Effects of Poisoning on the Dynamics of Fixed Bed Reactors. 1. Isothermal in a Cyclic Policy of Operation

Constantin E. Megiris[†] and John B. Butt*

Department of Chemical Engineering, Northwestern University, Evanston, Illinois 60208-3120

The dynamic behavior of a fixed bed reactor has been examined with benzene hydrogenation on Ni/kieselguhr, poisoned by thiophene, as a model exothermic reaction. The reactor was operated isothermally, with exit conversion declining with time to a preset lower limit, and then temperature increased to restore the initial conversion level. This procedure was repeated over several cycles. The overall results are interpreted in terms of wave propagation in the fixed bed, combined with the complex nature of thiophene chemisorption on Ni. It is found that successive temperature cycling increases the effective thiophene capacity of the catalyst (increasing temperature). A geometric blockage variation, suggested before, seems to be a reasonable interpretation. A simulation model based on this variable poison adsorption capacity is in excellent accord with experimental results. It is found that an integral guardbed, growing with time, is formed at the entrance to the reactor entrance, and this to a large extent governs the cyclic behavior.

Many industrial processes are seriously constrained or even dominated by catalyst deactivation, yet there are relatively few direct experimental studies reported (Butt et al., 1971). Since catalyst deactivation changes steady-state processes into unsteady-state processes, the transient behavior of a fixed bed reactor subject to poisoning is reflected in a wavelike propagation of temperature, concentration, and activity profiles through the catalyst bed, resulting in a decrease in exit conversion. The objective of this research is, first, to obtain experimental information on the relationship of the poisoning mechanism to its effects on the dynamics of the reactor and, second, to model in an a priori fashion the dynamic behavior of the fixed bed reactor by formulating an appropriate simulation model in which the parameters involved are determined via separate experimentation where possible.

Here we explore a cyclic policy of reactor operation, in which conversion is allowed to decline under deactivating conditions to a preset minimum and then readjusted to initial conditions by increasing the reactor temperature. This cyclic policy is an initial approach to further study of the constant conversion policy of operation often employed industrially. As will be seen, the analysis of cyclic operation is complex enough in its own right.

Experimental Section

Materials. Harshaw Ni-0104T (58% Ni on kieselguhr) was used as the hydrogenation catalyst, supplied in the form of 1/8-in. pellets which were crushed and sieved to specific size ranges. Harshaw reports the active nickel surface to be approximately 24 m²/g. Glass shot microbeads supplied by Ferro and sieved to the same size ranges were used to dilute the catalyst bed. Thiophene-free reagent-grade benzene supplied by J. T. Baker and reagent-grade thiophene supplied by Eastman Kodak were used as liquid feeds. Prepurified-grade hydrogen and nitrogen and high-purity-grade helium, supplied by Linde, were used in all experiments.

Flow System and Reactor. This experimental flow system is similar to that described previously (Weng et al., 1975; Frycek, 1984). It employs a parallel feed arrangement, with one stream containing a pure benzene/hydrogen mixture and the second a thiophene/benzene/hydrogen mixture. Both streams are passed through a four-way valve which allows the selection of the stream that flows through the reactor and diverts the other to a bypass line with the same pressure drop.

A multiple heating zone tubular fixed bed reactor was used to maintain the temperature profile of the catalyst bed. A catalyst bed, suitably diluted, was used to minimize local heat generation and was approximately 48 cm in length. The reactor, was zone-heated to maintain isothermality; details of the design, data acquisition, and system control are as described by Megiris (1987).

Operation. Catalyst pretreatment consisted of purging the bed (ca. 100 cm³ of catalyst) at room temperature with nitrogen at 1000 mL/min for 1 h and then purging with hot nitrogen at 150 °C for 4 h more to remove CO_2 from the non-pyrophoric catalyst. The reactor temperature was then increased to 375 °C and hydrogen flow at 1000 mL/min for 6 h was used to activate the Ni catalyst. This procedure was repeated before each experimental run. For the cyclic policy of operation, the pure benzene stream was first fed to the isothermal reactor until steady-state conversion was established. The feed was then switched to introduce the thiophene-containing mixture. Conversion was allowed to decline, and the axial temperature profile and exit conversion were monitored at periodic time intervals. When a preset lower conversion limit was reached, the feed was switched back to the pure benzene steam and the reactor temperature was increased at a rate of 1 °C/min up to the temperature of the second cycle where the exit conversion was back to approximately that under initial conditions. This procedure was repeated for several cycles until significant thermal activation of the bed could

Table I. Experimental Operating Conditions

run	C1	C2	C5	C6	C7
mesh	60/70	60/70	100/120	80/100	70/80
temp, °C					
cycle 1	70	70	67.5	67.5	65
cycle 2	115.5	100	95	91	81.5
cycle 3	200	155	150	125	108
cycle 4					170

flow rate, mol/s	~6.81 × 10⁻⁷
av pressure, Pa	~12.3 × 10⁴ ± 8%
benzene mole fraction	~0.0215
ppm thiophene	~133
bed length, m	~0.48
catalyst wt, g	~2.00
glass beads wt, g	~153
reactor cross-sectional area, m²	2.068 × 10⁻⁴

(av values; actual exptl values are within ±3%)

---

*Author to whom correspondence should be addressed.

[†] Present address: Koninklijke/Shell-Laboratorium, 1003 AA Amsterdam, The Netherlands.

Table II. Benzene Hydrogenation Kinetic Parameters (Equation 1)

$k^\circ = 1.30 \times 10^{-2}$ kmol/(kg cat·s·Pa)	$K^\circ = 2.01 \times 10^{-14}$ Pa^{-1}
$E = 5.47 \times 10^7$ J/kmol	$Q = 8.94 \times 10^7$ J/kmol

Table III. Thiophene Poisoning Kinetic Parameters (Equation 3)

$k^\circ_D = 1.80 \times 10^{-4}$ (Pa·s)$^{-1}$	$E_D = 4.53 \times 10^6$ J/kmol

no longer be achieved. Experimental conditions for a series of five runs are summarized in Table I.

Reaction Kinetics

The benzene hydrogenation reaction over the Ni/kieselguhr catalyst is exothermic and irreversible in the temperature range 60–200 °C and at a pressure of 1 atm. Kehoe and Butt (1972) correlated the kinetics by the form

$$-r_B = \frac{k^\circ K^\circ \exp[(Q - E)/RT]P^2 x_B x_H}{1 + K^\circ \exp(Q/RT)Px_B} \qquad (1)$$

At low temperatures, the rate expression can be simplified to

$$-r_B = kPx_H \qquad (2)$$

These forms provide a good correlation of the kinetic data for the catalyst used in these experiments. The corresponding parameters obtained by linear least-squares analysis are summarized in Table II. The kinetics of the poisoning reaction have been correlated with a separable form of the rate equation, linear in the concentration of poison and availability of active sites

$$-r_D = k^\circ_D \exp[-E_D/RT]PX_T(s) \qquad (3)$$

Similar forms of the poisoning kinetics for thiophene chemisorption on Ni catalysts have been used by Richardson (1971), Zrncevic and Gomzi (1983), and Baiker et al. (1986). The parameters for this rate expression are given in Table III.

Three characteristics of the intrinsic kinetics of the hydrogenation and deactivation reactions have been found to exert significant influence on the dynamics of the fixed bed reactor induced by poisoning.

(a) In the temperature range 55–120 °C, the rate expression for benzene hydrogenation is zero order in benzene concentration.

(b) The rate equation for benzene hydrogenation exhibits a maximum around 180 °C under typical experimental conditions.

(c) The activation energy of the poisoning kinetics is quite low (1.1 kcal/mol), and therefore, the chemisorption of thiophene on Ni depends only weakly on temperature. Consequently, the rate of catalyst poisoning is controlled by the value of the preexponential factor, k°_D, and the activation energy parameter, E_D, exerts only a minor influence. In effect, the low value of E_D tells us that the uptake of poison is rapid and irreversible regardless of temperature.

Results and Simulation

Experimental Results. Typical experimental results are presented in Figures 1 and 2 in the form of conversion versus poison time on stream for experiments C2 and C6. Experiment C2 is more representative of the constant conversion conditions discussed later and is common for all models tested, so most comparisons given below are for that experiment. The first data point of each cycle represents the steady-state conversion measured while the pure benzene stream was fed to the reactor. The useful
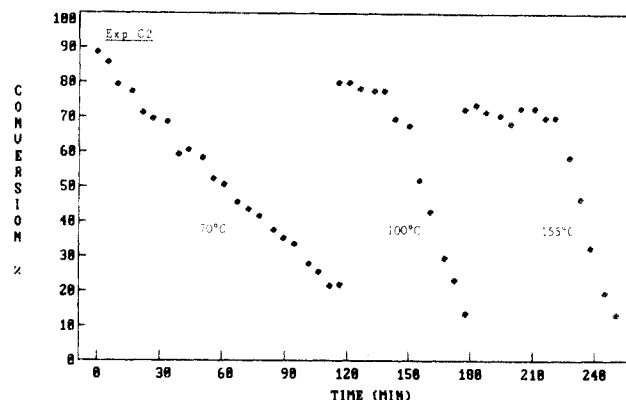

Figure 1. Experimental data for run C2. Conversion versus time for successive reactor temperature cycles.
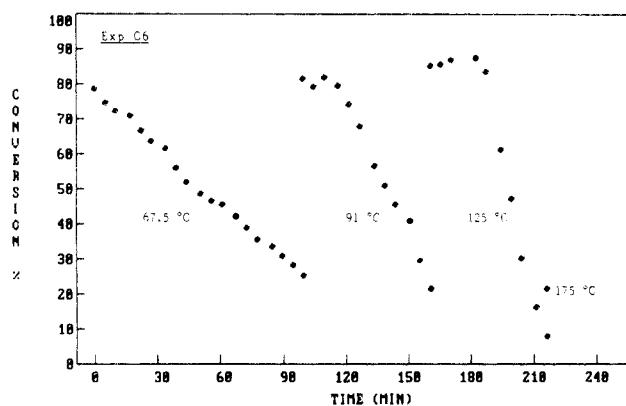

Figure 2. Experimental data for run C6. Conversion versus time for successive reactor temperature cycles.
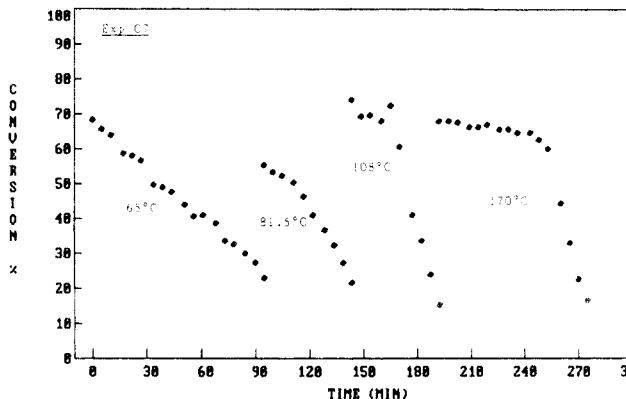

Figure 3. Experimental data for run C7. Conversion versus time for successive reactor temperature cycles.

lifetime of the catalyst bed in all experiments was usually exhausted in three cycles of reactor operation, as shown. The four cycles of C7 (Figure 3) were accomplished because the exit conversion alternated within a narrower range of high and low levels. In all cases, no significant thermal activation of the bed could be achieved after the last cycle of reactor operation.

Two very significant features of the dynamics induced by poisoning are revealed. During the first cycle of reactor operation, benzene conversion declines with time in a linear way. In subsequent cycles, exit conversion remains constant for an initial period of time in spite of the poisoning conditions, and the duration of this period becomes longer with increasing bed temperature. After this, the conversion drops rapidly to the low level of the cycle. Any reasonable interpretation should then predict both of these characteristics of the transient behavior.

Table IV. Reactor Model (One Site)

mass balance, benzene

$$\frac{\partial x_B}{\partial t} = -u\,\frac{\partial x_B}{\partial z} + \frac{\rho_c MW_g}{\epsilon \rho_g} r_B(x_B,T)s$$

mass balance, thiophene

$$\frac{\partial x_T}{\partial t} = -u\,\frac{\partial x_T}{\partial z} + \frac{\rho_c MW_g}{\epsilon \rho_g} r_T(x_T,T,s)$$

activity decay

$$\partial s/\partial t = r_D = r_T/M_T = -k_D{}^\circ \exp[-E_D/RT]Px_T s$$

boundary conditions

at $z = 0$, $x_B = x_B{}^\circ$ $(t > 0)$
at $z = 0$, $x_T = x_T{}^\circ$ $(t > 0)$

initial conditions

at $t = 0$, $x_B(z,0) = x_B(a)$ at steady state
$x_T(z,0) = 0$ $s(z,0) = 1$

Simulation: One-Site Model. A one-dimensional pseudohomogeneous plug flow reactor model was used to simulate the transient behavior. The system of coupled balances of the model is shown in Table IV. The model consists of mass balances for benzene and thiophene, an activity decay equation, and a set of boundary and initial conditions for reactor operation. Major assumptions are omissions of the hydrogen mass balance and neglect of volume changes during reaction, justified by the large excess of hydrogen employed in all experiments. The model also ignores axial mass dispersion effects and radial temperature gradients and assumes that interphase and intraphase gradients are negligible. The validity of these assumptions for the experimental conditions shown here has been shown by Weng et al. (1975) and Frycek (1984).

The reactor model is widely used in the literature. In this application, it also considers the sites active for hydrogenation to be active for chemisorption and is so characterized as a "one-site" model. The poison adsorption capacity of the catalyst, M_T, is particularly important for the modeling results. It has been measured in separate experiments (Price and Butt, 1977; Billimoria and Butt, 1981) and depends on temperature, ranging from 3.50 to 6.15 × 10⁻⁴ kmol of thiophene/kg of catalyst for 50–180 °C. For initial simulation purposes, a value of 4 × 10⁻⁴ kmol of thiophene/kg, well within the reported range, resulted in the best model predictions via the one-site model.

Comparison between experiment and model is shown in parts a and b of Figure 4 for the examples of runs C2 and C6. The deficiences are informative; this model simulates successfully the linear decline of conversion with poison time on stream during the first cycle of reactor operation but fails to describe the observed experimental behavior in all subsequent cycles. During the second cycle, experimental measurements decay in a convex manner, while simulated results decay exponentially. Moreover, the model fails to predict the existence of a third cycle of reactor operation.

Simulation: Two-Site Model. An empirical two-site model was also used by Weng et al. (1975) to simulate the dynamic behavior of a nonisothermal, nonadiabatic fixed bed for this system. It considered the sites active for thiophene chemisorption to be the sum of those active for hydrogenation and chemisorption (sites A) and those active for chemisorption alone (sites B). This assumption leads to two separate activity decay equations that correspond to two sites, A and B, respectively, as shown in Table V. Two additional parameters are involved in the two-site model, the rate constant for the poisoning of site B, k_{DB}, and the thiophene adsorption capacity on site B, M_{TB}. No separate experimental information is available about the
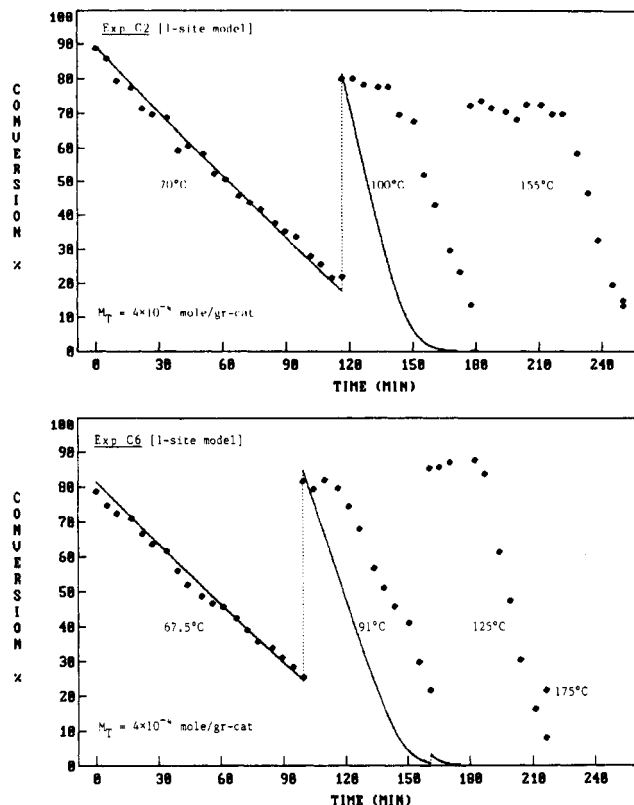

Figure 4. (a, top) Simulation of experimental results for run C2. One-site model. (b, bottom) Simulation of experimental results for run C6. One-site model.

Table V. Two-Site Model for Thiophene Chemisorption

mass balance, benzene

$$\frac{\partial x_B}{\partial t} = -u\,\frac{\partial x_B}{\partial z} + \frac{\rho_c MW_g}{\epsilon \rho_g} r_B(x_B,T)\theta_A$$

mass balance, thiophene

$$\frac{\partial x_T}{\partial t} = -u\,\frac{\partial x_T}{\partial z} + \frac{\rho_c MW_g}{\epsilon \rho_g}[r_{TA}(x_T,T,\theta_A) + r_{TB}(x_T,T,\theta_B)]$$

activity decay

site A: $\partial \theta_A/\partial t - r_{DA} = r_{TA}/M_{TA} = -k_{DA}Px_T\theta_A$

site B: $\partial \theta_B/\partial t = r_{DB} = r_{TB}/M_{TB} = -k_{DB}Px_T\theta_B$

boundary conditions

as in Table IV

initial conditions

as in Table IV, except now
$\theta_A(z,0) = 1$ $\theta_B(z,0) = 1$

values of these parameters, so here the set of parametric values for k_{DB} and M_{TB} must be adjusted for best fit of simulation to experiment.

Representative experimental and calculated profiles with this model are compared in Figure 5. Excellent results are obtained for the first two cycles of reactor operation including both the initial constant conversion period of the second cycle as well as the subsequent rapid drop of benzene conversion. However, while the two-site model predicts the existence of a third cycle, its failure to predict the conversion-time history here suggests further difficulties in modeling poisoning kinetics, as discussed below.

Poisoning Mechanism. Both the one- and two-site models are at best empirical approximations in view of the inadequacies above. This is further reflected in the apparent variation of the thiophene adsorption capacity of the catalyst with temperature. More detailed views of
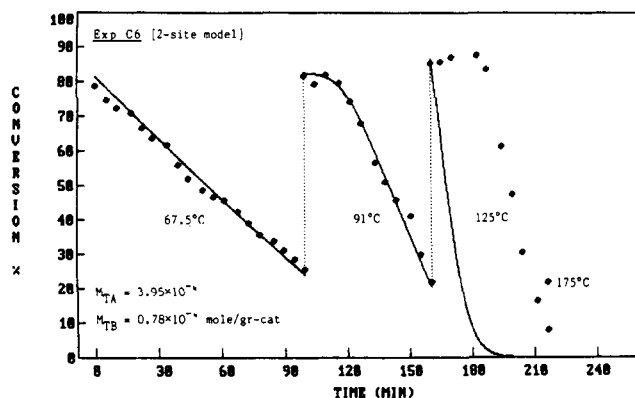
Figure 5. Simulation of experimental results for run C6. Two-site model.
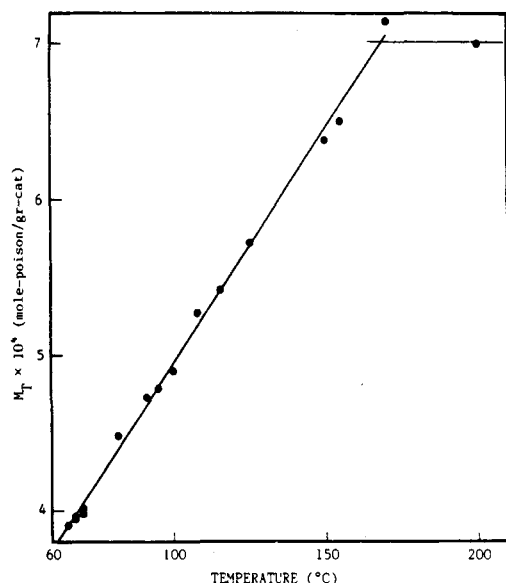

Figure 6. Variation of equilibrium thiophene adsorption with temperature.

thiophene adsorption have been set forth by Lyubarskii et al. (1962) and Ahmed et al. (1987). The former suggested that at room temperature the thiophene molecule is strongly adsorbed on the Ni surface in a planar orientation in which five Ni atoms are blocked, but at higher temperatures (100–150 °C), the molecule is hydrogenated to thiophane and bonded to the surface via the sulfur atom. The remaining saturated part of the molecule has an upright or "anchor" position above the surface. The part of the Ni surface formerly occupied by the flat-lying unsaturated ring is freed for additional poison adsorption. The sulfur capacity of the catalyst was reported to increase 1.5–2 times over this temperature range. At a temperature of 300 °C, thiophene undergoes hydrogenolysis to n-butane, leaving only the sulfur atom bonded to the surface. At this stage, all steric hindrance effects of the ring have been removed (Bourne et al., 1965). On this basis, a more sophisticated view of the chemisorption would be that of a series of transformations that are strong functions of temperature and tend to increase the apparent thiophene capacity of the catalyst with increasing temperature. As shown below, a variable capacity model provides a successful approach to this.

Simulation: Variable Poison Adsorption Capacity Model. A model incorporating the increase of poison adsorption capacity with temperature includes two activity parameters as indicated in Table VI. The activity for benzene hydrogenation, s, is related only to sites active for
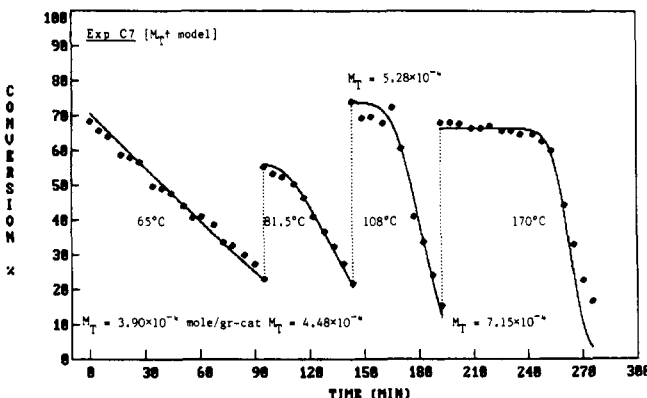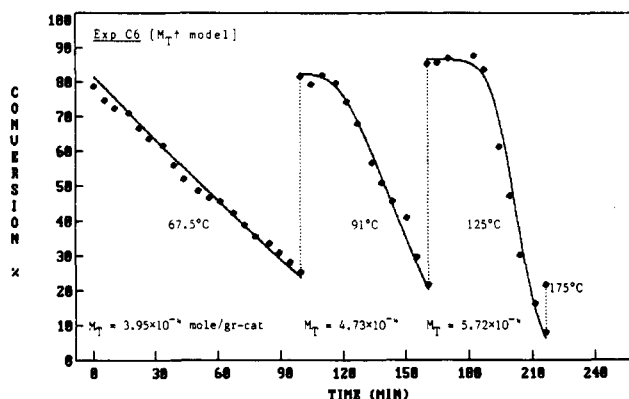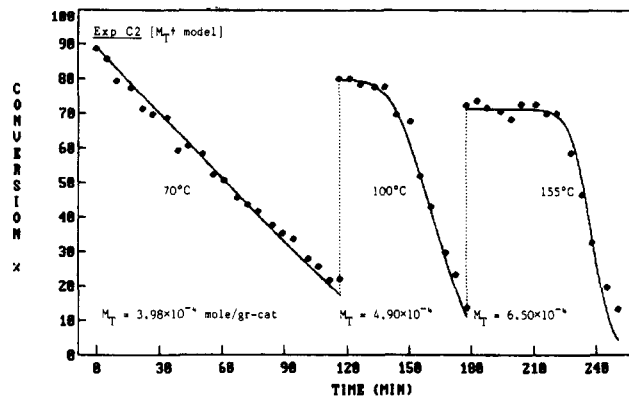

Figure 7. Fit to experimental data for various conditions with the variable poison adsorption capacity model. (a, top) Run C2; (b, middle) run C6; (c, bottom) run C7.

hydrogenation and is not significantly dependent upon temperature. A relative activity for poison adsorption, α, is taken to increase approximately linearly with temperature, and $M_T = f(\alpha)$ is shown in Table VI. This can be rewritten for the present experiments from cycle n to cycle $n + 1$ as

$$(1 - \alpha_{n-1})(M_T)_{n-1} = (1 - \alpha_n)(M_T)_n$$

to account for the increase in poison adsorption capacity between two cycles caused by the increase in the reactor temperature.

The results of this approach are shown in Figure 6, where adjustment of the parameter M_T has been used to obtain the best fit to experimental data. Modeling results are compared with data from the example experiments given previously in Figure 7. In Figure 7, it is seen that agreement between simulation and experiment is excellent, both with respect to the linear decline in conversion during the first cycle of reactor operation, the constant conversion period during the initial portion of subsequent cycles, and the breakpoint of conversion decrease. This follows the

Table VI. Variable Poison Adsorption Capacity Model

mass balance, benzene
    as in Table IV
mass balance, thiophene

$$\frac{\partial x_T}{\partial t} = -u\frac{\partial x_T}{\partial z} + \frac{\rho_c MW_g}{\epsilon \rho_g} r_T(x_T, T, \alpha)$$

activity for benzene hydrogenation
    $\partial s/\partial t = -k_D P x_T s$
relative activity for thiophene adsorption

$$\frac{\partial \alpha}{\partial t} = \frac{r_T}{M_T} = -k_D P x_T \alpha$$

$$\alpha(T_2) = 1 - [M_T(T_1)/M_T(T_2)][1 - \alpha(T_1)]$$

boundary conditions
    as in Table IV
initial conditions
    at $t = 0$ $x_B(z,0) = x_B(a)$ at steady state
    $x_T(z,0) = 0$, $s(z,0) = 1$, $\alpha(z,0) = 1$
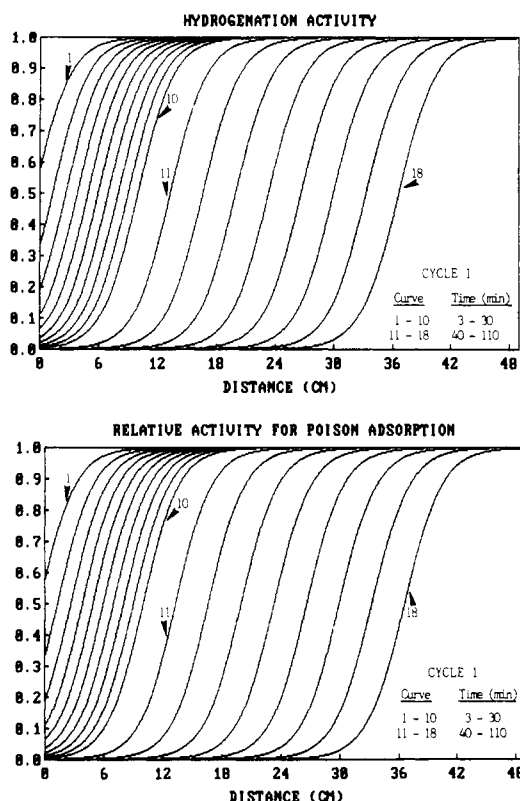

Figure 8. Simulation results for fixed bed reactor dynamics; variable adsorption capacity model, conditions of run C2. Hydrogenation activity and poison adsorption capacity. Cycle 1.

behavior shown in Figure 6, where M_T is approximately linear with temperature, attaining a saturation value at temperatures in the range ~ 200 °C.

Two factors should be examined regarding the internal consistency of this modeling approach. First is the physical reasonableness of the temperature variation of M_T, and second is the apparent saturation observed. We are satisfied that the first represents the smooth temperature transition from multiple- to single-site blocking noted by others and that the second is the apparent saturation capacity attained at higher temperatures, characteristic of decomposition to a surface sulfur species. Since 1 cm^2 of Ni accommodates an average of 1.55×10^{15} Ni atoms (Lyubarskii et al., 1962), unit stoichiometry for S adsorption per surface Ni is suggested via these results. Apparent saturation coverage is then calculated to be 7.06×10^{-4} mol of poison/g of catalyst in the 170–200 °C range. According to Bourne et al. (1965), this corresponds to a Ni/S atom
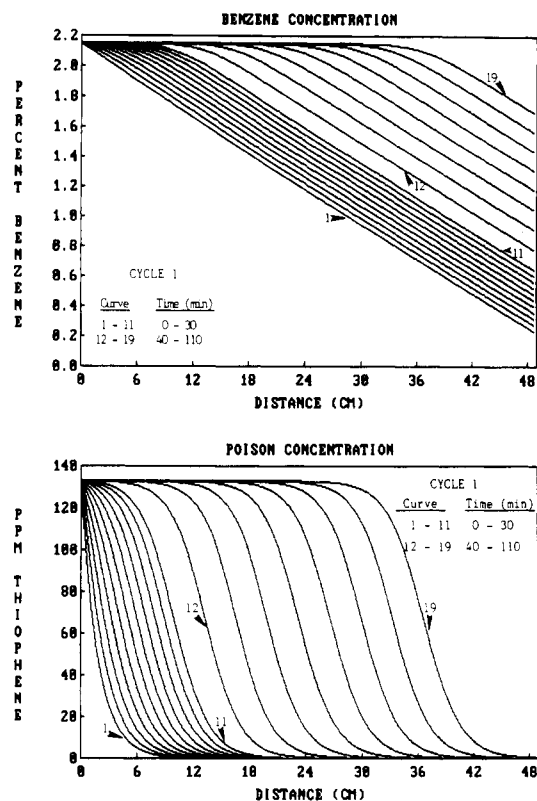

Figure 9. Simulation results for fixed bed reactor dynamics; variable adsorption capacity model, conditions of run C2. Benzene concentration and poison concentration. Cycle 1.

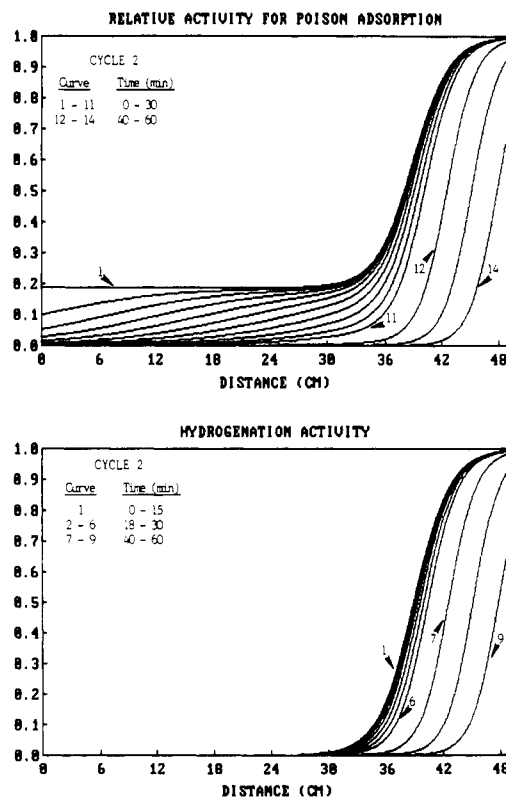**Figure 10.** Simulation results for cycle 2. Cf. Figure 8.

ratio of 1:1. For an active Ni surface of approximately 24 m^2/g, one calculates the number of adsorbed sulfur atoms to be 1.8×10^{15} cm^{-2}. Everything appears to be internally consistent in this interpretation.

Dynamic Simulation: Activity and Concentration Profiles. Following this, it is worth exploring some details
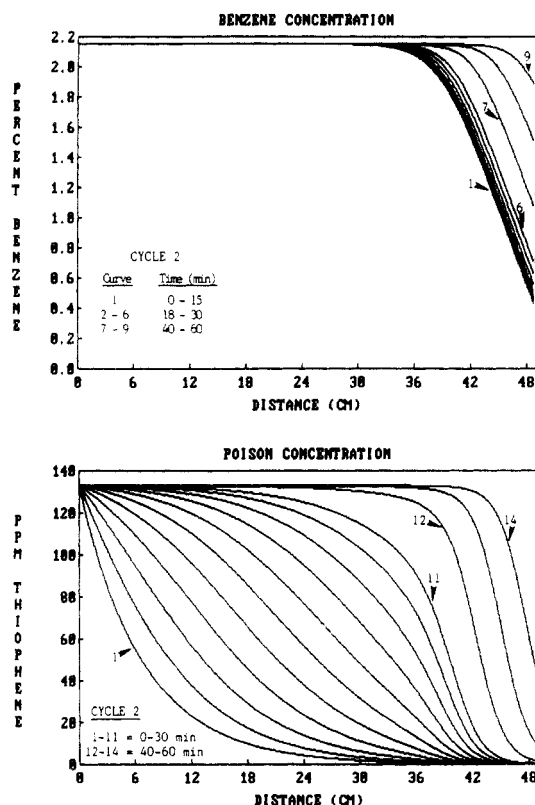
BENZENE CONCENTRATION

CYCLE 2

Curve	Time (min)
1	0 - 15
2 - 6	18 - 30
7 - 9	40 - 60

POISON CONCENTRATION

CYCLE 2
1-11 = 0-30 min
12-14 = 40-60 min

Figure 11. Simulation results for cycle 2. Cf. Figure 9.

RELATIVE ACTIVITY FOR POISON ADSORPTION

CYCLE 3

Curve	Time (min)
1 - 11	0 - 30
12 - 15	40 - 70

HYDROGENATION ACTIVITY

CYCLE 3

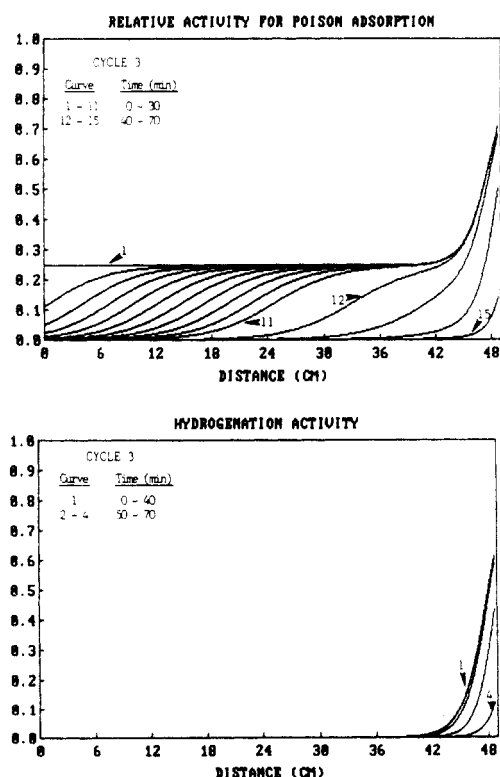| Curve	Time (min)
1	0 - 40
2 - 4	50 - 70

Figure 12. Simulation results for cycle 3. Cf. Figure 8.

of what this model predicts concerning the dynamic behavior of activity and concentration profiles. Simulation results based on typical experimental conditions (experiment C2) are presented in Figures 8–13. In general, the transients induced by poisoning are reflected in a wavelike propagation of concentration and activity profiles through the catalyst bed.

First Cycle of Reactor Operation. The reactor dynamics are composed of three distinct time domains, il-

BENZENE CONCENTRATION

CYCLE 3

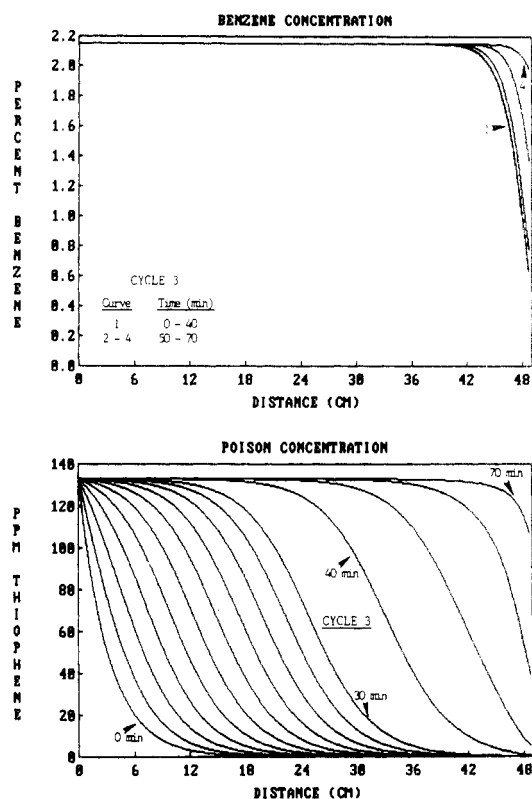| Curve	Time (min)
1	0 - 40
2 - 4	50 - 70

POISON CONCENTRATION

CYCLE 3

Figure 13. Simulation results for cycle 3. Cf. Figure 9.

lustrated in Figures 8 and 9. The first domain is a fast concentration response (FCR) (Price and Butt, 1977) of thiophene, which very rapidly establishes a quasi-steady profile from its zero initial condition. This time domain in fact cannot be shown well because the quasi-steady profile is established in less than two residence times of reactor operation. However, during the FCR time period, the activity and benzene concentration profiles do not change significantly from their initial steady-state values.

The other two time domains can be identified as two different types of slow concentration response (SCR). During the first SCR, which lasts about 30 min (Figure 9), the activity and concentration profiles slowly develop a characteristic shape. During the second SCR period, which lasts until the end of the cycle, the activity and concentration profiles travel through the catalyst bed at constant velocity and without any change in their characteristic shape. The hydrogenation activity profiles of Figure 8 assume a fixed shape, approaching step functions, and hence, the length of the active catalyst bed is a linear function of the poison time on stream. On the other hand, the observed linear benzene concentration profiles of Figure 9 reflect the zero-order kinetics with respect to benzene at the low temperature of the first cycle. Therefore, the exit conversion is also a linear function of the length of the active catalyst bed. It follows that the exit conversion is a linear function of poison time on stream, and thus the simulation predicts the linear decline in conversion observed experimentally during the first cycle.

Second Cycle of Reactor Operation. The increase in reactor temperature required for the second cycle results in a corresponding increase in the poison adsorption capacity of the catalyst bed. As shown in Figure 10, the entrance of the bed becomes active again for thiophene chemisorption but remains inactive for hydrogenation. As a consequence, the catalyst bed can be divided into two different parts. The bed entrance is only active for poison

Table VII. Comparison between the Total Amount of Poison Fed to the Bed and the Poison Adsorption Capacity of the Catalyst

expt	reactor temp last cycle, °C	$10^4 M_T$, mol/g cat	total poison × 10^4, mol/g cat
C1	200	7.06	7.16
C2	155	6.60	6.82
C5	150	6.45	6.65
C6	125	5.70	5.89
C7	170	7.06	7.50

adsorption and acts as a guard bed that strips poison from the feed before it reaches the second part of the bed. The rest of the bed is active for benzene hydrogenation and, since it is protected by the guard bed, operates under poison-free conditions during the initial stages of the second cycle. Indeed, catalyst removed from the bed entrance after this second cycle shows no activity for benzene hydrogenation.

The overall picture of reactor dynamics in cycle 2 (Figures 10 and 11) shows four distinct time domains. The first is a FCR of thiophene exactly the same as for the first cycle. The next two domains can be classified as differing types of SCR of thiophene. During the first of these (0–15 min), poison concentration and adsorption activity profiles develop within the guard bed and travel through the guard bed. The hydrogenation activity and benzene concentration profiles established within the main bed remain unchanged because of the adsorption capacity of the guard bed. Therefore, the main bed operates under poison-free pseudo-steady-state conditions and benzene conversion remains constant.

During the second SCR of thiophene (15–30 min), the tail of the poison concentration and adsorption activity profiles passes the guard-bed exit, causing a slow movement of the hydrogenation activity and benzene concentration profiles in the main bed. The relatively slow changes occurring in the main bed manifest themselves as a slight decrease in exit conversion at the back of the conversion decay curves (Figure 7).

The fourth time domain is a third SCR (40–60 min) resulting from the poisoning of the main bed. The poison concentration and adsorption activity profiles have entered the main bed, and therefore, the guard-bed section is not capable of adsorbing more poison. During this period, all profiles move through the main bed at constant velocity without changing shape, and the exit conversion of benzene decays rapidly with poison time on stream.

Third Cycle of Reactor Operation. The general characteristics of dynamics in the third cycle (Figures 12 and 13) are similar to those for the second cycle, but now the first and second SCR of thiophene are fused into a single, slow thiophene concentration response. Again, initially (0–40 min), the guard-bed strips the poison fed to the reactor, while the main bed operates under poison-free pseudo-steady-state conditions, and the exit conversion remains constant. The poison concentration and adsorption activity profiles also propagate along the guard bed with constant velocity and fixed shape. The second SCR time domain (40–70 min) is characterized by the rapid decline in benzene conversion, since the guard bed is inactive for thiophene chemisorption and poisoning of the main bed occurs.

The simulation results on dynamics also lead to a mass balance test of model reliability. All poison fed to the reactor is adsorbed by the catalyst bed except for the last few minutes of the second and third cycles, during breakthrough. On the other hand, at the end of each experiment, the catalyst bed is dead for all practical

purposes. Therefore, the total amount of poison fed to the reactor (parameter measured experimentally) should be only slightly higher than the poison adsorption capacity of the catalyst bed evaluated at the temperature of the reactor during the last cycle of operation (M_T parameter determined by best simulation fitting). Good results are obtained from this comparison, as shown in Table VII.

Conclusions

The cyclic technique appears to be an efficient tool for exploring the specifics of deactivation. The present work shows clearly that the successive transformations of the thiophene molecule on the Ni catalytic surface serve to increase the poison adsorption capacity of the catalyst with increasing temperature and that this is very important in determining the overall reactor behavior. Simulation results on this basis were excellent.

An important feature of the dynamics induced by poisoning is the formation of an integral guard bed at the entrance of the reactor. The guard bed, although inactive for benzene hydrogenation, is capable of adsorbing poison and strips the poison from the feed before it reaches the main bed, which is active for the hydrogenation reaction. The main bed operates under poison-free pseudo-steady-state conditions, and the exit conversion remains constant until the guard bed is saturated with poison.

The behavior of the fixed bed under temperature-cycled operation is seen to be composed of a complex interaction of waves associated with reactant and poison concentrations and bed activity for both hydrogenation and poison chemisorption. It is interesting that such an experiment turns out to be a rather sensitive diagnostic for the mechanism of catalyst poisoning.

The most severe test of the approach, however, would be in the prediction of time-temperature histories required to achieve constant conversion. Such T–t trajectories are compared with the results in part 2 (Megiris and Butt, 1990).

Nomenclature

E = activation energy of the main reaction, J/kmol
E_D = activation energy for poisoning, J/kmol
k = rate constant for the hydrogenation reaction, kmol/(kg of catalyst·s·Pa)
$k°$ = preexponential factor for the hydrogenation reaction, kmol/(kg of catalyst·s·Pa)
K = adsorption constant for benzene, 1/Pa
$K°$ = preexponential factor of adsorption constant for benzene, 1/Pa
k_D = poisoning rate constant, 1/(Pa·s)
$k°_D$ = preexponential factor for poisoning, 1/(Pa·s)
k_{DA}, k_{DB} = poisoning rate constants for the two-site poisoning model, 1/(Pa·s)
M_T = catalyst adsorption capacity for thiophene, kmol of poison/kg of catalyst
M_{TA}, M_{TB} = catalyst adsorption capacity for thiophene on sites A and B, kmol of poison/kg of catalyst
M_{T_n} = catalyst adsorption capacity for thiophene at the temperature of cycle n, kmol of poison/kg of catalyst
MW_g = molecular weight of gas, kg/kmol
P = pressure, Pa
Q = benzene heat of adsorption, J/kmol
R = universal gas constant
r_B = rate of benzene hydrogenation, kmol/(kg of catalyst·s)
r_D = rate of poisoning, s⁻¹
r_{DA}, r_{DB} = rate of deactivation of sites A and B, s⁻¹
r_T = rate of thiophene chemisorption, kmol/(kg of catalyst·s)
r_{TA}, r_{TB} = rate of thiophene chemisorption on sites A and B, kmol/(kg of catalyst·s)
s = catalyst relative activity for benzene hydrogenation

t = time, s
T = temperature, °C
u = superficial gas velocity, m/s
x = benzene conversion
x_B, x_T, x_{H_2} = mole fractions of benzene, thiophene, and hydrogen
x_B°, x_T° = inlet mole fractions of benzene and thiophene
z = length variable, m

Greek Symbols

α = relative activity for poison adsorption
ϵ = bed voidage
θ_A, θ_B = fractional occupancy of hydrogenation-active and -inactive sites by thiophene (two-site model)
ρ_c = bulk density of catalyst, kg/m^3
ρ_g = gas density, kg/m^3

Registry No. Ni, 7440-02-0; benzene, 71-43-2; thiophene, 110-02-1.

Literature Cited

Ahmed, K.; Chadwick, D.; Kershenbaum, L. S. *Stud. Surf. Sci. Catal.* **1987**, *34*, 513.
Baiker, A.; Epple, D.; Wokaun, A. *Chem. Eng. Sci.* **1986**, *41*, 779.
Billimoria, R. M.; Butt, J. B. *Chem. Eng. J.* **1981**, *22*, 71.
Bourne, K. H.; Holmes, P. D.; Pitkethly, R. C. *Proc. 3rd Int. Congr. Catal.* **1965**, *2*, 1400.
Butt, J. B.; Joyal, C. L.; Megiris, C. E. The Poisoning of Catalysts: Experimental Observations and Modeling. In *Catalyst Deactivation*; Petersen, E. E., Bell, A. T., Eds.; Marcel Dekker: New York, 1987.
Frycek, G. J. Experiment and Modeling of Poisoning Effects in Temperature-Increased Fixed Bed Reactor Operation. Ph.D Dissertation, Northwestern University, Evanston, IL, 1984. Available from University Microfilms, Inc.
Kehoe, J. P. G.; Butt, J. B. *J. Appl. Chem. Biotechnol.* **1972**, *22*, 23.
Lyubarskii, G. D.; Andeeva, L. G.; Kul'kova, N. V. *Kinet. Catal.* **1962**, *3*, 102.
Megiris, C. E. Effects of Poisoning on the Dynamics of Fixed Bed Reactors. Ph.D Dissertation, Northwestern University, Evanston, IL, 1987. Available from University Microfilms, Inc.
Megiris, C. E.; Butt, J. B. *Ind. Eng. Chem. Res.* **1990**, following paper in this issue.
Price, T. H.; Butt, J. B. *Chem. Eng. Sci.* **1977**, *32*, 393.
Richardson, J. T. *J. Catal.* **1971**, *21*, 130.
Weng, H. S.; Eigenberger, G.; Butt, J. B. *Chem. Eng. Sci.* **1975**, *30*, 1341.
Zrncevic, S.; Gomzi, Z. *Chem. Eng. Sci* **1983**, *38*, 1351.

Effects of Poisoning on the Dynamics of Fixed Bed Reactors. 2. Constant Conversion Policy of Operation

Constantin E. Megiris[†] and John B. Butt[*]

Department of Chemical Engineering, Northwestern University, Evanston, Illinois 60208-3120

The dynamic behavior of a fixed bed reactor subject to strong, irreversible poisoning has been investigated. In this work, the nature of the reaction and reactor and deactivation characteristics have been incorporated into a study of fixed bed operation at constant conversion. Experiments and simulation results are presented, showing in a severe test that the variable capacity model for chemisorption of thiophene on Ni can explain the results. The constant conversion, temperature increased requirement (TIR) experiment is quite sensitive to the energetics of deactivation and, overall, provides a good measure of the worth of both the reactor simulation model and the approach to poisoning kinetics. Simulation of transients under TIR further illustrates the wavelike propagation of activity and concentration profiles through the bed. These resemble the cyclic operation of part 1 but differ importantly in end-of-bed behavior because of the constant-conversion requirement. Guard-bed behavior is observed but is modified by the constant conversion requirement and concomitant increase in bed temperature.

Many instances of catalyst deactivation require reactor operation at constant conversion conditions accomplished by increasing the reactor temperature with time to compensate for deactivation while there is a constant feed rate to the reactor. The result is a temperature–time history, often called the "temperature increased requirement" (TIR), that represents a measure of the resistance of the catalyst to deactivation.

Krishnaswamy and Kittrel (1979) and Sadana (1980, 1982) have presented simple mathematical models based on two different criteria for optimum reactor operation and the assumption that at any instant the reactor is isothermal and the deactivation rate is concentration independent. Subsequently, both groups of investigators extended their approach to include severely intraparticle diffusion-limited systems (Krishnaswamy and Kittrell, 1982; Henley and Sadana, 1986; Sadana, 1987). Gonzalez-Velasco et al.

(1984) and Romero et al. (1981) applied the analysis of Krishnaswamy and Kittrell (1979) to the dehydrogenation of benzyl alcohol to benzaldehyde on Cu/SiO_2 with good results. However, the assumption of concentration independence of deactivation is often a serious limitation to the general applicability of such models.

In cases where the deactivation rate is a concentration-dependent function, the analysis of Butt and Rohan (1968) applies. That approach is based on the fixed bed modeling via a series of perfect mixing cells and was later extended (Butt, 1970, 1971) to poisoning of bifunctional catalysts. Recently, Hong and Lee (1985, 1986) presented a new approach for estimating the extent of catalyst deactivation and maintaining the exit conversion within a band about the desired level from on-line measurements of inlet temperature and outlet concentration. The method is a feedback control scheme and does not require knowledge of the deactivation kinetics to maintain the desired conversion.

This work follows part 1 (Megiris and Butt, 1990) in an extension to TIR operation. Such operation can be con-

---

[*] Author to whom correspondence should be addressed.
[†] Present address: Koninklijke/Shell Laboratorium, 1003 AA Amsterdam, The Netherlands.