EFFECTS OF POISONING ON THE DYNAMICS OF FIXED BED REACTORS:
Cyclic and Temperature-Increased Operational Policies

C. E. Megiris and J. B. Butt

Department of Chemical Engineering
Northwestern University
Evanston, IL 60208 USA

ABSTRACT

The dynamic behavior of a fixed bed reactor has been examined using benzene hydrogenation on Ni/kieselguhr, poisoned by thiophene, as a model reaction. Reactor operation, cyclic at constant temperature (CO) and fixed conversion with increasing temperature (TIR), has been studied. It is shown that CO provides a rather sensitive means for identification of the mechanism of poisoning, and TIR gives a severe test of such interpretation.

KEYWORDS

Dynamic behavior; poisoning; fixed bed reactor; traveling waves; cyclic operation; constant conversion

INTRODUCTION

Deactivation is very important industrially, but there are relatively few experimental studies that deal with reactor behavior confronting simulation/ modeling results. In fixed beds deactivation leads to transient, wave-like behavior (Froment and Bischoff, 1962; Weng et al., 1974; Wheeler and Robell, 1969) that in general defies intuition as to a priori predictions of performance. In this work we examine two types of dynamics, 1) constant temperature with variable conversion (CO) and 2) variable temperature with constant conversion (TIR). In each case simulation and experimental results are compared both with respect to the reactor operation itself and to the nature of the information conveyed by the experiment regarding deactivation. The thiophene-nickel system used for poisoning here has been widely investigated and is rather complex. A good summary is provided by the work of Lyubarskii et al., (1962).

EXPERIMENTAL - CATALYSTS AND KINETICS

The benzene hydrogenation reaction is an interesting model system to use for deactivation studies because it involves large thermal effects, is irreversible over a conveniently accessible experimental range, and is subject to rapid poisoning by sulfur compounds with a number of metal catalysts. The kinetics of ths reaction over Ni/kieselguhr at temperatures below ca. $230^\circ C$ are well correlated (Weng et al., 1974; Megiris, 1987) by an expression of the form:

$$(-r)_B = \frac{k^o K^o \exp[(Q-E)/RT]\ P^2 x_B x_{H_2}}{1 + K^o \exp(Q/RT)\ Px_B} \quad \frac{kmol}{kg\text{-}cat\text{-}sec} \tag{1}$$

where $k^o = 1.3 \times 10^{-2}$ kmol/kg-cat-sec-Pa, $E = 5.47 \times 10^4$ kJ/kmol, $K^o = 2.02 \times 10^{-14}$ Pa^{-1} and $Q = 8.94 \times 10^4$ kJ/kmol. The kinetics of the poisoning reaction are given by:

$$(-r)_D = k_D^o \exp(-E_D/RT)\ Px_t \quad s = -\frac{ds}{dt} \ sec^{-1} \tag{2}$$

where s is the activity variable (1 for fresh catalyst and zero for completely deactivated catalyst), $k_D^o = 1.8 \times 10^{-4}$ (Pa-sec)$^{-1}$ and $E_D = 4.5$ kJ/kmol. In this separable formulation (Szepe and Levenspiel, 1971) the deactivation kinetics are followed by the model that, at any time:

$$k^o(t) = k^o \cdot s \tag{3}$$

Although forms such as equation (1) are common and rather well understood, for the benzene hydrogenation (paramater values as above) the rate behavior turns turns out to be fairly complicated, as shown in Figure 1 for a typical range of concentrations and temperatures of interest. The experimental results investigated by us fall in the region from zero order benzene kinetics [$K^o \exp(Q/RT)\ Px_B \gg 1$] to transition to first order kinetics, dependent upon

temperature level and benzene concentration, roughly from 60 - 200° as shown in Figure 1.
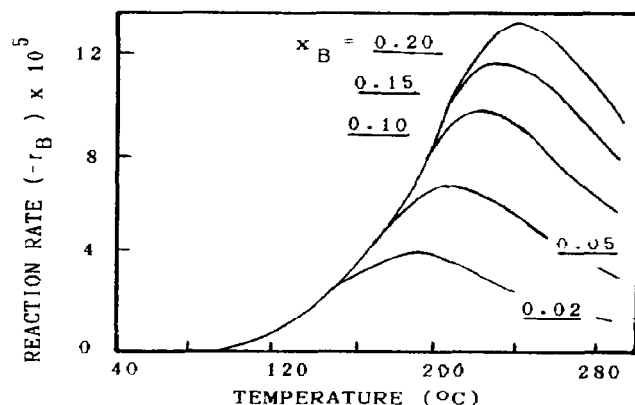

Figure 1.   Intrinsic Kinetics of Benzene Hydrogenation, Equation (1).   P = 1 atm.

The reaction experiments were conducted in a fixed bed reactor operated under plug flow conditions with provision for axial temperature measurement and a five zone computer-operated temperature control system to ensure isothermality.   Complete details of the reactor system are given by Megiris (1977).   All experiments were conducted with catalyst particle size < 80 mesh to eliminate diffusional effects (Kehoe and Butt, 1972; Price and Butt, 1977).

REACTOR DYNAMICS UNDER CYCLIC OPERATION

In CO conversion was allowed to fall to a preset minimum, the bed temperature then increased to regain the initial conversion level, and the experiment repeated.   In the following we present example results for an experiment [C2 of Megiris (1987)] run at a total pressure, P, of 12.3 x 10^4 Pa, inlet concentration of benzene, x_B, of 2 x 10^{-2} (mol fraction, remainder hydrogen and 113 ppm thiophene = x_T^o) and an initial temperature of 70°C.   Such results are shown in Figure 2a for three cycles.   If it is assumed that the deactivation kinetics are separable, then a plug reactor approach, with inlet conditions of fixed benzene and thiophene
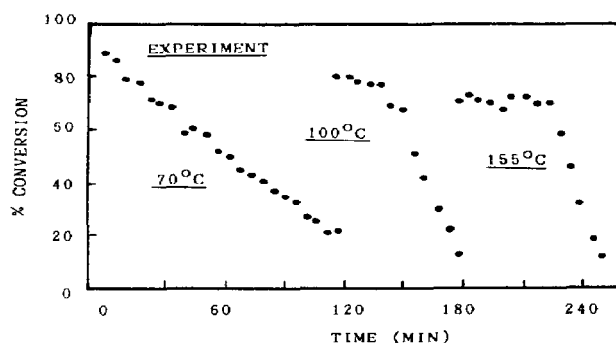

Figure 2a.   Cyclic Operation Data for Run C2 Example; 3 cycles.

concentration ($x_B = x_B^o$; $x_T = x_T^o$) and initial conditions of steady state reaction profile of benzene through the reactor, no thiophene present, and uniform bed activity (s = 1) gives the simple model of Table 1, assuming as stated ("constant deactivation") a single molecule of thiophene adsorbed relates to a constant decrease in activity for the hydrogenation reaction. Now the equations in Table 1 are mass balances, and in order to be made consistent with the

Table 1.   Reactor Model for Constant Deactivation

Mass balance, benzene: $\dfrac{\partial x_B}{\partial t} = - \nu \dfrac{\partial x_B}{\partial z} + \dfrac{\rho_c MW_g}{\varepsilon \rho_g} r_B(x_B,T) \cdot s$

Mass balance thiophene: $\dfrac{\partial x_T}{\partial t} = - \nu \dfrac{\partial x_T}{\partial x} + \dfrac{\rho_c MW_g}{\varepsilon \rho_g} r_T(x_T,T,s)$

Activity decay: $(r_T/M_T) = (-r)_D$

activity decay correlation of equation (2), the thiophene mass balance must be related to the
change in activity by proportionality between activity and uptake of poison, M_T. Interpreted
literally, M_T is the level of poison on the catalyst surface at which the activity for reaction
has been reduced to zero. It has been shown by Weng et al. (1974) that this is the "time driver"
of the fixed bed response to poison and ultimately determines the bed life; as such, it stands
as the single most important parameter in determination of the isothermal, fixed-bed time res-
ponse and it shows up (with different names and other notation) in all analyses of time response
to irreversible deactivation of which we are aware. Practically, M_T serves to convert the
change in absolute activity, sec^{-1} of equation (2), to an uptake of poison such as kmol poison/kg
catalyst - sec.

Given this, for the experiments shown in Figure 2a, M_T was determined as 4×10^{-4} kmol/kg cata-
lyst at 100°C, and according to the constant deactivation model, this value is independent of
temperature. Results of the CO simulation to the experiment of Figure 2a are shown in Figure 2b.
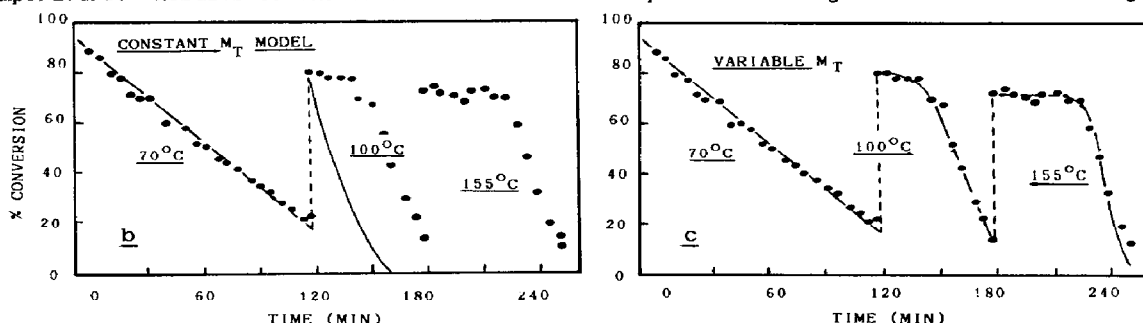
Figure 2b.   Fit of Simulation Model to Run C2, $M_T = 4 \times 10^{-4}$ kmol/kg.

Figure 2c.   Fit of Simulation Model to Run C2, Variable M_T, 70°C - $M_T = 4 \times 10^{-4}$;
             100°C - $M_T = 4.9 \times 10^{-4}$; 155°C - $M_T = 6.5 \times 10^{-4}$ kmol/kg.

It should be noted that this not is a "best fit" parameter model. All parameters for the reactor
simulation and the kinetic parameters have been determined in separate experimentation [Megiris
(1987)]. It is seen in the figure that agreement with the first cycle is excellent but the
model fails for both time scale and conversion beyond this. The difficulty resides in the para-
meter, M_T. This is resolved in simulation if M_T is considered to be a function of temperature,
where equation (2) is modified to:

$$\frac{\partial \alpha}{\partial z} = (r_T/M_T) = - k_D P x_T \alpha \qquad (4)$$

and:

$$\alpha(T_2) = 1 - \frac{M_T (T_1)}{M_T (T_2)} [1 - \alpha (T_1)] \qquad (5)$$

In this formulation the value of α represents the progressive modification of the activity
function s as the change in M_T with temperature is incorporated into the model. The reasons
for considering $M_T = f(T)$ reside in the work of Lyubarskii et al. (1962) and are discussed
later. Comparison of the variable M_T model with experiment is shown in Figure 2C. This gives a
satisfactory fit to the data.

On the basis of these results and a number of experiments under other conditions, one is in fact
able to extract the variation of poison adsorption capacity with temperature, as shown in
Figure 3. In view of the good agreement of simulation with experiment in cyclic operation using
the variable M_T model, it is now reasonable to proceed with a more severe experiment as below.
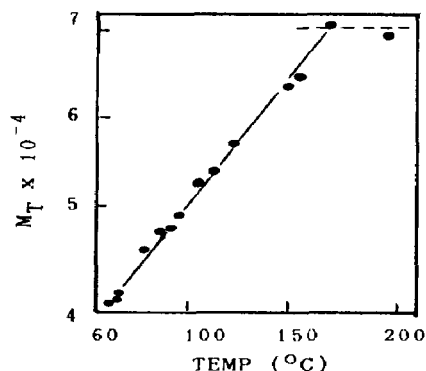
Figure 3.   Thiophene Adsorption Capacity Variation with Temperature Obtained from
             Simulation Results

REACTOR DYNAMICS WITH CONSTANT CONVERSION

Here the conservation equations are the same as in Table 1, but the conversion is fixed and
one uses the simulation with given parametric values to determine the temperature-time
relationship (TIR) required to maintain this. A summary of typical results for a conversion
fixed at 50% and other conditions as Run C2 is given in Figures 4a and 5b, comparing the
constant and variable M_T models.   In this work, the temperature-time relationship required

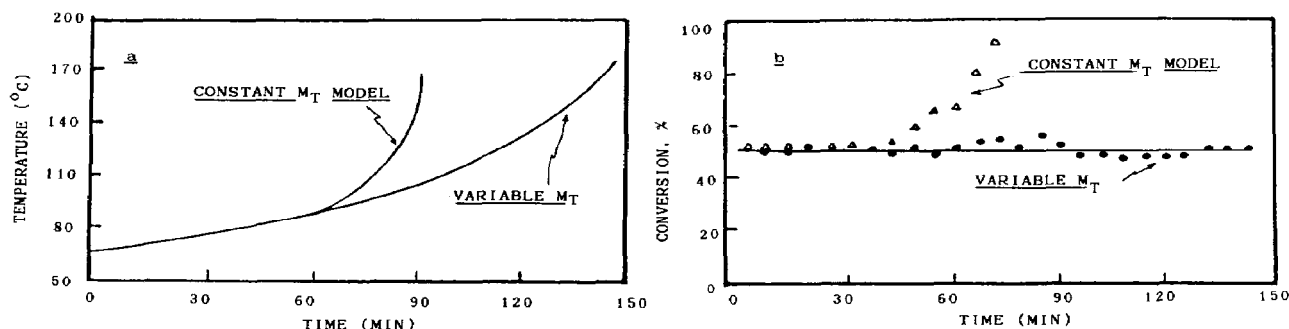
Figure 4.   a)   Temperature-time Required for Constant Conversion; Fixed and Variable
                  Capacity Models
             b)   Results of Application of the Operational Policies for the Two Models

to obtain constant conversion was generated by the reactor/deactivation model according to
both fixed and variable adsorption capacity interpretations. These predicted temperature
histories are shown in Figure 4a. The predicted TIR were then employed in experiments and the
resultant exit conversion vs. time measured. It is clear that the variable capacity model is
superior, and that this type of experiment makes a clear distinction between the models, as shown
in Figure 4b.

THIOPHENE CHEMISORPTION

Since both CO and TIR experiments demonstrate that M_T is a strong function of temperature and,
since this is important in determining the duration of the transients, details of the chemisorp-
tion should be considered. The results, as shown in Figure 3, agree generally with the postu-
lates of Lyubarskii et al. (1962) that thiophene graduates from a planar configuration (~ 5 Ni
blocked) to upright, linear (~ 1 Ni blocked) as the temperature increases. This is indicated by
the variation of M_T with temperature up to apparent saturation for $T \gtrsim 150°C$. The combination
of CO and TIR experiments thus provides a sensitive test of the details of deactivation.

WAVE MOTION

Operation in both CO and TIR modes is characterized by rather extreme types of wave behavior in
the reactor. Many examples are possible; we choose here to show the comparison between CO and

TIR for the simulation of the experimental run C2.   In Figure 5 is shown the nature of the internal profiles for CO after cycle 2 (initial temperature of 100°C), using the variable adsorption capacity model.   It is seen that the zones of activity for poison adsorption, hydrogenation activity and reactant adsorption are all compressed into a zone approaching the end of the bed and, after several such cycles much of the reactor acts as a guard bed only.   The time marks in the figure refer to the transients upon startup at 100°C after completion of the first cycle (70°C, Fig. 2a).   The last profile in each case represents the end of Cycle 2.   Action of the guard bed effect is particularly evident in Figures 5a and 5b.
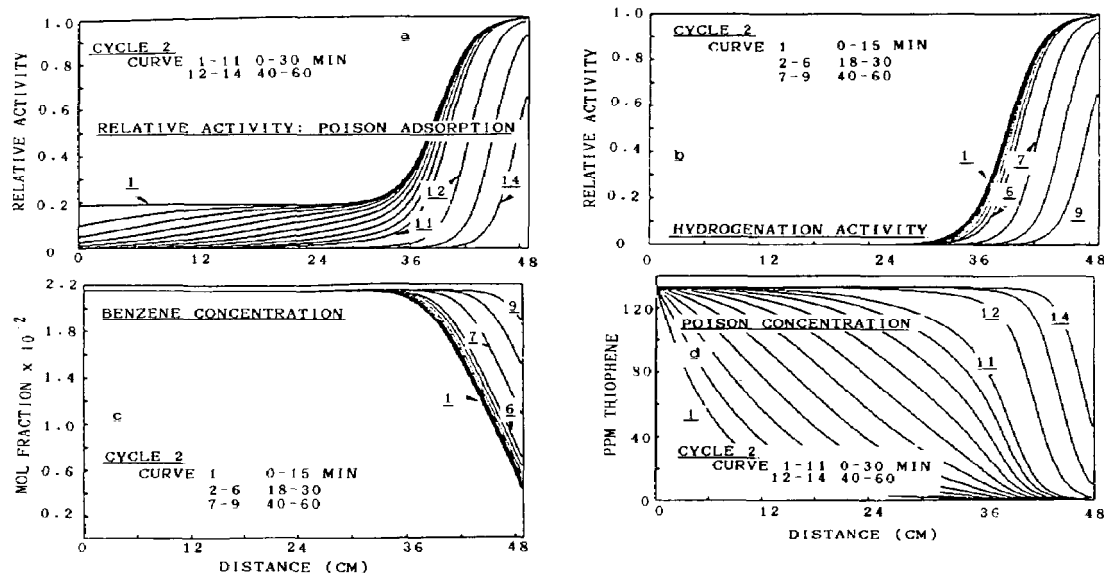

Figure 5.   Transient and Final Profiles for Cycle 2 of CO, Example Run C2.

For TIR the guard-bed is not so pronounced, but the increasing temperature leads to the evolution of quite complex poisoning and activity waves.   In Figure 6 are given profiles corresponding to the experiments of Figure 4.   Here it is seen that the activity wave precedes the poisoning, yielding the transition from wave to motonic behavior as shown for the poison concentration.   The interaction between reaction and deactivation kinetics is clearly shown in the benzene concentration profiles, where the zero order behavior of intrinsic kinetics under the experimental conditions is displaced by the poison wave.
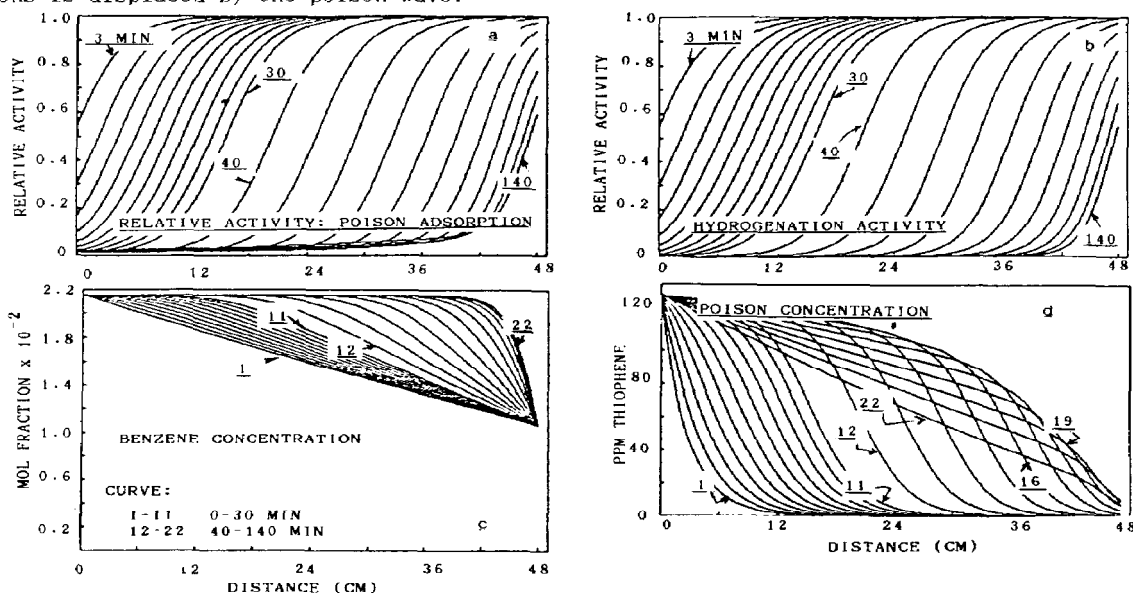

Figure 6.   TIR Profiles Corresponding to Run C2.

CONCLUSION

Reactor dynamics in the types of operation illustrated are complex and, though the observable results are simple enough and the operation is isothermal, the interior reactor profiles are complicated indeed. The combination of CO and TIR experiments in the fixed bed turns out to be a powerful diagnostic for evaluation of both the kinetic pathway and chemisorbed state of the poison molecule. Since the detailing of reactor models and the computational techniques are no longer the problem they once were, one can now look to the employment of real reactor operation as a means of study of the catalytic kinetics/deactivation problem in ways not deemed feasible before.

NOTATION

M_T = adsorption capacity at complete deactivation

MW_g = gas phase molecular weight

P = total pressure

$r_{T,B}$ = reaction rates of thiophene or benzene

t = time

$x_{T,B}$ = mole fractions of thiophene or benzene

t = bed void fraction

$\rho_{g,c}$ = gas phase density

υ = gas phase linear velocity

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