

BEHAVIOR OF A PILOT PLANT FIXED-BED REACTOR DURING CATALYST DEACTIVATION

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Dedicated to Professor W. Richarz on the occasion of his 60th birthday

ABSTRACT

The behavior of an non-adiabatic, non-isothermal fixed-bed reactor used for the hydrogenation of toluene has been studied under the influence of catalyst deactivation caused by continuous addition of thiophene to the reactant feed. Axial and radial temperature and concentration profiles were measured during deactivation. In spite of significant radial temperature gradients (Biot number = 5.25), it was possible to describe the reactor behavior with a one-dimensional pseudo-homogeneous model. Mean cross-sectional temperatures can be used since the measured radial profiles are parabolic. The activation energy for thiophene adsorption derived from the measured profiles (4.7 kJ/mole) agrees with previous direct determinations in the literature.

KEYWORDS

Fixed-bed catalytic reactor; toluene hydrogenation; catalyst deactivation; feed poisoning; radial and axial temperature and concentration profiles; mean cross-sectional temperature; reactor model.

INTRODUCTION

Although the behavior of fixed-bed reactors during catalyst deactivation has received considerable attention (Butt, 1980; Hughes, 1984), in particular because of its importance in industry, there is relatively little experimental work where axial and radial temperature and concentration profiles have been measured during catalyst deactivation. Pexidr, Cerny and Pasek (1968) measured axial temperature and concentration profiles for the benzene hydrogenation on a Ni catalyst during deactivation by CS_2 . Weng, Eigenberger and Butt (1975) studied the deactivation of a non-isothermal non-adiabatic fixed-bed reactor for the same reaction during thiophene addition to the feed. The employed reactor had a small inner diameter (0.8 cm); for this reason no radial temperature gradient existed. Price and Butt (1977) studied the factors which play a decisive role for an a priori simulation of the reactor behavior during deactivation. Richardson (1971) and Wheeler and Robell (1969) showed that for isothermal reactors with constant overall deactivation rate parameters the activity profiles could be described by the adsorption theory of Bohart and Adam (1920).

In the present work we have measured axial and radial temperature and concentration profiles in a fixed-bed reactor during deactivation by feed poisoning. An efficient modelling of the observed profiles was achieved by means of a simple pseudo-homogeneous one-dimensional model using a mean cross-sectional temperature. The basic concept is to estimate kinetic and heat transfer parameters from stationary profiles, and to assume that the only influence of thiophene adsorption is to reduce the active surface area of the catalyst. Thus the deactivation rate parameter can be determined by evaluating the profiles taken at a series of times after initiation of deactivation.

EXPERIMENTAL

The fixed-bed reactor pilot plant has been described by Baiker and Bergougnan (1985a, Fig. 1). It was operated as a continuous reactor with recycle of hydrogen. A jacketed reactor tube of 2.2 m length and 0.052 m inner diameter was employed. A diagram of the reactor showing the positions of the catalyst bed and measuring devices has been given by Baiker and Eppler (1986, Fig. 1). The catalyst bed of 0.7 m length was embedded in inert glass packings on both sides. Axial temperature and concentration profiles were measured at seven positions in the catalyst bed separated by 0.1 m (position 3: $z = 0$, catalyst bed entrance; position 9: $z = 0.6$ m; positions 1 and 2 were located in the inert glass bead packing at the reactor entrance). The radial temperature and concentration profiles were measured at five radial positions at $z = 0.25$ m and $z = 0.55$ m. The reactor wall temperature was controlled by circulating oil through the jacket. An infrared

analyzer (URAS) was utilized for the automatic analysis of the toluene concentrations. The plant operation and data acquisition were controlled by a PDP 11/10 process computer. A commercial silica supported Ni catalyst (ICI 42.1) was used. Properties of the cylindrical (3.4 x 3.4 mm) catalyst pellets were given elsewhere (Baiker and Epple, 1986). Before use the catalyst was reduced according to the procedure given by the manufacturer. Toluene (99.5 %), nitrogen (99.99%), and hydrogen (99.99%) were used without further purification.

Recording of the axial and radial profiles was started after steady-state conditions were reached in the reactor, typically after less than 20 minutes. Then poisoning by addition of thiophene to the reactor feed was initiated. Results of four deactivation experiments performed at 2 bar are presented in this paper. They were characterized by the following conditions. Run (A): temperature of oil in reactor jacket, $T_B = 381$ K; total flow rate (hydrogen and toluene), $F = 700$ moles/h; Reynolds number, $Re = 99$; toluene concentration, 2.4 vol-%; thiophene feed, 12 ml/h; total. Run (B): $T_B = 393$ K; $F = 850$ moles/h; $Re = 104$; toluene concentration, 1.8 vol-%; thiophene feed, 25 ml/h. Run (C): $T_B = 392$ K; $F = 690$ moles/h; $Re = 78$; toluene concentration, 1.5 vol-%; thiophene feed, 10 ml/h. Run (D): $T_B = 394$ K; $F = 640$ moles/h; $Re = 100$; toluene concentration, 2.8 vol-%; thiophene feed, 26 ml/h. The thiophene adsorption capacity of the catalyst at full deactivation was measured by means of the method described by Granatelli (1959), in which the amount of sulfur is determined. A mean sulfur content of 2.6 mg sulfur per g of catalyst was found. This corresponds to a thiophene adsorption capacity of 0.08 moles per g of catalyst.

MEASURED AXIAL PROFILES

Figure 1 depicts the time profiles of temperatures and toluene concentrations measured at the axial positions 3 - 9 (Fig. 1, Baiker and Epple, 1986) during deactivation experiment (A). The four-point interpolation procedure used to derive continuous axial and radial profiles from the measured data has been described by Baiker and Bergougnan (1985a).

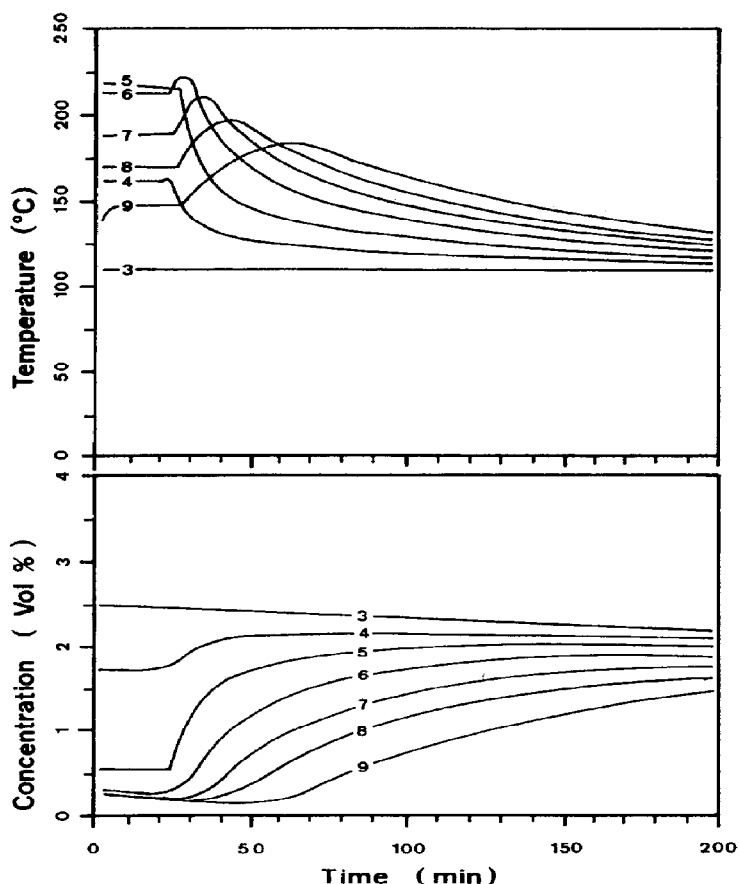


Fig. 1 Measured time profiles of axial temperatures and toluene concentrations at positions 3 - 9. Run (A).

Figure 2 shows the axial profiles of experiments (A) and (B). Note that in the initial period of deactivation ($t = 5$ min) the hot spot temperature was significantly higher than the one of the steady-state profiles ($t = 0$). With progressing deactivation, the hot spot shifted towards the end of the catalyst bed, the profiles were broadened, and the hot spot temperature decreased. The corresponding axial toluene concentration profiles indicated an inactive zone at the entrance of the catalyst bed, which is formed relatively late, i. e. after conversion decreased to about 20% of its initial value.

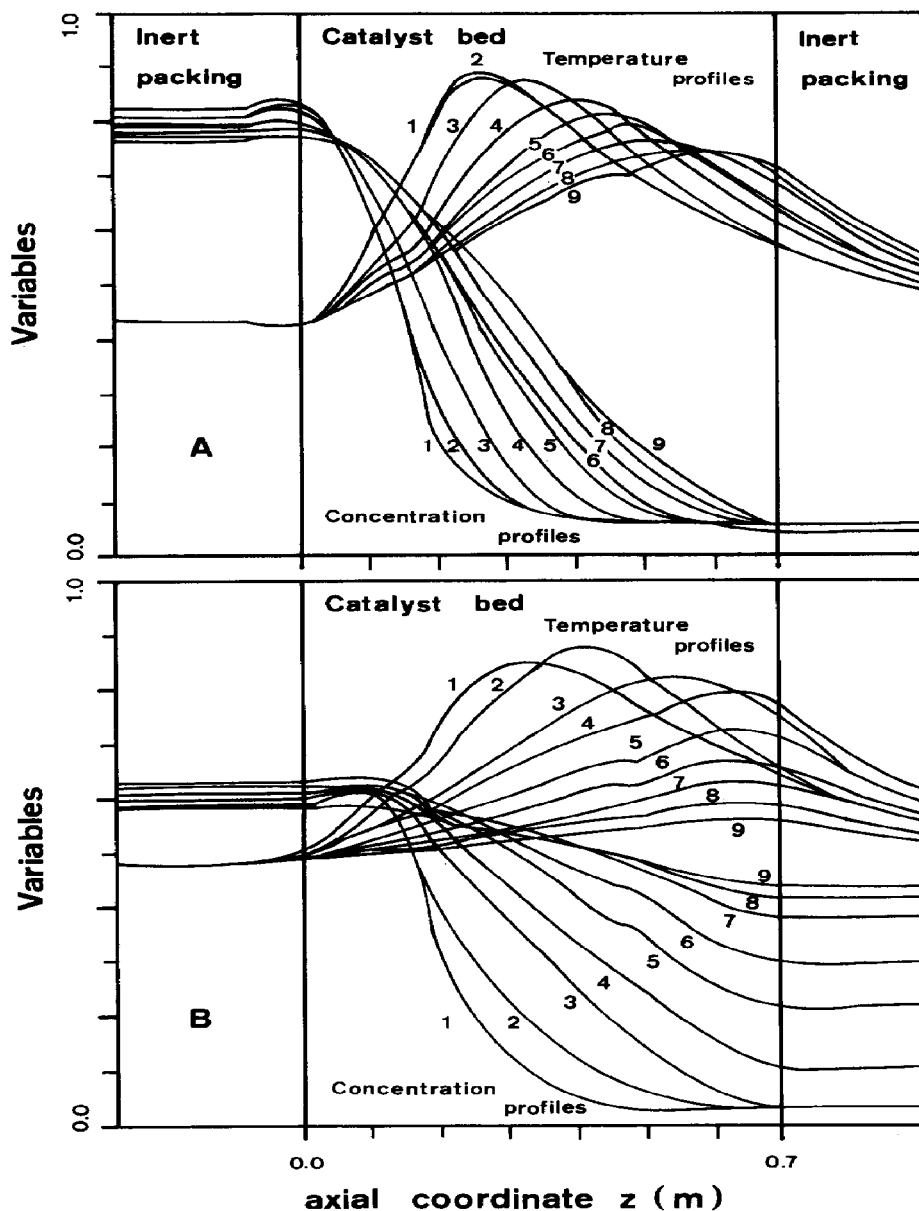


Fig. 2 Interpolated axial temperature and toluene concentration profiles of runs (A) and (B). Curve 1 corresponds to steady-state before deactivation. Curves 2 - 9 represent reactor profiles during deactivation measured in intervals of five minutes after initiation of thiophene addition to the feed. Variable ranges: temperature, 0 - 250 °C; toluene concentration, 0 - 3 vol%.

MEASURED RADIAL PROFILES

The radial temperature profiles measured during deactivation experiments (Fig. 3) were similar in shape to those found during steady-state operation, for which a Biot number $h_w R / k_p = 5.25$ was calculated. As a consequence of the parabolic shape found in all experiments, mean cross-sectional temperatures could be defined and applied for the reactor model. The procedure used for the estimation of the mean cross-sectional temperature has been described by Baiker and Eppe (1986). Measured radial toluene concentration profiles were flat, i.e. the mean cross section concentrations corresponded approximately to the concentrations in the center of the reactor tube.

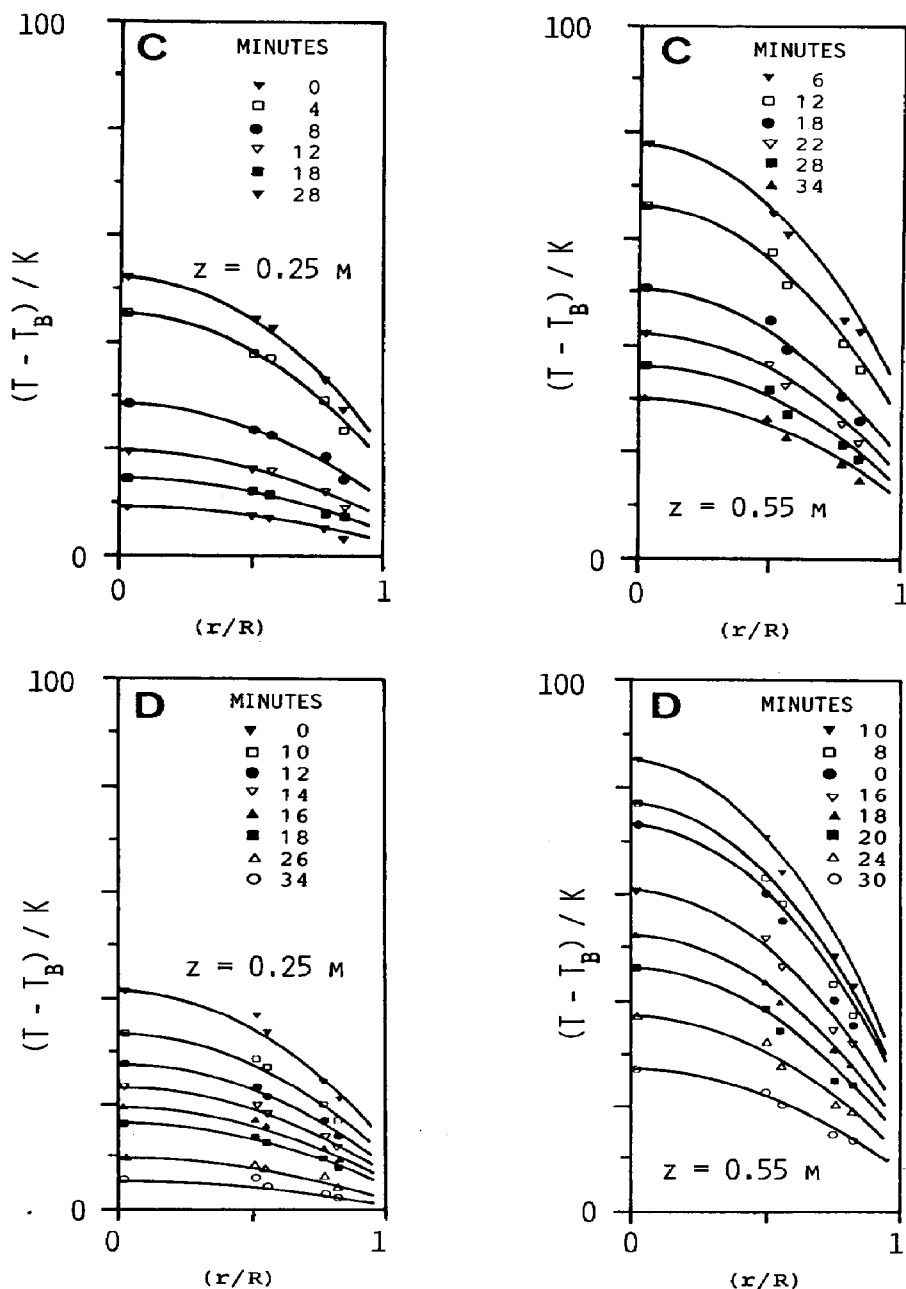


Fig. 3 Typical radial temperature profiles measured at axial positions $z = 0.25$ m and $z = 0.55$ m during deactivation experiments. (Runs C and D; T_B = temperature of oil in reactor jacket)

REACTOR MODEL

The reactor model is based on the assumption that the kinetic parameters of toluene hydrogenation are not affected by the deactivation process; thus the kinetic equations for toluene hydrogenation and for the catalyst deactivation are separable. Consequently the heat transfer parameter and the hydrogenation rate constant could be estimated from the initial steady-state of the reactor. In order to describe the deactivation behavior, the model was extended by introducing a linear differential equation for the poisoning of the active surface area, and a mass balance equation for thiophene.

The one-dimensional pseudo-homogeneous reactor model used to describe the behavior without deactivation is given by the following set of equations.

Heat balance:

$$\frac{\partial T}{\partial t} = - \frac{\epsilon u \rho_f c_{pf}}{(1-\epsilon) \rho_s c_{ps}} \frac{\partial T}{\partial z} + \frac{2 U (T_b - T)}{R (1-\epsilon) \rho_s c_{ps}} - \frac{\Delta H_r}{c_{ps}} r(T, P_T) \quad (1)$$

Mass balance:

$$\frac{\partial C}{\partial t} = - u \frac{\partial C}{\partial z} - \frac{(1-\epsilon) \rho_s}{\epsilon} r(T, P_T) \quad (2)$$

Boundary conditions: $T(z = 0, t) = T_{in}(t)$

$C(z = 0, t) = C_{in}(t)$

Initial conditions: $T(z, t = 0) = T_{in}(t = 0)$

$C(z, t = 0) = 0$

The kinetic rate equation used for the toluene hydrogenation has been discussed in an earlier investigation (Baiker and Bergougnan, 1985b).

$$r(T, P_T) = \frac{K_1 (P_T/\bar{P}_T)}{1 + (P_T/\bar{P}_T) \exp\{K_2 (1/T - 1/K_3)\}} \quad (3)$$

For the description of the reactor behavior during deactivation, the time-dependent active fraction $\theta(t)$ of the catalyst was defined by the equation

$$\theta(t) = 1 - \frac{\text{thiophene adsorbed at } t}{\text{thiophene adsorbed at total deactivation}} \quad (4)$$

Richardson (1971) and Lyubarskii, Andreeva and Kul'kova (1962) have found a linear dependence of the deactivation rate on the active fraction $\theta(t)$. This suggests that the time-dependence of $\theta(t)$ is governed by an equation of the form

$$-d\theta(t)/dt = p_{thio} \theta(t) k(T_m) \exp[-E_a/R (1/T - 1/T_m)]. \quad (5)$$

The rate parameter $k(T) = k_0 \exp[-E_a/(RT)]$, of dimensions $\text{bar}^{-1} \text{s}^{-1}$, has been transformed to a mean temperature T_m according to the procedure of Himmelblau (1970), to reduce the correlation between the estimated parameters $k(T_m)$ and E_a . The second relationship required to describe deactivation is the thiophene mass balance,

$$dC_{thio}/dt = - u dC_{thio}/dz + [(1-\epsilon)/\epsilon] \rho_s M_T d\theta(t)/dt. \quad (6)$$

The following initial conditions were used ($t = 0$ is the time when deactivation is started by adding thiophene to the feed):

$$\begin{aligned} T(z, t = 0) &= T(z) && \text{(temperature in steady state before deactivation)} \\ C(z, t = 0) &= C(z) && \text{(toluene concentration in steady-state before deactivation)} \\ C_{\text{thio}}(z, t = 0) &= 0 && \text{(thiophene concentration)} \\ O(z, t = 0) &= 1 && \text{(initial activity).} \end{aligned}$$

Furthermore the following boundary conditions were applied:

$$\begin{aligned} T(z = 0, t) &= T_{\text{in}} && \text{(temperature at entrance to catalyst bed)} \\ C(z = 0, t) &= C_{\text{in}}(t) && \text{(toluene concentration in feed)} \\ C_{\text{thio}}(z = 0, t) &= C_{\text{thio}}(t) && \text{(thiophene concentration in feed)} \end{aligned}$$

Numerical Solution

The method of orthogonal collocation (Villadsen and Michelsen, 1978) was used to reduce the partial differential equations to a set of ordinary differential equations. In the present work 8 collocation points were used. The resulting system consists of 24 differential equations, 8 algebraic equations for the deactivation, and the deactivation equation at bed entrance ($z = 0$). This system of equations was simultaneously integrated using Gear's variable integration step algorithm, as provided in the software package IMSL. These integration routines were used together with the nonlinear multiresponse regression program RKPEs (Klaus and Rippin, 1979). This program is based on the "maximum likelihood" method (Bard, 1974). RKPEs was used with the option of an unknown non-diagonal covariance matrix. The experimentally measured data were interpolated with respect to time and space previous to use in the regression program, since the positions of the measurements did not correspond to the positions of the collocation points, and a simultaneous recording of all measurement points was not possible.

Estimated Parameters from Steady-State Profiles

The kinetic parameters and the overall heat transfer coefficient were estimated from steady state experiments and reported elsewhere (Baiker and Eppe, 1986). Mean parameter values found were: k_1 , 8.8 ± 1.1 mole /kgs; k_2 , 7.3 ± 1.8 K; k_3 , 4.25 ± 0.03 K. The heat transfer parameter U was found to depend on the Reynolds number (cf. Fig. 4 in Baiker and Eppe, 1986).

Estimated Deactivation Parameters

Deactivation parameters $k(T_m)$ and E_a were estimated from eight deactivation experiments by the procedure described above. The data set used consisted of the profiles determined at times 10, 20, 30, and 40 minutes after initiation of the deactivation process. Mean parameter values found were: $k(T_m)$, 1.05 ± 0.08 s; E_a/R , 530 ± 145 K. Note the relatively large standard deviation of E_a/R , which is due to the small absolute value of the activation energy. The activation energy of 4.7 kJ/mole indicates a weak temperature dependence of the deactivation.

DISCUSSION

Calculated and Experimental Profiles

Experimental and calculated profiles of runs (A) and (B) are compared in Fig. 4. The model provides a good representation of the measured temperature and concentration profiles. The deviation between experimental and simulated axial concentration profiles in run (A) at the reactor outlet can be ascribed to a systematic error in the measurement of very low toluene concentrations.

Deactivation kinetics

The quality of the description of the reactor behavior showed a different sensitivity on the two estimated deactivation parameters. It was very sensitive to the pre-exponential factor $k(T_m)$, which in turn was found to be strongly correlated with the thiophene adsorption capacity. In contrast, the parameter E_a had only a minor influence on the quality of the fit, which indicates a very shallow optimum. This activation energy of the deactivation kinetics, i.e. the adsorption rate of thiophene on Ni, is quite low (4.7 kJ/mole). Our value derived from the measured profiles agrees well with direct determinations in the literature. Weng, Eigenberger and Butt (1975) found a value of 4.5 kJ/mole, while Zrnecvic and Gomzi (1983) gave a value of 5.3 kJ/mole. Considering the fact that the thiophene adsorption rate depends only weakly on temperature, an isothermal treatment of the deactivation reaction may lead to satisfactory results.

No definite conclusions have been reached concerning the question whether the toluene hydrogenation rate and the deactivation rate can be considered to be separable. However this assumption will only lead to significant errors in the description of the profiles when the catalyst activity

is low, i.e. when the conversion in the reactor has dropped to values less than 20 % of the initial conversion. In contrast to Weng, Eigenberger and Butt (1975) who used a semi-empirical two-site mechanism for the deactivation kinetics, we have employed a simple linear dependence between the toluene hydrogenation activity and the adsorbed amount of thiophene. This leads to a considerable reduction of computation time. Consequences of this simplifying assumption are noticeable only for high degrees of deactivation, which are generally of less importance in practical applications. It appears that under the conditions given, the one-dimensional pseudo-homogeneous reactor model can be considered as accurate enough for most practical purposes.

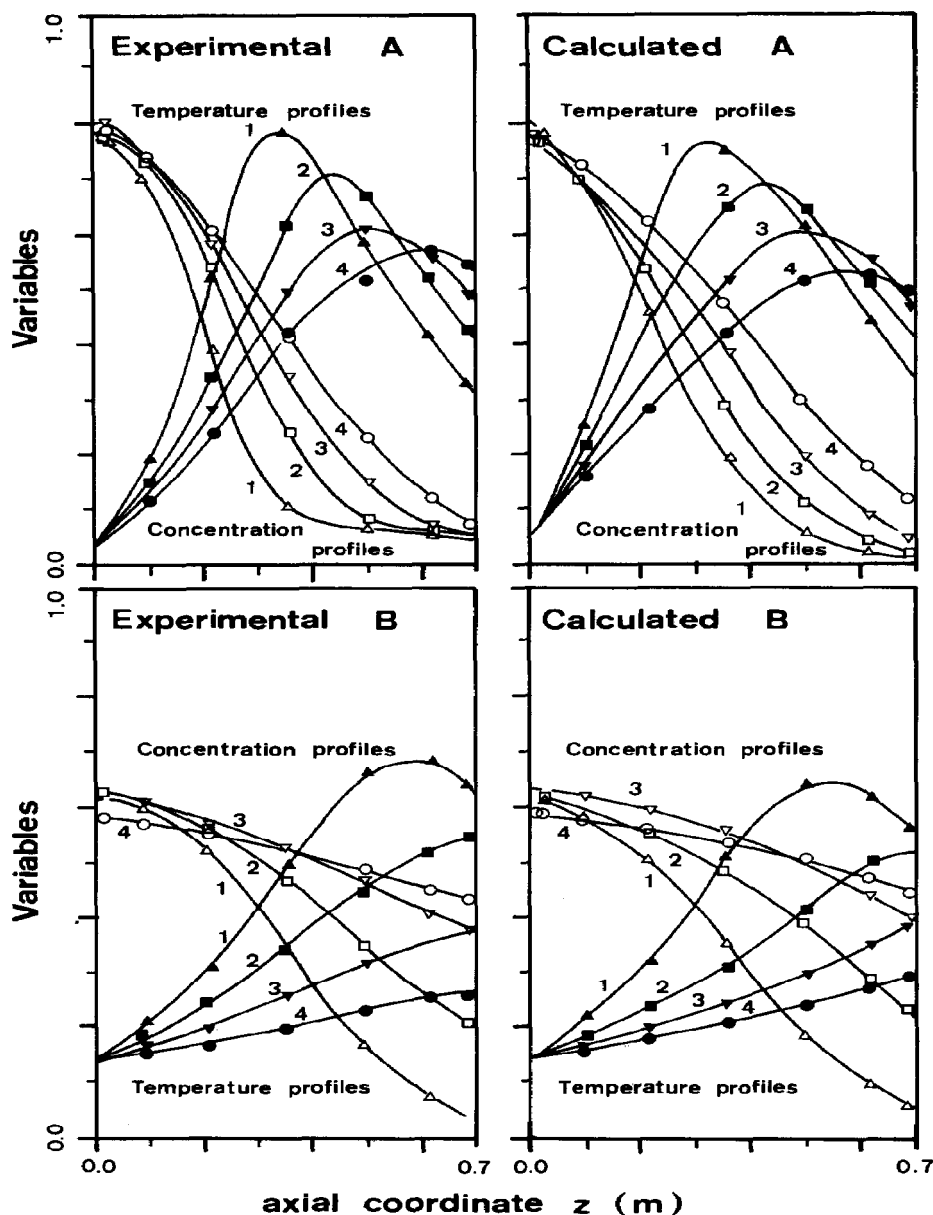


Fig. 4 Experimental and calculated axial temperature and toluene concentration profiles of runs (A) and (B). Symbols in calculated curves represent T and C values calculated at collocation points. Variable ranges: temperature, 100 - 250 °C; toluene concentration, 0 - 3 vol%. Curves 1, 2, 3, and 4 correspond to times of 10, 20, 30, and 40 minutes, respectively, after initiation of thiophene addition to the feed.

CONCLUSIONS

The behavior of a fixed-bed reactor during deactivation has been investigated. Measured axial temperature and concentration profiles were described by a pseudo-homogeneous one-dimensional model. Description with a one-dimensional model was appropriate because the measured radial temperature profiles exhibited a parabolic shape during the entire course of deactivation. The use of a mean cross-sectional temperature is justified if the radial position corresponding to the mean cross-section temperature is constant. This condition is fulfilled for radial profiles of the form $T(r) = T(0) + a(r/R)^n$.

A first order rate expression was found to be appropriate to describe the deactivation caused by thiophene adsorption on the supported Ni catalyst. The thiophene adsorption rate was found to be only weakly dependent on temperature, indicating that in several situations of practical importance the use of an isothermal deactivation kinetics may be sufficiently accurate. This simplification is very well justified for moderately deactivated catalyst beds. At high degrees of deactivation a more complex two-site model may be more appropriate.

LIST OF SYMBOLS

C	toluene concentration, mol m ⁻³
C ^{thio}	thiophene concentration, mol m ⁻³
c _{ps}	specific heat of catalyst, J kg ⁻¹ K ⁻¹
c _{pf}	specific heat of fluid phase, J kg ⁻¹ K ⁻¹
d _p	catalyst particle diameter, m
G _p	mass flow rate, kg s ⁻¹
ΔH _r	reaction enthalpy, J mol ⁻¹
h _w	heat transfer coefficient through reactor wall, J m ⁻² s ⁻¹ K ⁻¹
k _e	radial heat conductivity, J m ⁻¹ s ⁻¹ K ⁻¹
K ₁	kinetic parameter, mol/kg
K ₂	kinetic parameter, K
K ₃	kinetic parameter, K
M _T	thiophene adsorption capacity, mol kg ⁻¹
P _T	toluene partial pressure, bar
\bar{P}_T	mean toluene partial pressure, bar
R _T	radius of reactor tube, m
Re	Reynolds number (G _p /u)
r	radial coordinate, m
r(T, P _T)	reaction rate, mol kg ⁻¹ s ⁻¹
t	time, s
T	temperature, K
U	overall heat transfer coefficient, J m ⁻² s ⁻¹ K ⁻¹
u	superficial gas velocity, m s ⁻¹
z	axial coordinate, m
ε	bed porosity
θ	active fraction of catalyst surface
ρ _f	density of fluid phase, kg m ⁻³
ρ _s	density of solid phase, kg m ⁻³

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