at the same time allows to operate under semirunaway conditions. For a constant split, there is an optimum period in which the reaction rate is at its highest value. The optimum period depends on the liquid holdup and composition, the gas velocity and the reaction and evaporation rate. This should be further investigated. Efforts are currently under way to study the impact of cycling operation variables in a wider range of values.

Modeling of the periodic operation taking into account the several steps involved in the process of drying with chemical reaction is also under consideration.

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Notation

$C_{\mathrm{AMS},0}$ = initial concentration of AMS
M_{CAT} = mass of catalyst
r_{PERIOD} = reaction rate under cycling conditions
R_g = overall reaction rate
S = split = T_2/T
T = period = $T_1 + T_2$
T_D = depletion time
T_1 = time of duration of the dry cycle
T_2 = time of duration of the wet cycle
T_{OPT} = optimum period
v_l = average liquid flow rate = v_L S
v_L = liquid flow rate
V_{TOT} = total volume of liquid
X_{cumene} = conversion

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