Model Validation in Chemical Process with Multiple Steady States

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Abstract: Pilot plant work is considered a reasonable intermediate step when chemical processes are moved from lab to commercial scale. Unfortunately, pilot plants are not easy or cheap to operate and modelers are faced with the problem of getting the most information out of the least expensive pilot plant experimental plan. We have developed a kinetic model for a catalytic reaction mechanism using lab scale experiments in an Accelerating Rate Calorimeter. Under isothermal conditions in a continuously stirred tank reactor, the catalyst exhibits three steady states, one of which is unstable. Our kinetic model is now part of steady state and dynamic models for reactors in the pilot plant. In this work, we compare the performance of our mechanistic models against that of empirical models obtained by analysis of the chosen statistical experimental design, we point out the potential pitfalls of the empirical models, and we suggest ways around those pitfalls for systems with complex dynamic behavior. The combination of mechanistic and empirical modeling offers a balanced approach. Mechanistic models provide insight that is useful in dealing with complex dynamic behavior, while empirical models allow analysis and optimization of system responses for which mechanistic models are not available.

Keywords: pilot plant, process scale up, state multiplicity, catalytic reaction mechanism, chemical reactor, reaction ignition and extinction, mechanistic and empiric models

1. INTRODUCTION

Using only lab data to design and build a commercial chemical plant is considered risky since limitations that are not present at the smaller scale can become dominant at the larger scale. Mass and heat transfer limitations, for example, play an increasing role during plant scale up. Pilot plants are useful in making the transition form lab to commercial scale. Unfortunately, pilot plants are viewed more as means to generate product samples for market testing than as devices to use for model validation, despite the great need to have models that can be scaled up reliably.

In our system, choosing the operating conditions and the catalyst level that will favor the desired stable steady state is difficult, since process economics demand low catalyst levels and this constraint pushes the system towards the low activity region. In other words, a delicate balance has to be established between process economics and the ability to control the process.

In the absence of a kinetic model for a strongly non-linear system like the one considered in this work, a purely empirical approach to experimental planning and plant scale up is at risk of failing or it has to be constrained to small regions in parameter space where linear approximations are valid and other stable steady states are far enough from the desired stable steady state. Unfortunately, these regions are likely to be of little or no value from a practical viewpoint.

2. METHODOLOGY

2.1. Accelerating Rate Calorimeter

In preparation for pilot plant experiments, kinetic modeling work was initiated in an Accelerating Rate Calorimeter (ARC). The ARC was developed at the Dow Chemical Company in the late 70's as a tool for thermal hazard evaluation [1]. Our system involves two reactants and a catalyst. Reactant A is nonvolatile while reactant B is highly volatile. The reaction is strongly exothermic and, for safety reasons, only low concentrations of B are allowed in pilot plant and commercial reactors. In a typical experiment, a spherical container with a mass of 16 grams would be loaded with a sample containing 20 parts per million catalyst, 4 grams of A, and 1 gram of B. The temperature profile observed during the reaction period is shown in Fig. 1. The ARC is particularly useful in systems where strongly exothermic reactions are possible and where a pressure build-up occurs because of the release of gaseous substances. In addition to providing a safeguard against thermal hazards during the phases of production, storage, and transport of chemicals, the ARC is also a valuable tool in thermokinetic analysis. It is with this application in mind that we selected the ARC.
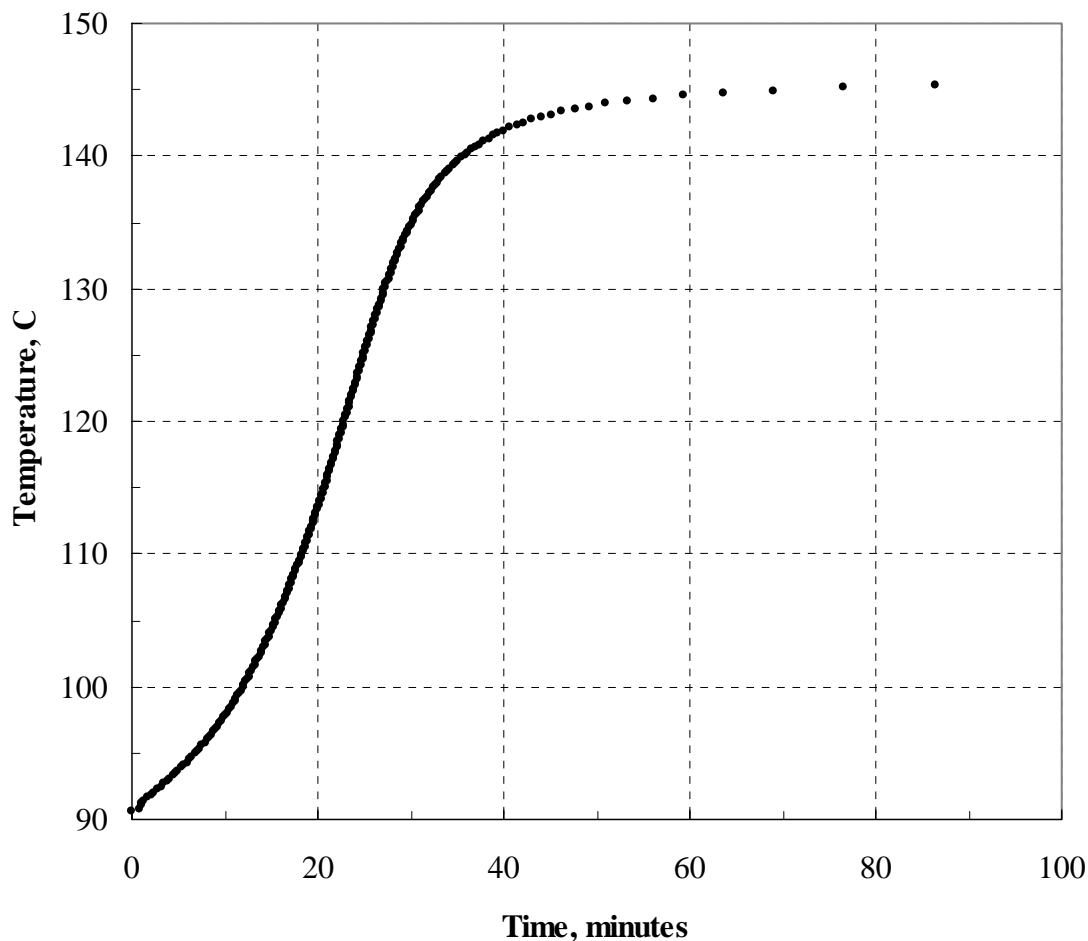

Figure 1. Temperature profile in ARC during exothermic reaction between 4 grams of A and 1 gram of B in the presence of 20 ppm catalyst

With catalyst concentration and initial weight fraction of B as factors, ARC experiments were chosen at the following conditions:

Run Number	Catalyst Level, ppm	Initial weight fraction of B
1	10	0.2
2	60	0.2
3	10	0.4
4	60	0.4

Temperatures observed in ARC experiments were transformed to weight fractions of B during the reaction by making use of Eq. (1), which assumes fixed values for heat capacities and heat of reaction.

$$w_B = w_{Bi} - \frac{(m_m C_{pm} + m_s C_{ps})(T - T_i)}{m_m \Delta H_{rxn}} \tag{1}$$

where w_B is weight fraction of B at a chosen temperature, w_{Bi} is weight fraction of B at the initial temperature, m_m is sample mass, C_{pm} is heat capacity of sample, m_s is sphere mass, C_{ps} is heat capacity of sphere, T is temperature, T_i is initial temperature, and ΔH_{rxn} is heat of reaction.

2.2. Pilot Plant

The pilot plant uses a continuous stirred tank reactor (CSTR) followed by a plug flow reactor (PFR). Additional tanks are available for storage of catalyst, reactants, and product. Near Infrared sensors provide measurements of the concentration of reactant B at points of interest. The pilot plant has been designed for temperatures in the range from 90 to 130 ºC and overall flowrates as high as 50 kilograms/hour. Unlike ARC experiments, the pilot plant experiments were conducted isothermally and with a continuous flow of materials. The factors chosen for study were in this case catalyst concentration and temperature in the CSTR. Conversion of B in the CSTR was chosen as the main system response.

3. RESULTS

3.1. Kinetic Mechanism

The results of ARC experiments show an important trend for this system: when the temperature of the sample reaches a high enough value, often in the neighborhood of 145 ºC, the reaction nearly dies. Based on this, we have suggested a kinetic mechanism where the catalytic sites are assumed to exist in two forms: fast and slow. When the catalyst is fresh, all sites are fast. Exposing the catalyst to reactant B and to high temperatures promote the irreversible transformation of fast sites into slow sites. This mechanism leads to Eqs. (2) and (3) for the rates of consumption of B in the main reaction and the rate of site transformation, respectively.

$$R_M = \left(k_P \theta_P + k_S (1 - \theta_P)\right) \frac{4 w_B^2}{(1 + 4 w_B)} \tag{2}$$

$$R_T = k_T \theta_P \frac{4w_B^3}{\left(1 + 4w_B\right)} \tag{3}$$

where θ_P is the fraction of fast catalytic sites, k_P is the reaction coefficient for the main reaction at the fast sites, k_S is the reaction coefficient for the main reaction at the slow sites, and k_T is the reaction coefficient for site transformation.

The rate expressions in Eqs. (2) and (3) can be used in macroscopic mass balances [2] describing the behavior of the reacting system in the ARC. The necessary balances are given by Eqs. (4) and (5).

$$\frac{dw_B}{dt} = -w_C R_M \tag{4}$$

$$\frac{d\theta_P}{dt} = -R_T \tag{5}$$

where t is time, and w_C is the concentration of catalyst.

In the system of Eqs. (1) through (5), the three reaction coefficients depend on temperature, as described by the Arrhenius expression: $k_i = k_{io} e^{-E_i / RT}$. There will be two adjustable parameters for each reaction coefficient, k_{io} and E_i, for a total of six adjustable parameters. As illustrated by Eq. (1), temperature is not an independent variable but is linked to the weight fraction of B. Fig. 2 shows the fit of this model to the experimental data obtained in the ARC, with conversion defined for the ARC runs as $X_B = 1 - w_B / w_{Bi}$.

3.2. CSTR Model

Macroscopic mass balances provide again a description of the dynamic behavior of the reacting system in a CSTR. Eqs. (6) through (8) correspond to balances for B, catalyst, and fast catalytic sites, respectively, assuming the density of the mixture is independent of composition and the reactor is always full:

$$\tau \frac{dw_B}{dt} = w_{Bf} - w_B - w_C \tau R_M \tag{6}$$

$$\tau \frac{dw_C}{dt} = w_{Cf} - w_C \tag{7}$$

$$\tau \frac{d\theta_P}{dt} = \left(1 - \theta_P\right) \frac{w_{Cf}}{w_C} - \tau R_T \tag{8}$$

where τ is reactor residence time, w_{Bf} is weight fraction of B in the feed stream, and w_{Cf} is concentration of catalyst in the feed stream. At steady state, the accumulation terms in the left hand sides of Eqs. (6) through (8) will be zero.

3.3. Steady State Multiplicity

At steady state, the system described by Eqs. (2), (3), and (6) through (8) leads to Eq. (9), which allows calculation of the concentration of catalyst needed in reaching a chosen degree of conversion of B, defined for the CSTR as $X_B = 1 - w_B / w_{Bf}$.

$$w_{Cf} = w_{Bf} X_B \frac{1 + \tau k_T \dfrac{4 w_{Bf}^3 \left(1 - X_B\right)^3}{\left(1 + 4 w_{Bf} \left(1 - X_B\right)\right)}}{\tau \left(k_P + k_S \tau k_T \dfrac{4 w_{Bf}^3 \left(1 - X_B\right)^3}{\left(1 + 4 w_{Bf} \left(1 - X_B\right)\right)} \right) \dfrac{4 w_{Bf}^2 \left(1 - X_B\right)^2}{\left(1 + 4 w_{Bf} \left(1 - X_B\right)\right)}} + c\left(1 - w_{Bf}\right) \qquad (9)$$

The second term on the right hand side is used to correct for the amount of catalyst that is killed by impurities. These are suspected to come in mostly through reactant A. Fig. 3 shows curves created using Eq. (9) at two temperatures. Reactor residence time is 5 hours and the weight fraction of B in the feed is 0.8. The curve at the lower temperature illustrates the behavior one would typically expect, with a monotonic increase in the degree of conversion of B as the concentration of catalyst is increased.
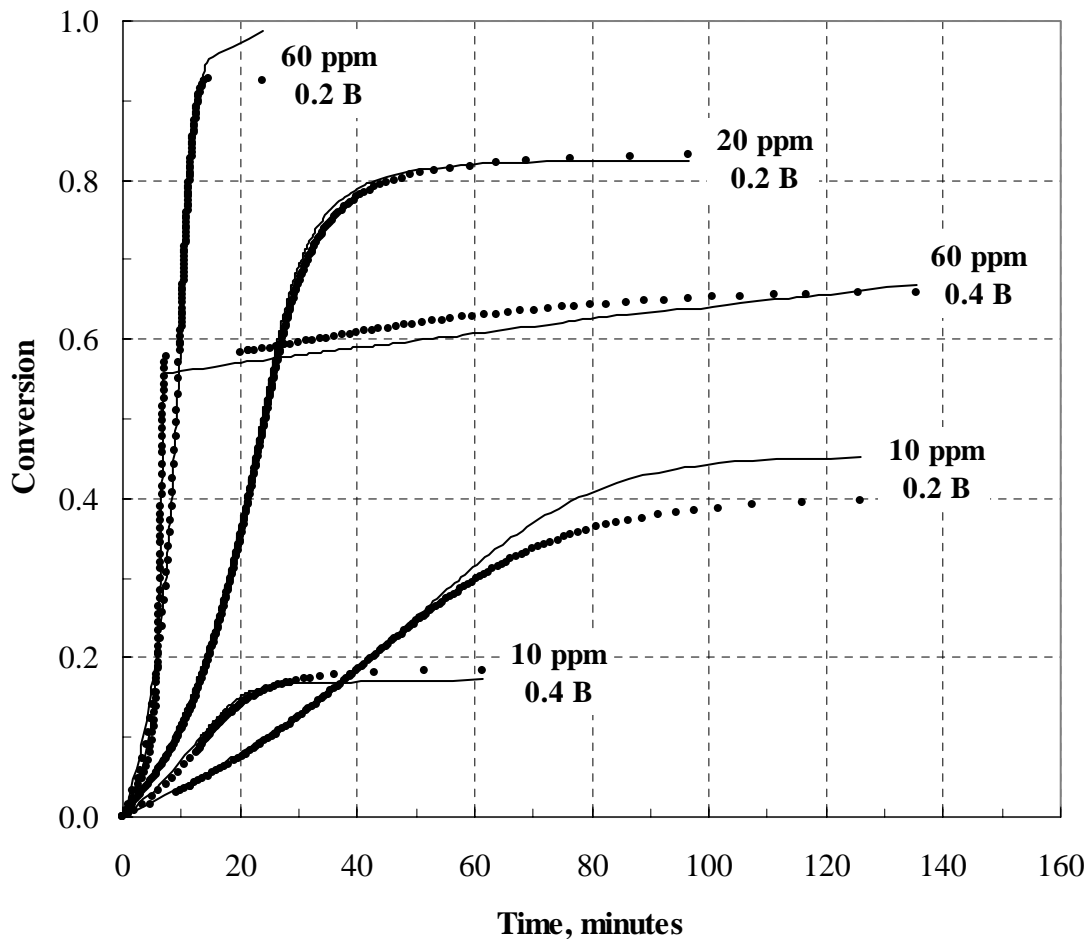

Figure 2. Experimental results and model predictions for conversion of B in ARC runs

The curve at higher temperature reveals that as many as three steady states are possible for a given concentration of catalyst. State multiplicity is thus more likely to appear at higher temperatures, when site transformation has a more noticeable effect on the main reaction.

Steady state multiplicity has been studied in great detail for non-isothermal reactors [3]. Isothermal reactors also display this kind of behavior [4]. Reaction mechanisms similar to ours have been reported in biochemical systems [5].

3.4. Model Validation

Eq. (9) was used in choosing the set of operating conditions for pilot plant experiments. Pilot plant experiments were allowed to reach steady state by running them for at least 25 hours, or five times the chosen residence time of 5 hours. The feed weight fraction of B was approximately 0.8 in all runs. These conditions were expected to lead to significant monomer conversion in the pilot plant, since conversions lower than 0.75 were considered unsafe. Slight differences in the type and quality of the reactants used in pilot plant experiments, when compared to the reactants used in ARC experiments, led however to lower catalyst activity than expected.
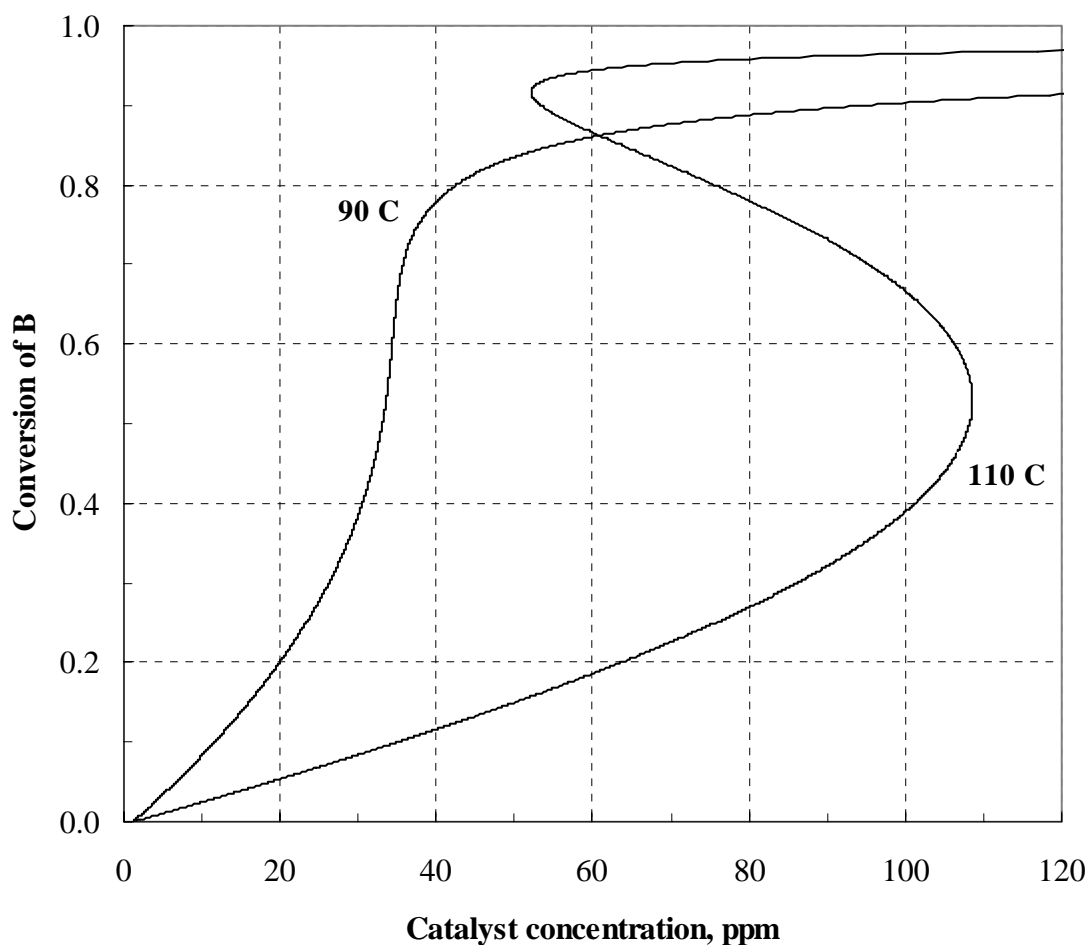

Figure 3. Effect of catalyst concentration on conversion of B at low and high temperatures

As implied by the first few pilot plant experiments, the estimates supplied by ARC experiments for the parameters of Eq. (9) could not accurately describe the behavior of the pilot plant. Because of these differences, the original experimental plan was not followed strictly and modifications were needed. The first modification involved an overall increase of 20 ppm in the concentration of catalyst. Additional complications led to further modifications in the experimental plan. Fig. 4 compares the runs of the original plan to the actual runs executed. Missing from the later set are some of the runs at low catalyst concentration and high reactor temperature. Various attempts at executing these runs were unsuccessful since the conversion of reactant B would quickly move away from conversion levels considered safe and the pilot plant had to be shut down. This is consistent with the trend displayed in Fig. 3 as the temperature goes up.

Despite all the complications, Eq. (9) was a good starting point since it provided reasonable estimates of the conditions to expect at steady state for all runs. When things did not go as expected, Eq. (9) still helped in locating problem causes and in choosing corrective actions. Additional help was provided by the full dynamic model described by Eqs. (2), (3), and (6) through (8).
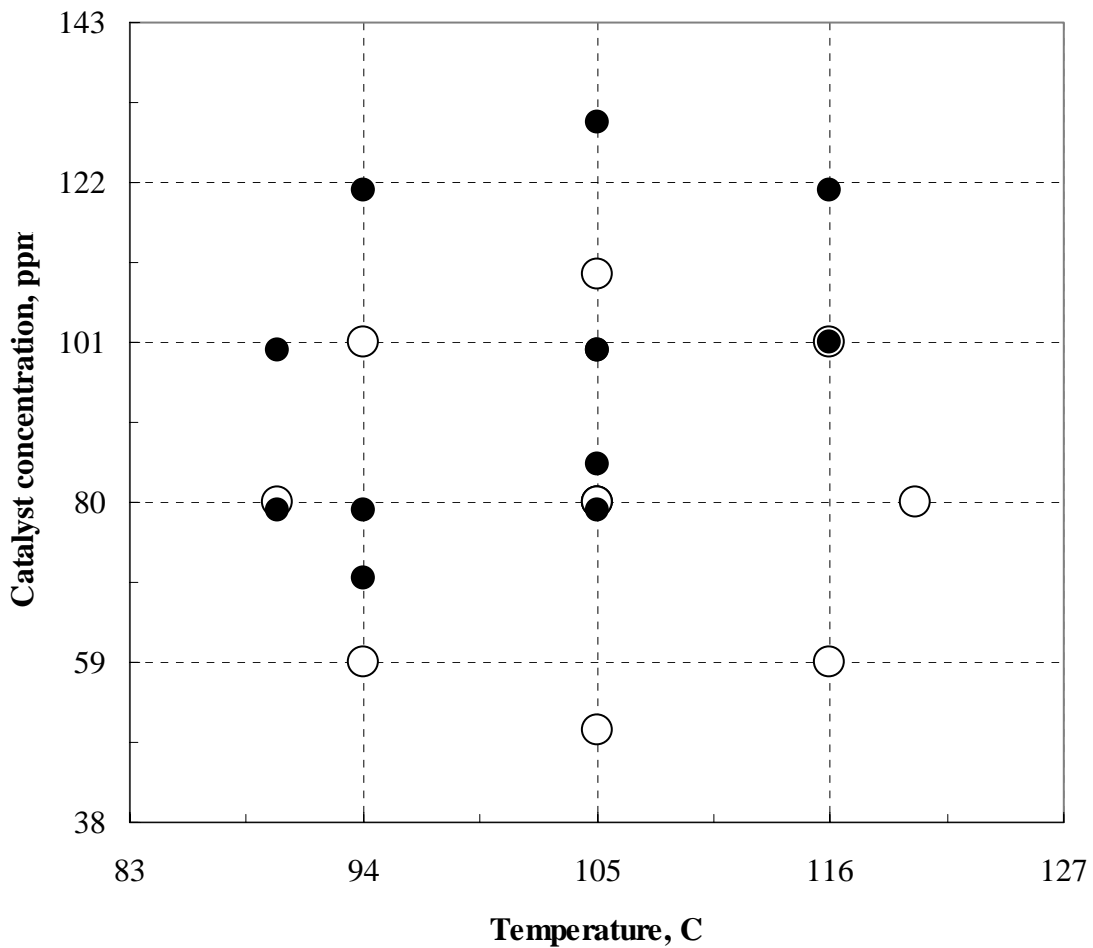

Figure 4. Planned (O) and actual (●) runs of experimental design for the pilot plant

3.5. Mechanistic vs. Empirical Models

Fig. 5 compares predicted and observed values of conversion of B during pilot plant experiments. One set of predictions was generated using Eq. (9) and the parameter estimates obtained by fitting the ARC data. This model has a tendency to underestimate the activity of the catalyst when it is present in high concentrations and to overestimate it at low concentrations. The other set was generated by a linear empirical model whose parameters were fitted to the pilot plant results.

The fit provided by the linear empirical model is excellent. Even though an improved fit is obtained when the parameters in Eq. (9) are adjusted to match the pilot plant results, the predictive ability of this mechanistic model can only get as good as that of the linear model, but not better. Add to this the fact that there are product properties for which only the empirical approach is possible and the advantages of this approach become clear. Unfortunately, in its current form the empirical model knows nothing about time. Eq. (9), on the other hand, includes the residence time as a variable. The dynamics of the system are modeled by Eqs. (2), (3), and (6) through (8), with the corresponding steady state solution provided by Eq. (9). One may argue, however, that data from dynamic pilot plant experiments could be used to include time as an independent variable in the empirical model.
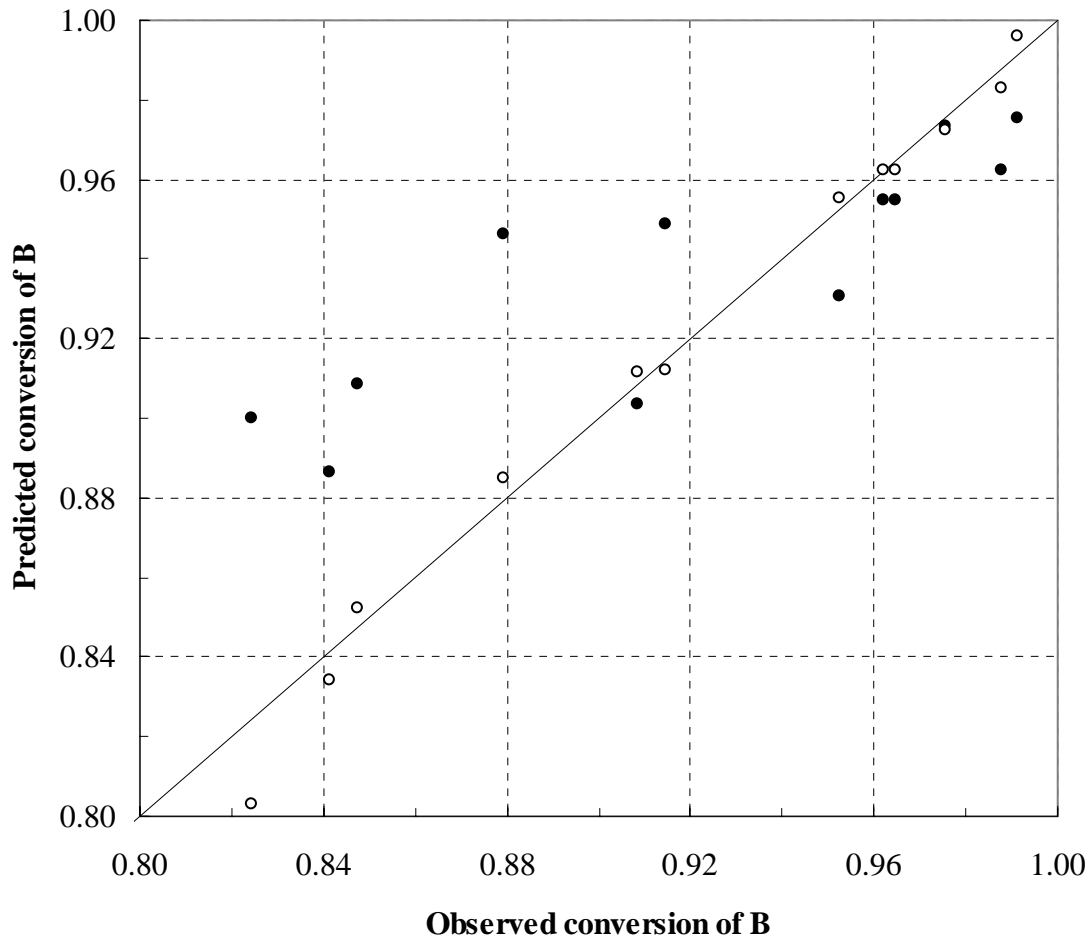

Figure 5. Fits generated by empirical (o) and mechanistic (●) models of conversion of B

The most troublesome aspect of the empirical model is the way it handles conditions of low catalyst activity, which correspond to high temperature and low catalyst concentration. At 116 °C and 79 ppm, for example, a conversion of B of 0.89 is predicted by the empirical model. In the pilot plant, however, the conversion had already dropped to 0.75 and would have continued dropping if a plant shut down had not been ordered. The chosen conditions thus fall in a region that the mechanistic model can handle better than the empirical model, as illustrated by Fig. 6.

An improved set of parameters for Eq. (9) was used to create the corresponding curve in Fig. 6. More impurities are expected in pilot plant experiments than in ARC experiments and for this reason a higher catalyst level at zero conversion is observed in Fig. 6 than in Fig. 3. This level, like the prediction of 0.5 for the conversion of B at 79 ppm are not supported by experimental data since conversions lower than 0.75 were not allowed in the pilot plant. Thus, while the mechanistic model is in principle capable of generating predictions over the entire conversion range, it can only be built by using high conversion data. ARC and dynamic experiments should provide, however, the information needed in validating a given kinetic mechanism and set of kinetic parameters for the mechanistic model.
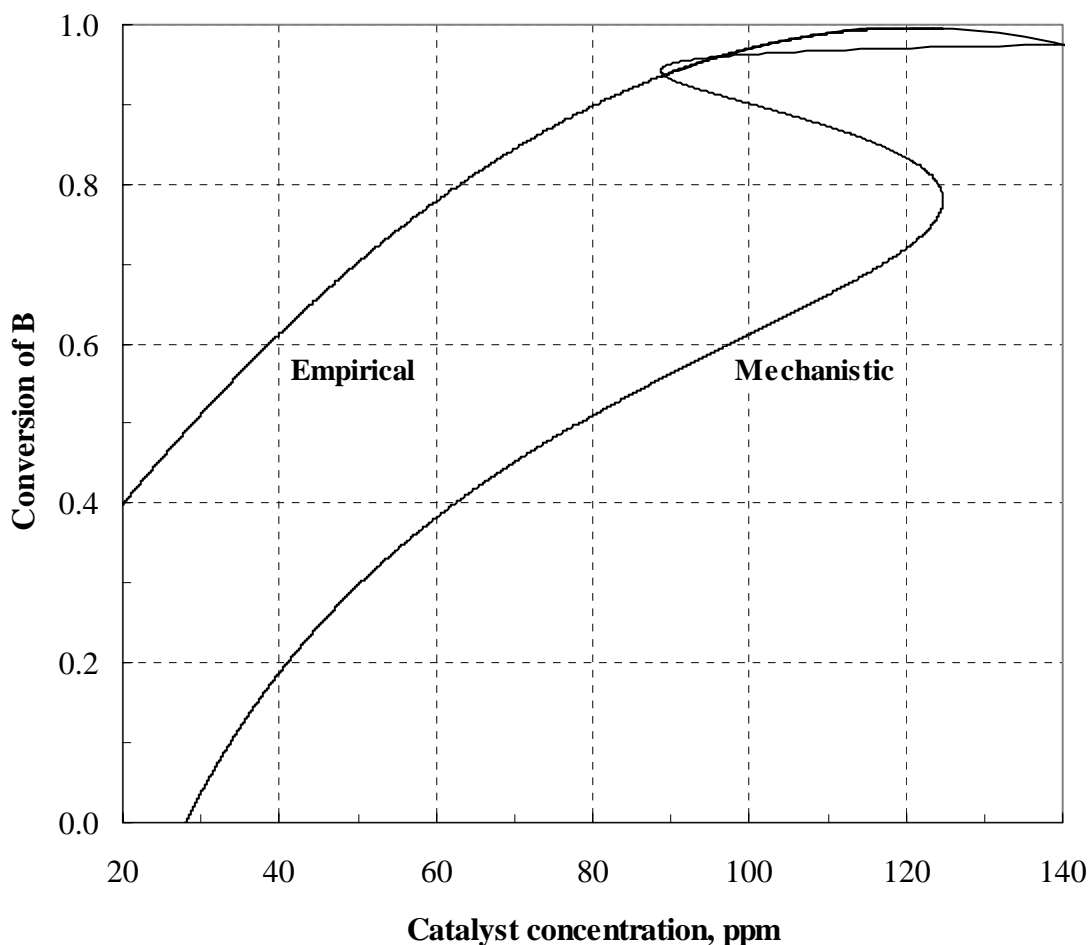

Figure 6. Conversion of B predicted by empirical and mechanistic models at 116 °C

4. DISCUSSION

Our validated reactor models are going to be used as part of a process intensification strategy that will search for optimum operating conditions of commercial plants and will choose product grade transition strategies for those plants. At the commercial scale, the energy balance plays a more important role and the combination of this balance with the reaction mechanism for the catalyst will introduce complications that process control systems will have to deal with. Those systems should be designed to avoid reaction extinction episodes or the cycling behavior that results from process configurations and process conditions that favor sustained oscillations.

We continue to develop empirical and mechanistic models for reactant conversion and for product properties of interest in this system. We view the approaches as complementary, rather than contrary. Empirical models can provide excellent fits over the experimental region and they are often the only available option. Mechanistic models, when properly validated and when extrapolated with care, can help in the analysis of possible scenarios at the commercial scale even before a commercial plant becomes available.

One of the key aspects of this work has been the early detection of state multiplicity during ARC experiments. Had it not been for such detection, execution of the pilot plant experimental plan would have been plagued by far too frequent reaction extinction episodes. Thanks in part to this knowledge we have been able to push our experiments to the lowest catalyst concentration and thus more economic operating region without considerable waste of resources.

We are dealing with a strongly exothermic reaction and a highly volatile reactant. We are thus constrained to low concentrations of unreacted B in pilot plant reactors and in larger reactors. This represents a major limitation in model validation since the low conversion region is rich in information but unreachable. Despite such limitation, we already have steady state and dynamic reactor models that are very helpful in evaluating multiple catalysts and products, and should be very helpful in facilitating the transition to commercial scale reactors.

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