Complex Dynamic Behavior during Polyol Preparation in Continuous Processes Using Heterogeneous Double Metal Cyanide Catalysts

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Abstract

The transition from batch to continuous processes for polyol production presents interesting challenges because of the unusual behavior of double metal cyanide (DMC) catalysts. One feature that is often observed in these catalysts is the need for an activation period whose length changes from one catalyst formulation to another[1]. When this activation occurs in the same reactor where the chain growth reaction is going to take place, the length of the activation period plays an important role in deciding the reactor residence time. Another feature that has been observed is the deactivation of the catalyst under some reactor conditions[1].

The monomer plays a central role in the main reaction steps: activation, chain growth, and deactivation. Even under isothermal conditions, the interaction between these steps can lead to complex behavior, like the existence of multiple steady states and sustained oscillations. The use of heterogeneous DMC catalysts in continuous processes thus requires careful selection of process conditions and operating policies during grade transitions and other dynamic events. In this work, we describe a non-isothermal model of a backmixed continuous reactor for the production of polyols using heterogeneous DMC catalysts. This reactor could be, for example, a mixed flow reactor or a loop reactor with a high recycle ratio[2]. We present experimental data that supports our model, and we discuss the impact that the observed behavior will have on reactor design and operation.

Behavior of DMC Catalysts

Some characteristics typical of DMC catalysts have a significant effect on the properties of the polyol product. One of these characteristics is a chain-length dependent effect that favors growth of short chains over long chains and keeps the molecular weight distribution as narrow as possible, even in continuous reactors[1]. A second characteristic is the generation of small fractions of high molecular weight chains[3]. In this publication, we focus on the activation and deactivation characteristics of DMC catalysts.

To date, reported DMC catalysts require an induction, or activation, period as illustrated in Figure 1. For this particular example, a non-activated catalyst preparation based on literature examples[1] was mixed with a 700 molecular weight triol in a semibatch reactor. The reactor was equipped with a feed tank so that propylene oxide could be added whenever the total pressure in the reactor dropped. Almost half of the reaction period passed before

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[1] Kim, I., Ahn, J., Sik Ha, C., Sik Yang, C., and I. Park, “Polymerization of propylene oxide by using double metal cyanide catalysts and the application to polyurethane elastomer”, *Polymer 44*, 3417–3428, 2003

[2] Zacca, J. J., Ray, W. H., “Modeling of the liquid phase polymerization of olefins in loop reactors”, Chem. Eng. Sci. 48(22), pp 3743-65, 1993

[3] Brons, J. F. J., Eleveld, M. B., “Process for preparing polyoxyalkylene polyether products”,EP 1,295,902, 2003

monomer consumption became noticeable. An exothermic reaction was observed during the second half of the reaction period, signaling the activation of the DMC catalyst.

The second characteristic of DMC we investigated is the loss of activity which, like the induction time, varies from one catalyst formulation to another. An example of DMC activity loss is illustrated in Figure 2 for a catalyst preparation based on literature examples[1], obtained during a calorimetric experiment where the mixture of catalyst, initiator, and monomer was held at 67 ºC until an adiabatic temperature rise was observed. Although a significant fraction of the initial monomer was still present in the calorimeter, full monomer conversion was not observed. The catalyst transitioned from a regime of high activity to one of low activity around 145 ºC.

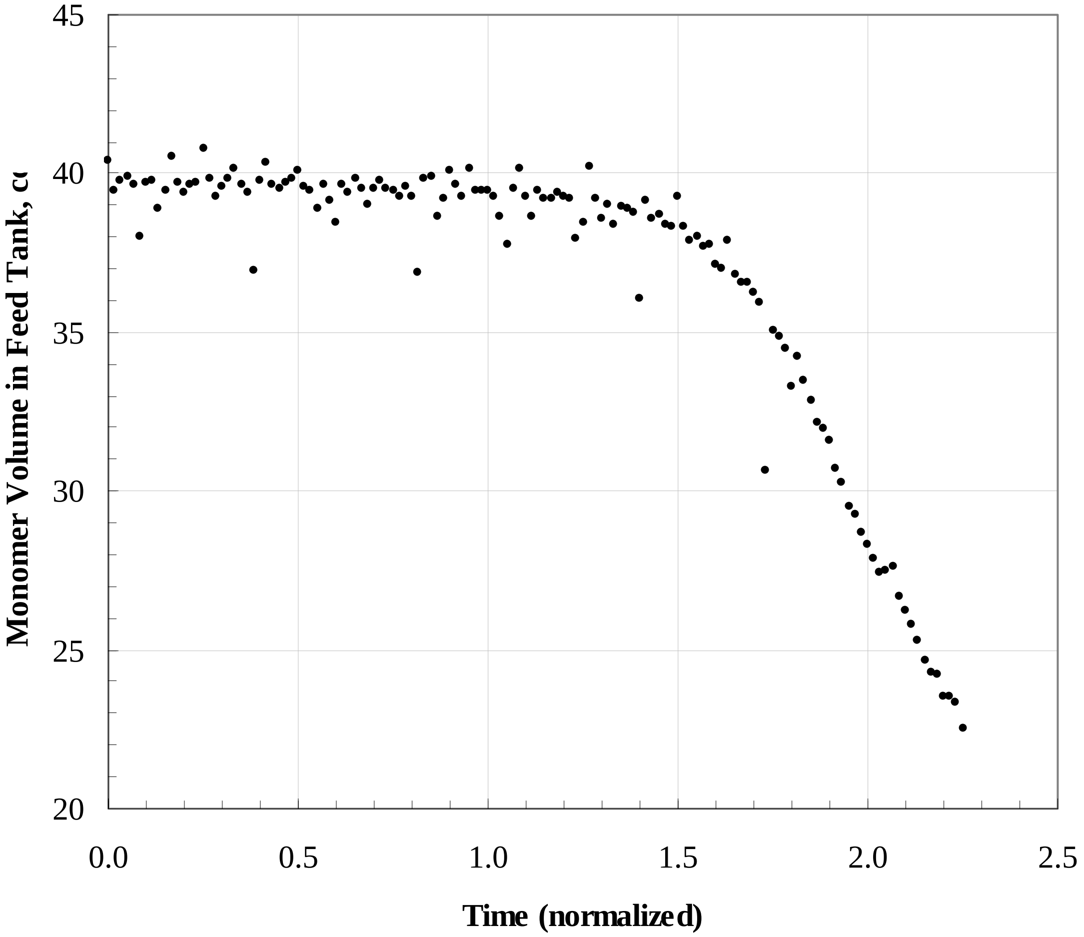

Figure 1. Catalyst activation and polymerization in semibatch reactor

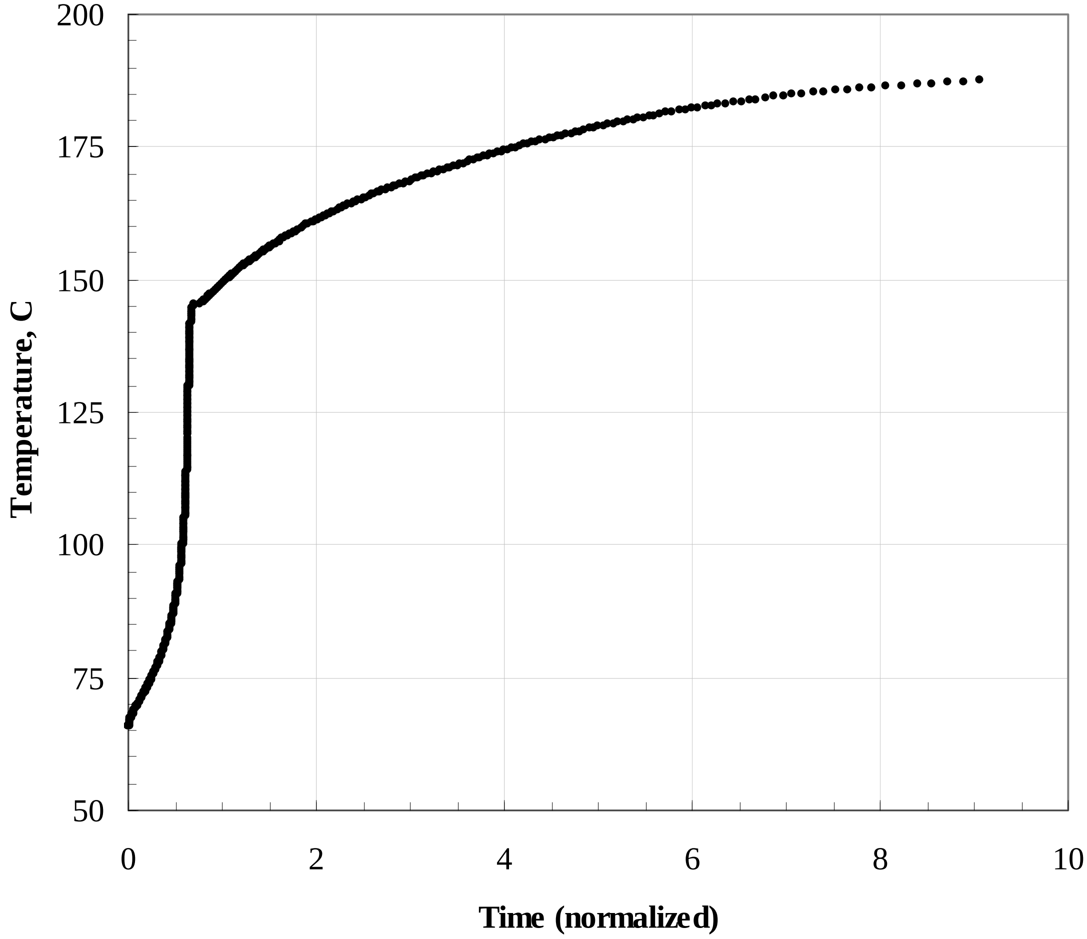

Figure 2. Adiabatic temperature rise during polymerization in calorimeter

Model Development

Kinetic Scheme

We have successfully modeled the performance of DMC catalysts in lab and pilot plant scale reactors, both batch and continuous, by making use of the mechanism described by Scheme 1. According to Scheme 1, DMC catalysts exist initially in a precatalyst form C_P that must be activated before it can be used in chain growth reactions. Once activated, the catalyst adopts a first form C_A that is very efficient at adding monomer to adsorbed polymer chains R_J. In addition, some reaction conditions can speed up the irreversible transformation of catalyst sites to a second form C_B, still capable of adding monomer to adsorbed polymer chains S_J but at a much lower rate than the first catalyst form.

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\begin{array}{ll}
C_P \rightarrow C_A & \textit{activation} \\
C_A + Q_J \leftrightarrow R_J & \textit{adsorption} - \textit{desorption} \\
R_J + M \rightarrow R_{J+1} & \textit{growth} \\
C_A \rightarrow C_B & \textit{transformation} \\
C_B + Q_J \leftrightarrow S_J & \textit{adsorption} - \textit{desorption} \\
S_J + M \rightarrow S_{J+1} & \textit{growth}
\end{array}
$$

Scheme 1

Kinetic Model

Quadratic autocatalysis provides a convenient form for modeling the behavior of catalysts that display an induction period[4]. In the case of DMC catalysts, the first step of Scheme 1 becomes:

$$C_P + C_A \rightarrow 2C_A \qquad \textit{activation}$$

For the irreversible steps in the mechanism, the reaction rates are thus:

$$R_A = k_A \theta_P \theta_A \qquad \textit{activation}$$

$$R_R = k_R \theta_A \frac{4w_M^2}{(1+4w_M)} \qquad \textit{chain growth at fast sites}$$

$$R_S = k_S \theta_B \frac{4w_M^2}{(1+4w_M)} \qquad \textit{chain growth at slow sites}$$

$$R_T = k_T \theta_A \frac{4w_M^3}{(1+4w_M)} \qquad \textit{site transformation}$$

where θ_P is fraction of precatalyst sites
θ_A is fraction of fast active sites
θ_B is fraction of slow active sites
w_M is mass fraction of monomer

These expressions were obtained by fitting data generated in calorimetric experiments and steady state data on monomer concentration in continuous pilot plant reactors. Figure 3 compares, for example, observed and predicted values of monomer concentration in pilot plant experiments. There are terms in our kinetic expressions that are reminiscent of functional

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[4] Gray, P., and S. K. Scott, “Chemical Oscillations and Instabilities”, Oxford University Press, First Edition, New York, 1990

forms observed in kinetic mechanisms involving adsorption of reactants to catalysts. It is important to keep in mind, however, that these expressions are strictly the product of data fitting and as such they should be interpreted with care.

Mass Balances for a Continuous Reactor

In a reactor that remains full and whose inlet and outlet flowrates are constant and equal to each other, mass balances are as follows:

$$\frac{d(V\rho w_M)}{dt} = Fw_{Mf} - Fw_M - w_C V\rho(R_R + R_S) \qquad \textit{monomer}$$

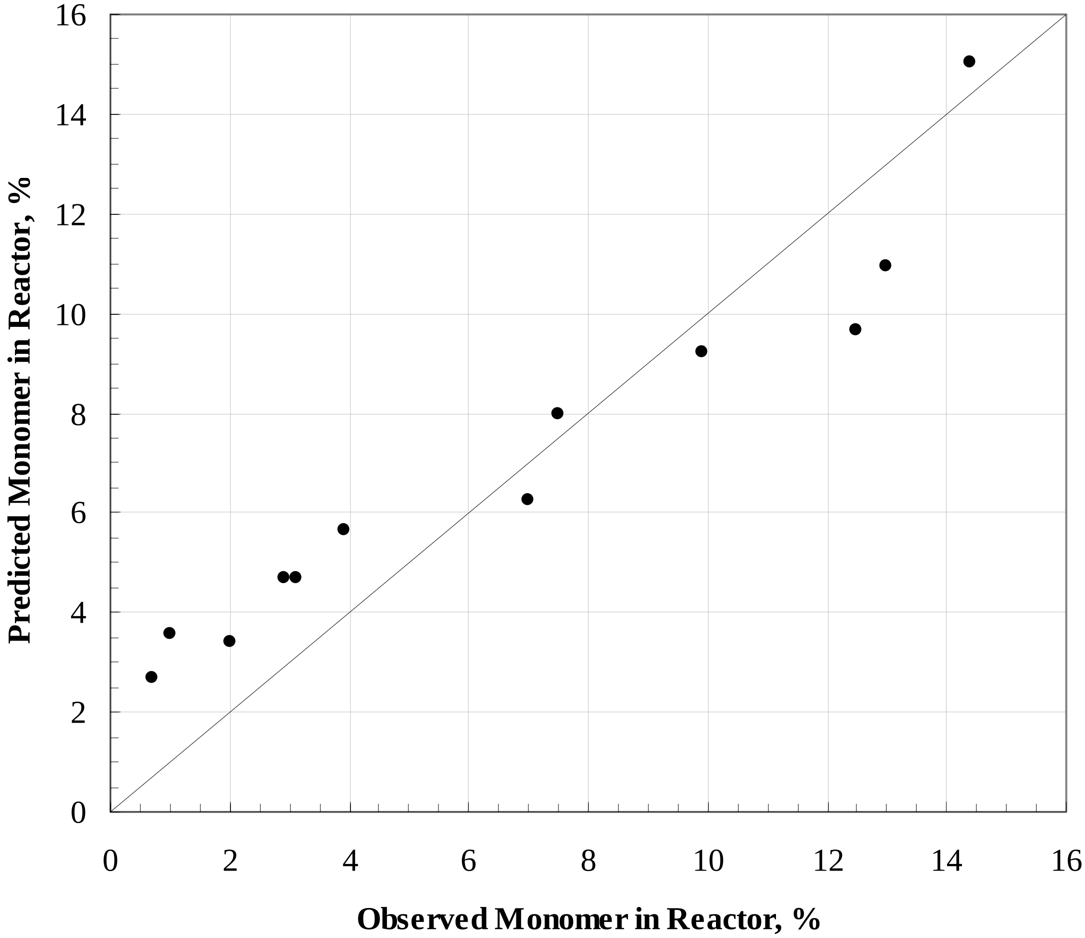

Figure 3. Results of pilot plant experiments and model predictions

$$\frac{d\left(V\rho w_C\right)}{dt} = Fw_{Cf} - Fw_C \qquad \textit{catalyst}$$

$$\frac{d\left(V\rho w_C \theta_P\right)}{dt} = Fw_{Cf}\theta_{Pf} - Fw_C\theta_P - w_C V\rho R_A \qquad \textit{precatalyst sites}$$

$$\frac{d\left(V\rho w_C \theta_A\right)}{dt} = Fw_{Cf}\theta_{Af} - Fw_C\theta_A + w_C V\rho R_A - w_C V\rho R_T \qquad \textit{fast active sites}$$

$$\frac{d\left(V\rho w_C \theta_B\right)}{dt} = Fw_{Cf}\theta_{Bf} - Fw_C\theta_B + w_C V\rho R_T \qquad \textit{slow active sites}$$

where

V	is reactor volume
ρ	is density of mixture in the reactor
t	is time
F	is total mass flow rate
w_{Mf}	is feed mass fraction of monomer
w_C	is catalyst concentration
θ_{Pf}	is feed fraction of precatalyst sites
θ_{Af}	is feed fraction of fast active sites
θ_{Bf}	is feed fraction of slow active sites
w_{Cf}	is feed catalyst concentration

Figure 4 shows the dynamic behavior observed and predicted by this model when the continuous pilot plant reactor starts up isothermally. The peak observed during the initial period of operation of the pilot plant is explained by the activation step of the mechanism. The minimum that is observed right after the peak corresponds to the point of maximum concentration of fast active sites. Slow active sites are then created at the expense of fast active sites until a steady state distribution of fast and slow active sites is approached.

Complex Dynamic Behavior

The kinetic mechanism considered in this work is similar to mechanisms reported in biochemical reactions where substrate and product-inhibited reactions are common[5]. In our case, the monomer participates both in the chain growth reactions and in the catalyst transformation reaction that slows down the growth. As a result, regions of steady state multiplicity are possible, as illustrated in Figure 5 for an isothermal continuous reactor.

In the case of a non-isothermal reactor, the energy balance must be solved too:

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[5] Ramachandran, P. A., Kulkarni, B. D., and A. Sadana, “Analysis of Multiple Steady States of Complex Biochemical Reactions”, *J. Chem. Tech. Biotechnol. 31*, 546-552, 1981

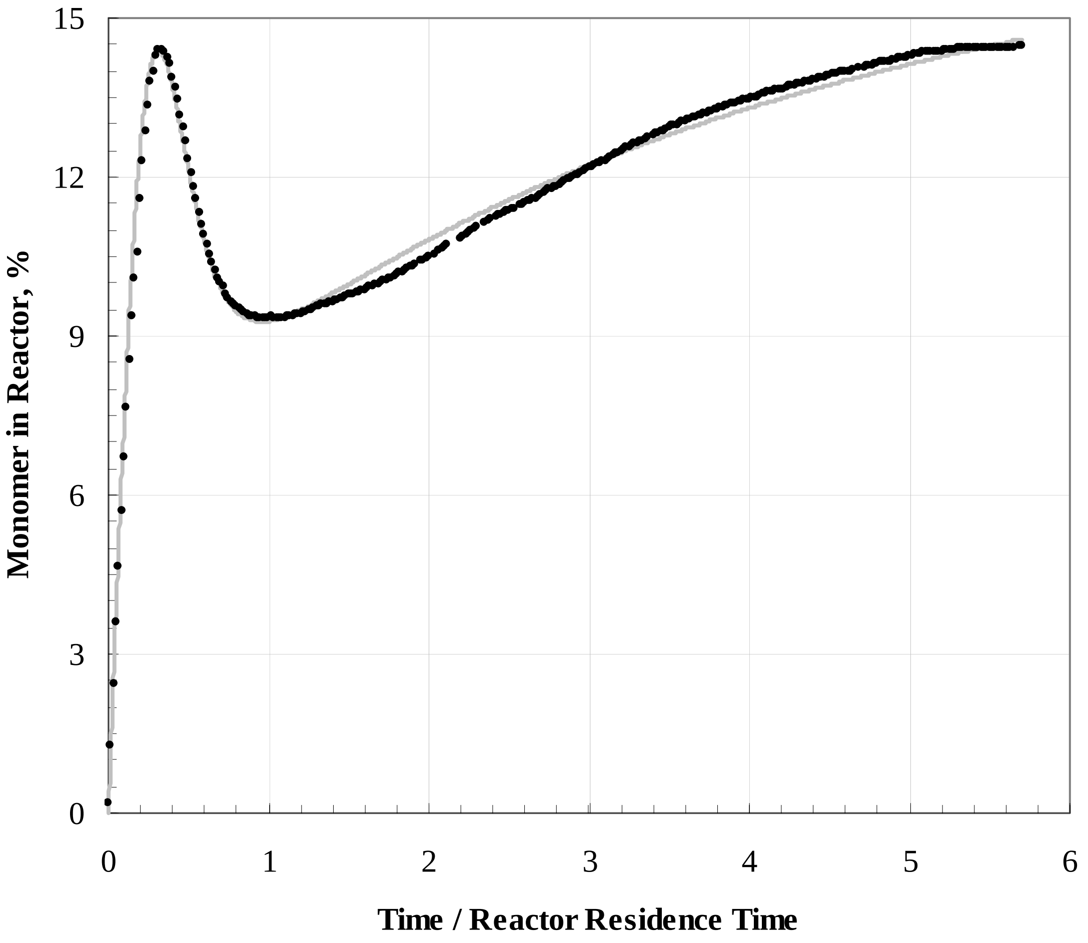

Figure 4. Pilot plant start up at constant temperature

$$\frac{d\left(V\rho c_p T\right)}{dt} = Fc_p\left(T_f - T\right) + w_C V\rho\left(R_R + R_S\right)\left(-\Delta H_r\right) - U_j A_j\left(T - T_j\right)$$

where c_p is heat capacity of reaction mixture

T is reactor temperature

T_f is feed temperature

ΔH_r is heat of polymerization

U_j is overall heat transfer coefficient between reactor and jacket

A_j is jacket heat transfer area

T_j is jacket temperature

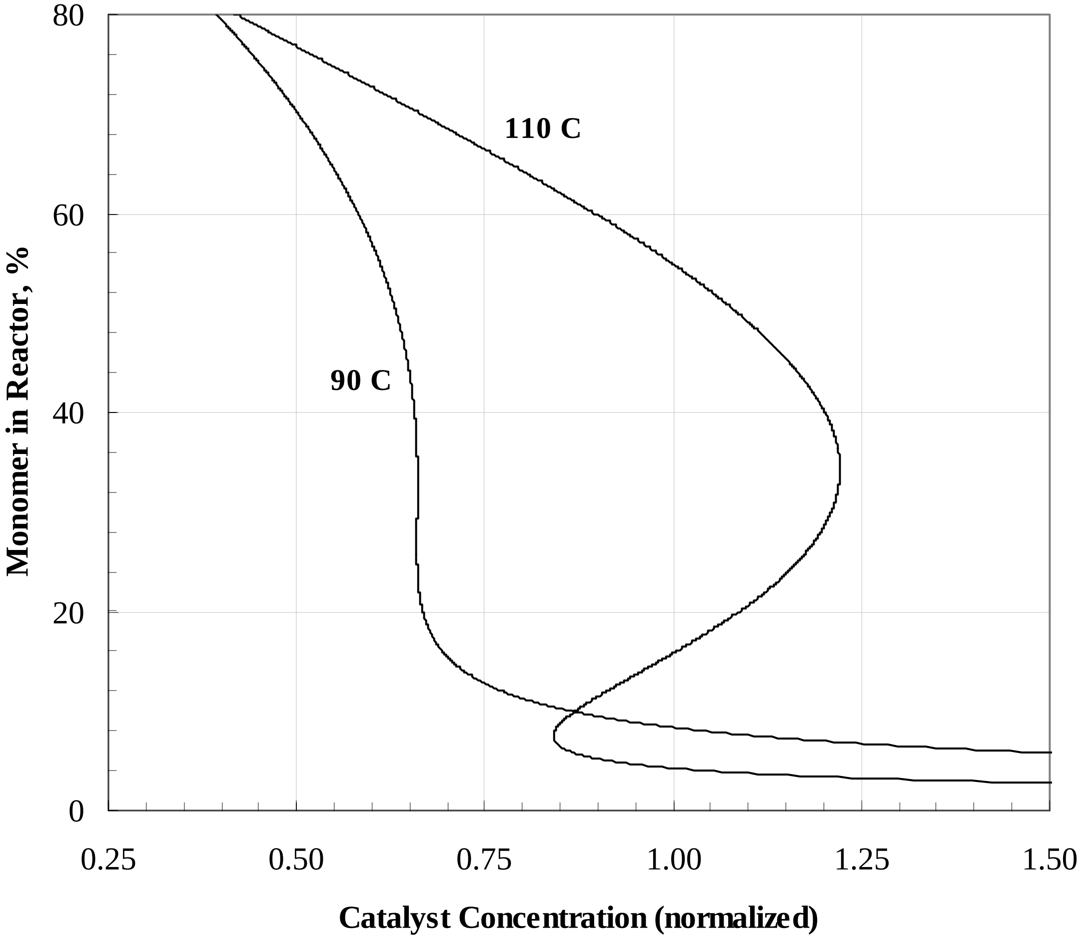

Figure 5. Steady states for continuous isothermal reactor

Figure 6 shows, for example, the steady state solutions at two jacket temperatures for a large scale reactor at typical operating conditions. With the additional complexity introduced by the energy balance, as many as 5 simultaneous steady states are possible at the lower jacket temperature.

Conclusions

The choice of operating conditions of a continuous process for poyol production is complicated by the unusual behavior of DMC catalysts. Optimum reactor performance is achieved when a kinetic model is available for the chosen catalyst formulation. This knowledge should be valuable during steady state operation, grade transitions, plant start-up, and troubleshooting.

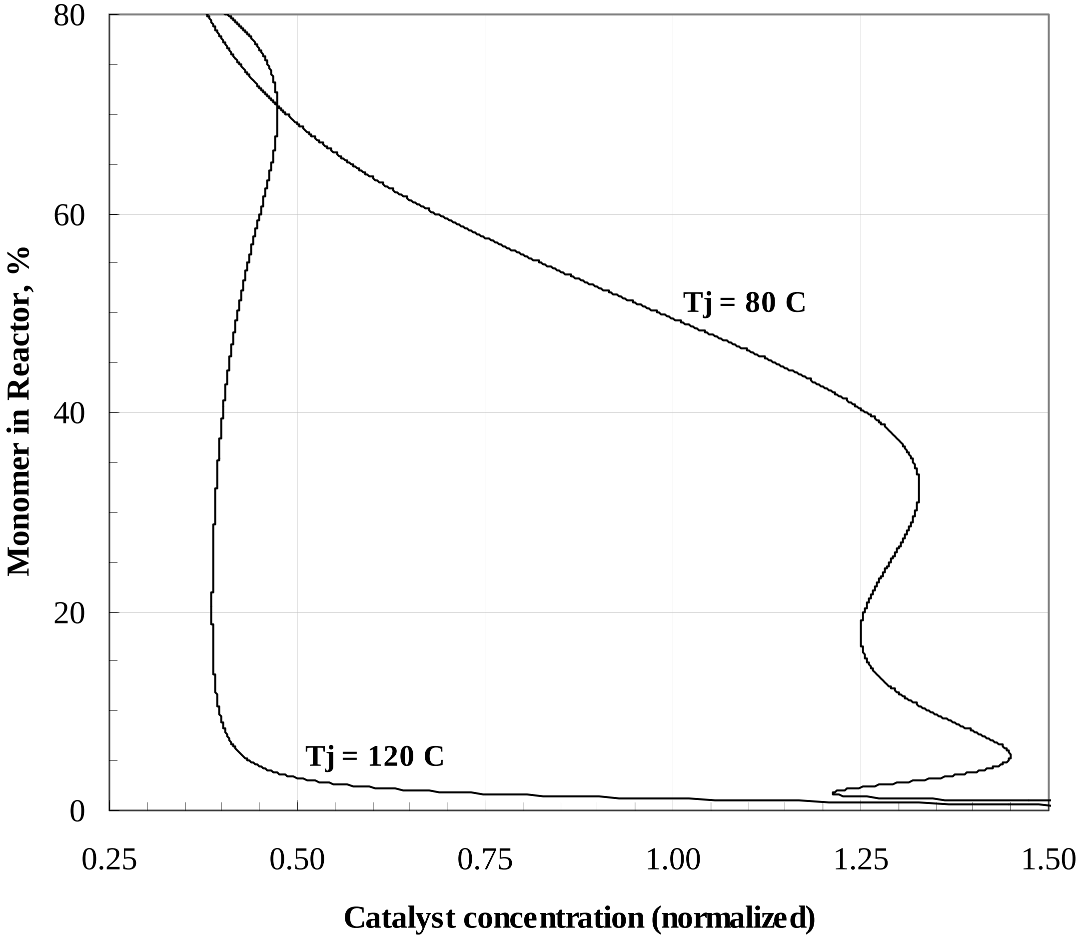

Figure 6. Steady states for continuous non-isothermal reactor