Evaluating and Estimating the Complex Dynamic Phenomena in Nonlinear Chemical Systems

Rama Rao Karri*
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Abstract

Successful operation and control of complex dynamic systems heavily rely on the availability of fast and accurate evaluation of the system performance. The measurement problems and the delays associated with these systems require the need for on-line state estimators as alternative measurement tools. In this work, a state estimation method based on extended Kalman filter (EKF) is presented for nonlinear dynamical systems that are characterized by complex dynamic phenomena such as multiple steady state behavior, limit cycle oscillations and chaos. The estimator uses the mathematical model of the process in conjunction with the known process measurements to provide the unmeasured process states that capture the fast changing nonlinear dynamics of the process. The design and performance of the state estimator is evaluated by applying two typical continuous non-isothermal nonlinear processes, a chemical reactor and a polymerization reactor, which show rich dynamical behavior ranging from stable situations to chaos. In order to understand the dynamic phenomena and to analyze the conditions that lead to an improved operation, prior to state estimation, these processes are thoroughly analyzed for multiplicity, stability and bifurcation studies. The sensitivity of the state estimator is also studied towards the effect of the design parameters involved in the method. The results demonstrate the efficacy of the model based method for state estimation in nonlinear chemical processes associated with complex dynamic behavior.

KEYWORDS: complex phenomena, nonlinear analysis, chemical reactor, state estimator, chaotic behavior

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1. Introduction

Nonlinear dynamical systems can present a variety of behavioral patterns depending on the values of the physical parameters and intrinsic features. One such behavior includes the limit cycle oscillations which frequently emerge as a steady state loses its stability through a change in operating condition. Another type of behavior involves the appearance of more complicated dynamic responses when the limit cycle becomes unstable. These exotic dynamic patterns may include multiperiodic and nonperiodic responses showing irregular dynamic phenomena termed as chaos. This unconventional dynamic phenomena exhibited by the chemical systems can be attributed to the nonlinear interaction between several quantities caused due to the perturbations in inputs and parameters that can be stored or sometimes inter-converted within these systems. Among the dynamical systems, continuous chemical reactors and continuous polymerization reactors have received special attention due to their complicated dynamics and economic importance. Understanding the dynamic phenomena of these systems is important in order to analyze the conditions that lead to an improved operation. Several researchers have analyzed continuous stirred tank chemical reactors to characterize the phenomena of multiple steady states, simple and modulated oscillations and chaos (Uppal et al., 1974; Schmitz et al., 1979; Doedel and Heinemann, 1983). Halbe and Poore (1981) have shown how the periodic solutions bifurcate from the steady state according to the Hopf criterion. Lynch et al. (1982) have treated two independent reactions and shown how complicated the structure of the periodic and chaotic regimes may be in a transition from stability to instability of the steady state. Kahlert et al. (1981) have studied period doubling and chaos for the consecutive reactions A→B→C with one exothermic and one endothermic reaction. Pismen (1980) has reviewed many of the situations in which chaotic solutions arise. Jorgensen and Aris (1983) have shown the complex pattern of multiplicities present in a stirred tank reactor in which A→B→C takes place and illustrated how the repeated bifurcation of limit cycles leads into a pattern of periodic and chaotic behavior that returns to a simple limit cycle and then reflects itself. The reviews by Razon and Schmitz (1987) and Doherty and Ottino (1988) have provided many details about the steady state multiplicities, oscillatory dynamics and chaos in chemical processes. Recently, Gamboa-Torres and Flores-Tlacuahuac (2000) have studied the effect of inclusion of the jacket energy balance on the nonlinear behavior of CSTR, in which two exothermic irreversible first order reactions in series take place. Polymerization reactors exhibit highly nonlinear dynamics because of the complicated reaction mechanisms associated with the large number of interactive reactions. Several researchers have investigated the existence of steady state multiplicities, self sustained oscillations and chaos in continuous solution polymerization reactors.
(Jaisinghani and Ray, 1977; Schmidt et al., 1984; Pinto and ray, 1995). Teymour and Ray (1991) observed that the dynamic behavior of continuous solution polymerization reactors may be very complex and identified the operating conditions that provide multiple stable oscillatory solutions and chaotic behavior for vinyl acetate (VA) homopolymerization. Kim et al. (1991) observed that chaotic oscillations may develop when different types of initiators are mixed during the solution polymerization of styrene in two CSTRs in series. Nonlinear analysis and bifurcation studies have also been carried out for various industrial systems, especially polymerization reactors to determine the operating conditions for stable and unstable behavior, and to investigate the steady state multiplicity and oscillatory dynamics (Keane, 1972; Borman, 1991; Lewin and Bogle, 1996; Flores-Tlacuahuac et al., 2005).

Bifurcation and stability theories provide very useful conceptual and computational guidance in investigating complex dynamic phenomena and their evolution in chemical reaction systems. Period doubling bifurcation, originally suggested by Feigenbaum (1978) is the most common bifurcation that causes chaos in chemical reactions. In this type of bifurcation, the period of oscillations doubles as the running parameter value is changed. As the period doubling continues, the period quickly approaches infinity leading to chaos. The unstable, oscillatory and chaotic phenomenon displayed by the chemically reacting systems has desirable as well as undesirable features. The desirable feature of multiple steady state condition is that one of the unstable steady state may correspond to higher rate of reaction/yield and this becomes the preferred state to operate on it to enhance the process performance. The desirable feature of chaos is that it enhances mixing and chemical reactions and provides a vibrant mechanism for transport of heat and mass. On the other hand, the intrinsic features of the reacting systems with the interactive influence of chemical or thermal energy may cause irregular dynamic behavior leading to degraded performance. In such situations, chaos is considered as undesirable and should be avoided. Chaotic processes show extreme sensitivity to initial conditions and the process trajectories can diverge exponentially. However, chaos offers great flexibility to operate chemical systems because there are an infinite number of unstable periodic orbits (UPOs) embedded in a chaotic attractor, in which one can choose a specific UPO along with its time averaged pre-specified performance defined in terms of conversion, yield or selectivity and the process can be stabilized to operate it on the chosen UPO.

Successful operation, control and optimization of complex dynamic processes heavily rely on fast and accurately available real time process variable information. However, in most systems, the state variables desired by the on-line optimizers/controllers cannot be easily available through measurement or available with large measurement delays. Such inaccessible or non-measurable state variables can be made available by using on-line state estimators. Methods
based on filtering or observation can deliver reliable on-line estimates for state variables defining a process on the basis of available process knowledge including a dynamic model and the incoming data from process measurement sensors. The problem of model based state estimation for nonlinear processes that do not exhibit much complicated dynamical phenomena has been extensively covered in literature (Choi and Khan, 1988; Valliere and Brown, 1990; Venkateswarlu and Gangiah, 1992; Schelur and Schmidt, 1993; Gudi et al., 1995; Venkateswarlu and Avantika, 2001; Park et al., 2002; Li et al., 2004; Sumana and Venkateswarlu, 2009). However, this problem has not been thoroughly investigated for nonlinear systems associated with complex dynamical phenomena.

The objective of this work is to develop a state estimator for nonlinear dynamical systems that exhibit complex dynamic phenomena such as multiple steady state behavior, limit cycle oscillations and chaos. The design and use of such an estimator has several advantages for systems that are characterized by complicated dynamic behavior. The estimator plays a significant role in monitoring, optimization and control of these processes. The estimated process states can serve as inferential measurements to the conventional/advanced controllers (Patwardhan et al., 2007). They can be incorporated into the nonlinear control laws derived from the mathematical model of the process. These states can also be incorporated into the on-line optimizing control schemes aimed at improving the process performance. However, this study is focused towards state estimation, and estimation based optimization and control is not in the scope of the present work. Nonlinear dynamical systems involving chemical reactions operate under fast changing dynamic conditions. It’s a challenging task to design an estimator for such systems where the estimated states have to converge fast to the actual process dynamics. Methods based on filtering/observation that involve mathematical models of the process in their design are found to provide faster convergence in the presence of noise in the measurements and process uncertainties. In this study, an extended version of Kalman filtering approach is used to develop a state estimator for chemical systems associated with complex dynamic behavior. This model based estimator employs the mathematical model of the process in the estimator design thus enabling it to effectively capture the rapidly changing dynamics of the process and reflecting these changes in the estimated states. The design and implementation of the state estimator is studied by choosing two typical continuous nonlinear dynamical systems, a chemical reactor and a homopolymerization reactor, which show rich dynamic behavior ranging from stable situations to chaos. Prior to design of state estimator, the processes are thoroughly analyzed by performing multiplicity, stability and bifurcation studies. The effectiveness of the estimator is evaluated by comparing the estimation results with the actual ones. The sensitivity of the state estimator is also studied towards the effect of the design parameters involved in the method.
2. Nonlinear dynamical systems: mathematical models

Two typical continuous nonlinear chemical systems, a chemical reactor and a homopolymerization reactor, that exhibit complicated dynamic behavior are chosen to perform nonlinear analysis and state estimation studies.

2.1 Chemical reactor

A non-isothermal, irreversible, first order series reaction $A \rightarrow B \rightarrow C$ in a CSTR with load disturbances is described by the following dimensionless mass and energy balance equations (Kahlert et al., 1981):

\[
\frac{dx_1}{dt} = 1 - x_1 - Da x_1 \exp\left[\frac{x_3}{1 + \varepsilon_A x_3}\right] + d_1
\]

\[
\frac{dx_2}{dt} = -x_2 + Da x_1 \exp\left[\frac{x_3}{1 + \varepsilon_A x_3}\right] - Da S x_2 \exp\left[\frac{k x_3}{1 + \varepsilon_A x_3}\right] + d_2
\]

\[
\frac{dx_3}{dt} = -x_3 + BDax_1 \exp\left[\frac{x_3}{1 + \varepsilon_A x_3}\right] - DaB \alpha S x_2 \exp\left[\frac{k x_3}{1 + \varepsilon_A x_3}\right] - \beta (x_3 - x_{3c}) + d_3
\]

The variables $x_1$ and $x_2$ denote the dimensionless concentrations of species $A$ and $B$ respectively, and $x_3$ is the dimensionless temperature. The parameter $x_{3c}$ represents the reactor coolant temperature. The load disturbances in feed compositions are denoted by $d_1$ and $d_2$, and the load disturbance in the reactor temperature is denoted by $d_3$. This reactor system exhibit multi-stationary behavior, oscillations and chaos for the parameter values shown in Table 1.

Table 1 - Characterization of steady states.

<table>
<thead>
<tr>
<th>Set No.</th>
<th>Parameter values</th>
<th>$x_1^s$</th>
<th>$x_2^s$</th>
<th>$x_3^s$</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$Da=0.06, S=0.0005, \varepsilon_A=0, k=1, \alpha=0.426, \beta=7.7, B=55.0$</td>
<td>0.0378</td>
<td>0.9501</td>
<td>6.0500</td>
<td>Unstable</td>
</tr>
<tr>
<td>II</td>
<td>$Da=0.26, S=0.5, \varepsilon_A=0, k=1, \alpha=0.426, \beta=7.7, B=57.77$</td>
<td>0.0729</td>
<td>0.1259</td>
<td>3.8900</td>
<td>Stable limit cycle</td>
</tr>
<tr>
<td>III</td>
<td>Same as Set II except $\beta=7.9999$</td>
<td>0.0819</td>
<td>0.1391</td>
<td>3.7627</td>
<td>Chaotic</td>
</tr>
</tbody>
</table>
2.2 Homopolymerization reactor

Continuous homopolymerization reactors represent one important class of dynamical systems. The homopolymerization reactions are characterized by high heat release, high viscosity and poor heat transfer. Vinyl acetate homopolymerization has shown complex dynamic behavior for certain ranges of operating conditions due to the large heat of polymerization, the gel effect and the large activation energy of the initiation step. These factors can readily produce phenomena such as multiple steady states, steady state instability, limit cycles and chaos.

The kinetic mechanism for free-radical vinyl acetate homopolymerization reaction is as follows.

\[
I \xrightarrow{k_i} 2R \quad \text{(Radical Initiation)}
\]

\[
R + M \xrightarrow{k_e} P_1
\]

\[
P_i + M \xrightarrow{k_e} P_{i+1} \quad \text{(Chain Propagation)}
\]

\[
P_i + P_n \xrightarrow{k_e} \Lambda_{i+n} \quad \text{(Chain Termination)}
\]

The mathematical model for homopolymerization reaction of vinyl acetate in tertiary butanol using AIBN as initiator is described by the following equations (Pinto and Ray, 1995):

**Monomer Mass Balance**

\[
\frac{dv_m}{d\tau} = \frac{\rho_m v_m}{\rho_m} - q_o q_i v_m - \frac{(MW)_m R_m \theta}{\rho_m} + \nu_m \rho_m \frac{dT}{d\tau} \frac{dT}{d\tau}
\]  

**Solvent Mass Balance**

\[
\frac{dv_s}{d\tau} = \frac{\rho_s v_s}{\rho_s} - \nu_s q_o q_i + \rho_s \nu_s \frac{dT}{d\tau} \frac{dT}{d\tau}
\]

**Initiator Mass Balance**

\[
\frac{dc_i}{d\tau} = c_{\theta} - c_i (q_o q_i + k_\theta \theta)
\]

**Energy Balance**

\[
\frac{dT}{d\tau} = \frac{j (T_f - T)}{\rho} + \frac{\theta}{\rho C_p (MW)_m} v_m \rho_m k_p P - \frac{\theta}{\rho C_p} \frac{UA (T - T_c)}{V}
\]
In the above equations, $q_0 q_i$ is a term that takes into account changes in the density of the reactive mixture and is defined by

$$q_0 q_i = \frac{\rho_m \nu_m'}{\rho_m} + \frac{\rho_p \nu_p'}{\rho_p} + \theta (MW) p \rho_m R_{\theta} - 1 \left( \rho_m - 1 \right) + \frac{d}{dT} \left( \rho_p \frac{d \langle \rho_p \rangle}{dT} + \rho_m \nu_m \frac{d \langle \rho_m \rangle}{dT} + \rho_p \nu_p \frac{d \langle \rho_p \rangle}{dT} \right)$$

(8)

The overall density and specific heat of the mixture are

$$\rho = \rho_m v_m + \rho_p v_p$$

$$C_p = y_m C_{pm} + y_p C_{pp}$$

Under quasi steady state assumption for the free-radical species ($R$ and $P$), the normalized rate of monomer reaction is expressed as

$$Rate_m = k_p P + R_{ckr}$$

(9)

where concentration of species $P$ can be written as

$$P = \sqrt{\frac{R_{ckr} M}{k_p}}$$

(10)

The $R_{ckr}$ is the normalized rate of initiation as given by

$$R_{ckr} = \frac{2 f k_{a} c_i}{M}$$

(11)

By substituting the value of $R_{ckr}$ from Eq. (11) in Eq. (9)

$$Rate_m = k_p P + \frac{2 f k_{a} c_i}{M}$$

$$= R_m \frac{(MW)_m}{\rho_m v_m}$$

(12)

where $R_m$ is the rate of monomer consumption expressed by
\[
R_m = \frac{k_p P \rho_m v_m}{(MW)_m} + 2 f k_d c_i
\]  

(13)

The termination and propagation constants \( (k_t, k_p) \) used in the above equations include gel effect with the form

\[
k_t = k_t^0 g_t \\
k_p = k_p^0 g_p
\]  

(14)

The gel effect correlations are

\[
g_p = 1 \\
g_t = \exp(-0.4407x_t - 6.753x_t^2 - 0.3495x_t^3)
\]  

(15)

In Eq. (14), the \( k_t^0 \) and \( k_p^0 \) are the kinetic constants at zero polymer concentration, and \( g_t \) and \( g_p \) are the gel effect correlations that take into account the effects of increasing polymer concentration. The other parameters involved in simulation are presented in Table 2.

**Table 2 - Parameters for the Homopolymerization of VA.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho_m(T) )</td>
<td>( 958.4 - 1.3276(T - 273) ) (g/l)</td>
</tr>
<tr>
<td>( \rho_s(T) )</td>
<td>( \frac{74120}{(60.21 + 0.116T)} ) (g/l)</td>
</tr>
<tr>
<td>( \rho_p(T) )</td>
<td>( 1211 - 0.8496(T - 273) ) (g/l)</td>
</tr>
<tr>
<td>( C_{pm} )</td>
<td>0.470 (cal/g K)</td>
</tr>
<tr>
<td>( C_{ps} )</td>
<td>0.3453 + 9.55 \times 10^{-4}(T - 298) (cal/g K)</td>
</tr>
<tr>
<td>( C_{ps} )</td>
<td>0.716 (cal/g K)</td>
</tr>
<tr>
<td>( k_p^0 )</td>
<td>( 82.212 \times 10^8 e^{\frac{-6100}{RT}} ) (lt/gmol.s)</td>
</tr>
<tr>
<td>( k_d^0 )</td>
<td>( 94.8 \times 10^{15} e^{\frac{-30800}{RT}} ) (lt/gmol.s)</td>
</tr>
<tr>
<td>( k_t^0 )</td>
<td>( 469.392 \times 10^{10} e^{\frac{-2462}{RT}} ) (lt/gmol.s)</td>
</tr>
<tr>
<td>( \Delta H )</td>
<td>21000 (cal/gmol)</td>
</tr>
<tr>
<td>( UA )</td>
<td>12 (cal/min K)</td>
</tr>
<tr>
<td>( V )</td>
<td>500 (ml)</td>
</tr>
<tr>
<td>( f )</td>
<td>0.8</td>
</tr>
</tbody>
</table>
3. Multiplicity and stability analysis

The usual form of the differential equation representation of the process is

$$\frac{dx_i}{dt} = f(x_i) \quad (16)$$

A steady state $x_{is}$ of the system is defined if eq. (16) satisfies the condition

$$f(x_{is})=0 \quad (17)$$

A Jacobian matrix $A$ of $f$ is evaluated at the $x_{is}$ of interest

$$A = \frac{\partial f(x_{is})}{\partial x_i} \quad (18)$$

Local stability is assured if all the eigen values of $A$ have negative real parts; if any value have positive real part the steady state is unstable. To determine the stability at each point of the curve, local stability of the system need to be verified by using the stability criterion based on Routh-Hurwitz.

3.1 Chemical reactor

3.1.1 Stability analysis

The steady state equations of the system, eqs. (1)-(3) with $\varepsilon_A = 0$ and $k = 1$ is

$$x_{1s} = \frac{1}{1 + Da \exp(x_{3s})} \quad (19)$$

$$x_{2s} = \frac{1 - x_{1s}}{1 + DaS \exp(x_{3s})} \quad (20)$$

$$x_{3s} = \frac{B(1 - x_{1s}) - \alpha B (1 - x_{1s} - x_{2s}) + \beta x_{3s}}{1 + \beta} \quad (21)$$

For fixed values of $\alpha$, $\beta$, $B$, $S$, $x_{3c}$, the dependency of the steady state conversion, $x_{3s}$, on the Damkholer number, $Da$, will have certain possible shapes as shown in Fig. 1, where curve (a) shows the situation in which multiple steady
states exists for some values of $Da$, while curve (b) shows the situation when only a single steady state may exist.

![Figure 1](image_url)

**Figure. 1.** Locus of reactor steady states indicating: (a) multiplicity; (b) no multiplicity.

The Jacobian matrix for the system, eqs. (1)-(3) is given by

$$
A = \begin{bmatrix}
 a_{11} & a_{12} & a_{13} \\
 a_{21} & a_{22} & a_{23} \\
 a_{31} & a_{32} & a_{33}
\end{bmatrix}
$$

where $a_{ij}$'s are the elements (Appendix A) obtained by taking the partial derivatives of the model, eqs. (1)-(3), with respect to the state vector. The nature of the behavior of the system is determined from the roots of the characteristic equation,

$$
|A - \lambda I| = -\lambda^3 + S_1 \lambda^2 - S_2 \lambda + S_3 = 0
$$

(22)

where $S_1 = a_{11} + a_{22} + a_{33}$; $S_2 = a_{11} a_{22} - a_{12} a_{21} + a_{11} a_{33} - a_{13} a_{31} + a_{22} a_{33} - a_{23} a_{32}$; $S_3 = \text{det } A$. 

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$S_1$ and $S_2$ are the trace and the sum of the principle minor elements of the matrix. The Routh table for eq. (22) is defined by

\[
\begin{array}{ccc}
1 & S_2 & 0 \\
-S_1 & -S_3 & 0 \\
(S_1 S_2 - S_3) & 0 & 0 \\
S_1 & 0 & 0 \\
-S_3 & 0 & 0 \\
\end{array}
\]

According to Routh-Hurwitz stability criterion, the eigen values/the characteristic roots of eq. (22) should fall in the left half complex plane. The necessary and sufficient conditions for the steady state to be locally asymptotically stable are:

(i) $S_1 = \text{tr } A < 0$

(ii) $\frac{(S_1 S_2 - S_3)}{S_1} > 0$

(iii) $S_3 = \text{Det } A < 0$

The characteristics of the matrix $A$ are intimately connected to the issue of steady state multiplicity. A unique steady state always satisfies the condition (iii). If either of the $S_1$ or $S_3$ has the opposite sign, the steady state is unstable. When eigen value is zero or purely imaginary, the condition for static bifurcation existing in multiple steady states is $S_3 = \text{Det } A = 0$. The subfigures (a), (b) and (c) in Fig. 2 represents the steady state stability curves for the parameter values specified in Table 1 for sets I, II and III, respectively.
Figure 2. Stability profiles for sets I, II and III in Table 1.
3.1.2 Bifurcation analysis

For complex dynamic systems, bifurcation arises due to perturbations in system parameters that change the stability characteristics of the steady state solutions. Thus stability and bifurcation impact each other. The bifurcation diagram for the system is built by varying the parameters, $\alpha$, $\beta$, $B$, $S$ while keeping the others constant. These parameters completely define the state of the CSTR system. A bifurcation diagram for $x_{3s}$ vs. $Da$ can be drawn as shown in Fig. 3 by choosing the process parameters as $S=0.0005$, $\varepsilon_d=0$, $k=1$, $\alpha=0.426$, $\beta=7.7$ and allowing $B$ to vary as $B=B(1+\Delta)$ with $\Delta$ as a perturbation in $B$. Here, $B$ is the dimensionless number signifying the adiabatic temperature rise defined by $B = \frac{(-\Delta H_f)C_A E_1}{\rho C_p RT_f^2}$.

Figure 3. Shifting of single steady state to multiple steady states for different values of $B$. 

http://www.bepress.com/ijcre/vol9/A94
The $x_{3s}$ vs. $Da$ plot for $B=55$ in Fig. 3(a) shows the presence of multiple steady states, however, on considering a perturbation in $\Delta$ such that $B = 30$, the $x_{3s}$ vs. $Da$ plot in Fig. 3(a) shows the existence of a single steady state. The $x_{3s}$ vs. $Da$ plot in Fig. 3(b) depicts how the steady state behavior of the system changes for different perturbations in $B$. These curves can be used to infer the influence of the parameters involved in the definition of $B$ on the reaction system.

Figure 4. Effect of $\alpha$ and $\beta$ on the steady state behavior of CSTR system.
Similar observations can be made on the effect of $\alpha$ defined as $\alpha = -\Delta H_{1}/\Delta H_{1}$ The $x_3$ vs. $Da$ curves in Fig. 4(a) show how the steady state behavior of the system changes with respect to the changes in $\alpha$. The increase of $\alpha$ implies higher enthalpy change in $B \rightarrow C$ reaction indicating that $B$ is consumed faster than it is produced. As more heat is evolved in the second reaction, conversion of $B$ increases as temperature increases. Decrease of $\alpha$ will have the opposite effect. Similarly, the $x_3$ vs. $Da$ curves in Fig. 4(b) depicts the effect of $\beta$ defined in terms of $\beta = UA/\rho C_p V$ on the dynamics of the system. If $\beta$ increases, better heat transfer rates occur between coolant and reactor.

3.2 Polymerization reactor

3.2.1 Stability analysis

The steady state model of the system can be obtained from eqs. (4)-(7) as

**Monomer Mass Balance**

$$\frac{\rho_{mf}v_{mf}}{\rho_m} - q_o q_m v_m = \frac{(MW)_m R_m \theta}{\rho_m} = 0$$

**Solvent Mass Balance**

$$\frac{\rho_{sf}v_{sf}}{\rho_s} - v_s q_o q_i = 0$$

**Initiator Mass Balance**

$$c_o - c_i (q_o q_i + k_d \theta) = 0$$

**Energy Balance**

$$\frac{\rho}{\rho} [T_f - T] + \frac{\theta}{\rho C_p (MW)_m} v_m \rho_m k_p \rho - \frac{\theta}{\rho C_p} \frac{UA(T - T_e)}{V} = 0$$

In the above equations, $q_o q_i$ is a term that takes into account changes in the density of the reactive mixture and is defined by

$$q_o q_i = \frac{\rho_{mf}v_{mf}}{\rho_m} + \frac{\rho_{sf}v_{sf}}{\rho_s} + \theta (MW)_m \rho_m R_{m} \left( \frac{\rho_m}{\rho_p} - 1 \right)$$
3.2.2 Steady state solution

The steady state solution for the homopolymerization reactor model is not as simple as the chemical reactor system. Since direct solution is difficult due to interdependency of variables, an indirect approach is employed to obtain the steady solution for the variables $v_s$, $v_m$, $c_i$, and $T$ as illustrated below.

Step 1: An initial value of temperature is guessed and the temperature dependent parameters in Table 2 are solved.
Step 2: An initial value of $v_s$ is assumed.
Step 3: Using the values in steps 1 and 2, $q_o q_i$ is found from eq. (24):

$$q_o q_i = \frac{\rho_{sf} v_{sf}}{\rho_s v_s}$$  \hspace{1cm} (28)

On rearranging eq. (23),

$$\frac{\rho_{mf} v_{mf}}{\rho_m} = q_o q_i v_m + \frac{\theta (MW)_m R_m}{\rho_m}$$

On substituting $q_o q_i$ and $\frac{\rho_{mf} v_{mf}}{\rho_m}$ in eq. (27) and rearranging, we get

$$\theta = \frac{q_o q_i v_p \rho_p}{(MW)_m R_m}$$  \hspace{1cm} (29)

Substitute $\theta$ and $q_o q_i$ in eq. (27) to obtain $v_p$

$$v_p = \frac{\left( q_o q_i - \frac{\rho_{mf} v_{mf}}{\rho_m} \right) \rho_{sf} v_{sf} - \frac{\rho_{sf} v_{sf}}{\rho_s} q_o q_i}{q_o q_i \rho_p \left( \frac{1}{\rho_p} - \frac{1}{\rho_m} \right)}$$  \hspace{1cm} (30)

From monomer mass balance, Eq. (23) we get

$$\left( \frac{\rho_{mf} v_{mf}}{\rho_m} - q_o q_i v_m \right) \rho_m = \theta R_m$$  \hspace{1cm} (31)
From eqs. (10), (11) and (13), we have

\[ R_m = \frac{k_p P_m v_m}{(MW)_m} + P^2 k_i \]  

(32)

Eq. (26) can be put in a simplified notation:

\[ G_1 + G_2 \theta P - G_3 \theta = 0 \]  

(33)

where

\[ G_1 = \rho_f (T_f - T) C_p ; \quad G_2 = \frac{\Delta H v_m k_p P_m}{(MW)_m} ; \quad G_3 = UAV(T - T_c) \]

From Eqn. (33), we can evaluate the residence time (\( \theta \)) as

\[ \theta = \frac{G_1}{G_3 - G_2 P} \]  

(34)

Substituting Eqs. (32) and (34) in Eq. (31) and rearranging, we get

\[ P^2 G_i k_i + P \left( \frac{G_i k_p P_m v_m}{(MW)_m} + G_2 \theta R_m \right) - G_3 \theta R_m = 0 \]  

(35)

Eq. (35) is a quadratic expression where \( P \) is the molar concentration of free radical having two roots. By choosing the positive roots of \( P \), the values of \( c_i \) and \( \theta \) can be evaluated from Eqs. (10), (11) & (34). The \( c_i \) can also be evaluated from the initial mass balance steady state eq. (25) and compared with that evaluated from eqs. (10) & (11). If both these \( c_i \)s are equal, then the corresponding temperature and volume fraction of the solvent (\( v_s \)) is chosen, and the volume fraction of monomer \( v_m \) is computed from the relation \( v_m = 1 - (v_s + v_p) \). Thus the values of \( \theta \) and \( T \) can be established. If both the \( c_i \)s are not equal, then the procedure is repeated from step 2 with small increment in \( v_s \).

Step 4: The procedure is repeated from step 1 for all the temperatures in the given range with incremental guesses in temperature.

The temperature vs. residence time curve in Fig. 5, which is drawn for the fixed set of operating conditions, \( T_c = 318 \) K, \( T_f = 315 \) K, \( v_{mf} = 0.3 \) and \( c_{if} = 0.03203 \).
gmol/lt shows the multiple steady state behavior of the system. To determine the stability at each point of the curve, local stability of the system can be verified by forming the Jacobian matrix and evaluating the stability of the system based on Routh-Hurwitz stability criterion.

![Figure 5. Multiplicity curve for homopolymerization reaction.](image)

The Jacobian matrix, A for this system of equations is represented as:

\[
A = \begin{bmatrix}
    a_{11} & a_{12} & a_{13} & a_{14} \\
    a_{21} & a_{22} & a_{23} & a_{24} \\
    a_{31} & a_{32} & a_{33} & a_{34} \\
    a_{41} & a_{42} & a_{43} & a_{44}
\end{bmatrix}
\]

where \( a_{ij} \)'s are the elements obtained by taking the partial derivatives of the model equations (4)-(7), with respect to state vector. These elements are given in Appendix B. The nature of the behavior of the system is determined from the roots of the fourth order characteristic equation,

\[
|A - \lambda I| = \lambda^4 - S_1 \lambda^3 + S_2 \lambda^2 - S_3 \lambda + S_4 = 0
\]  

(36)
For the sake of notation simplicity, the elements of $A$ are denoted as:

$$A = \begin{bmatrix} a & b & c & d \\ e & f & g & h \\ i & j & k & l \\ m & n & o & p \end{bmatrix}$$

The characteristic equation has the form:

$$|A - \lambda I| = \lambda^4 - \lambda^3(a + k + p + f) + \lambda^2(ak + ap + af + kp + fp - ol - be - ci - dm - gj - hn) + \lambda(-akp - afk - afp + aol - fkp + fol + bek + bep - bgi - bgm - cfl - cfl + cip - cip - cml - cml - dem + dfm - dm + ag + ahm + gip = gl - hj + hhj + hnh)$$

$$(37)$$

Eq. (37) is in the form of eq. (36). The Routh table for eq. (36) is defined by

$$\begin{array}{cccc}
1 & S_2 & S_4 & 0 \\
-S_1 & -S_3 & 0 & 0 \\
C & S_4 & 0 & 0 \\
D & 0 & 0 & 0 \\
S_4 & & & \\
\end{array}$$

where $S_i$'s are the sums of the principal minors of $A$. It can be observed that $S_1$ represents the trace of $A$ and $S_4$ denotes the determinant of $A$. In the above table,

$$C = \frac{(S_2 S_2 - S_3)}{S_1} \quad \text{and} \quad D = \frac{C(-S_1) + S_1 S_4}{C}.$$
(iii) \( \frac{(S_1S_2 - S_3) - S_3}{S_1} + S_1S_4 > 0 \)

(iv) \( S_4 = \text{Det } A > 0 \)

Conditions (ii) & (iii) are satisfied if and only if \( S_2 > 0 \) and \( S_3 < 0 \). The characteristics of the A are intimately connected with the question of steady state multiplicity. A unique steady state always satisfies the condition (iv). If either of the \( S_1 \) or \( S_4 \) has the opposite sign, the steady state is unstable. When eigen value is zero or purely imaginary, the condition for static bifurcation existing in multiple steady states is \( S_4 = \text{Det } A = 0 \).

Figure 6. Period doubling bifurcation diagram.

### 3.2.3 Bifurcation analysis

For this fourth order system the conditions for Hopf bifurcation to limit cycles at imaginary eigen values \((\pm i\omega)\) can also be determined from the Routh-Hurwitz criterion when the condition (ii) is equal to zero, i.e.,

\[
S_1S_2S_3 - (S_3)^2 - S_1^2S_4 = 0
\]

(38)
Hopf bifurcation points are those points where a pair of complex eigen values crosses the imaginary axis, changing the stability characteristics of the steady state solutions. Periodic solutions are expected to evolve from these special bifurcation points. For a particular set of operating conditions, $T_c = 318$ K, $T_f = 315$ K, $I_{mf} = 0.3$ and $c_{inf} = 0.03203$ gmol/lt, the bifurcation diagram in Fig. 6 shows the multiple steady states, limit cycle and bifurcation points as well as stable and unstable zones that are generated with respect to the variation in residence time. For the same set of conditions, the transition from stable to unstable zone (beginning at $\theta = 24$) occurs causing oscillatory behavior that eventually lead to period doubling bifurcation cascade and chaos as depicted in Fig. 7(a). The magnification results of Fig. 7(a) are further explained in Figs. 7(b) and 7(c), which indicate the sequence of periodic windows of periods 2, 4, 8 and so on leading to chaotic region. It can be observed that at residence time, $\theta = 27.0$ min, the system exhibits limit cycles with sustained period oscillations. The sustained oscillatory behavior of the response in time domain is shown in Fig 8(a) and the corresponding phase plane plot is shown in Fig 8(b). The dynamic characteristics of the responses are further explained along with the state estimation results in the later sections.

4. Optimal state estimation

Successful operation and control of nonlinear dynamical systems rely heavily on the availability of a fast and accurate evaluation of the system performance. However, in many systems some of the state variables that are critical for efficient operation are not readily available by on-line measurement. The measurement problems and the delays associated with such systems therefore require the need for on-line estimation of unmeasured process states. In this work, model based method is presented for state estimation in nonlinear dynamic systems that display complex behavior ranging from stable situations to chaos.
Figure 7. One dimensional Poincare bifurcation diagram: (a) Transition from limit cycles to chaos; (b) minimum temperature; (c) maximum temperature.
Fig. 8 - Single periodic limit cycle behavior: (a) time domain response; (b) phase plane plot

4.1 Process representation

The mathematical model of the nonlinear dynamical system can be expressed by the following state space form

\[ \dot{x}(t) = f(x(t), t) + w(t), \quad x(0) = x_0 \]  \hspace{1cm} (39)
where \( x(t) \) is \( n \) dimensional state vector, \( f \) is a nonlinear function of state \( x(t) \) and \( w(t) \) is an additive Gaussian noise with zero mean. The nonlinear measurement model with observation noise can be expressed as

\[
y(t_k) = h(x(t_k)) + v(t_k)
\]  

(40)

where \( h \) is a nonlinear function of state \( x(t_k) \). The expected values of noise covariance matrices for the initial state \( x(0) \), process noise \( w(t) \) and observation noise \( v(t_k) \) are given by the following relations,

\[
\begin{align*}
P_0 &= E[(x_0 - x(0))(x_0 - x(0))^T] \\
Q(t) &= E[w(t)w^T(t)] \\
R(t_k) &= E[v(t_k)v^T(t_k)]
\end{align*}
\]  

(41)

where \( P_0 \) is initial state covariance matrix, \( Q(t) \) is process noise covariance matrix and \( R(t_k) \) is observation noise covariance matrix. The matrices \( P_0, Q(t) \) and \( R(t_k) \) are generally selected as estimator design parameters which are used to reflect errors in the initial state, process model and process measurements.

### 4.2 State estimation algorithm

State estimation methods based on filtering or observation can deliver reliable online estimates for state variables defining a process on the basis of available process knowledge including a dynamic model and the incoming data from process measurement sensors. In this study, an extended Kalman filter is employed to estimate the unmeasurable state variables in complex dynamic systems.

The extended Kalman filter (EKF) is computed in two steps. The first is a prediction step, which is used to extrapolate the previous best estimates, and the second is a correction step by which the updated estimates are formed. These prediction and correction equations are implemented recursively. Since prediction is based on process model, continuous prediction and discrete correction is employed in the estimation scheme.

#### 4.2.1 Prediction equations:

By starting with an initial estimate \( x_0 \) and its covariance \( P_0 \) at time zero and no measurements are taken between \( t_{k-1} \) and \( t_k \), the propagating expression for the state estimate and its covariance from \( t_{k-1} \) to \( t_k \) are,
\[
\dot{x}(t_{k-1}) = f(\hat{x}(t_{k-1}),t) \\
P(t_{k-1}) = F(\hat{x}(t_{k-1}),t)P(t_{k-1}) + P(t_{k-1})F^T(\hat{x}(t_{k-1}),t) + Q(t)
\]

where \( F(\hat{x}(t_{k-1}),t) \) is the state transition matrix whose \( i,j \)th element is given by
\[
F(\hat{x}(t_{k-1}),t) = \frac{\partial f_i(x(t),t)}{\partial x_j(t)} \bigg|_{x(t) = \hat{x}(t_{k-1})}
\]

The solution of the propagated estimate \( \hat{x}(t_{k-1}) \) and its covariance \( P(t_{k-1}) \) at time \( t_k \) are denoted by \( \hat{x}(t_k/t_{k-1}) \) and \( P(t_k/t_{k-1}) \). By using measurements at time \( t_k \), the update estimate \( \hat{x}(t_k/t_k) \) and its covariance \( P(t_k/t_k) \) are computed.

### 4.2.2 Correction equations:

The equations to obtain corrected estimates are:
\[
\hat{x}(t_k/t_k) = \hat{x}(t_k/t_{k-1}) + K(t_k) [y(t_k) - h(\hat{x}(t_k/t_{k-1}))]
\]
\[
P(t_k/t_k) = (I - K(t_k)H(x(t_k)))P(t_k/t_{k-1})
\]
\[
K(t_k) = P(t_k/t_{k-1})H^T(x(t_k))(H(x(t_k)))P(t_k/t_{k-1})H^T(x(t_k)) + R^{-1}
\]

where, \( H(x(t_k)) = \frac{\partial h_i(x(t_k))}{\partial x_j(t_k)} \bigg|_{x(t_k) = \hat{x}(t_k/t_{k-1})} \)

The recursive initial conditions for state and covariance are:
\[
\hat{x}(t_k/t_{k-1}) = \hat{x}(t_k/t_k) \\
P(t_k/t_{k-1}) = P(t_k/t_k)
\]

More details concerning the EKF for state estimation in nonlinear systems can be referred to elsewhere (Kozub and Macgregor, 1992; Venkateswarlu and Kumar, 2006).

### 5. Design of estimator

#### 5.1 Chemical reactor

The nonlinear dynamic model of the reactor system in its dimensionless form is used in conjunction with the temperature measurements to estimate the reactor
species concentrations. The design of soft sensor involves the following components:

*State vector*

The chemical species concentrations and the temperature define the state vector as

\[ x = [x_1 \ x_2 \ x_3] \]

(49)

*State transition matrix*

The elements \( f_{ij} \) of the state transition matrix, \( F \) are computed by taking the partial derivatives of \( f(x) \) defined by (1)-(3) with respect to the state vector:

\[
F = \begin{bmatrix}
  f_{11} & f_{12} & f_{13} \\
  f_{21} & f_{22} & f_{23} \\
  f_{31} & f_{32} & f_{33}
\end{bmatrix}
\]

(50)

*Measurement matrix*

The measurement relation for temperature is

\[
H = [0 \ 0 \ 1]
\]

(51)

The temperature state equation, Eq. (3) in its discrete form is used as the nonlinear measurement equation, \( h(x) \). The elements of the measurement transition matrix, \( H_x \) are computed by taking the partial derivatives of \( h(x) \) with respect to the state vector

\[
H_x = [h_{i1} \ h_{i2} \ h_{i3}]
\]

(52)

All these components are evaluated for chaotic reactor and used with the EKF estimator to obtain measured and unmeasured states of the reactor. The soft sensor uses the temperature data of every sampling time as measurements and provides the estimates of temperature as well as reactor species concentrations.

5.2 Polymer reactor

The nonlinear dynamic model of the VA homopolymerization system is used in conjunction with the temperature measurements to estimate the volume fraction of
monomer, solvent, concentration of initiator and reactor temperature. The design of soft sensor involves the following components:

**State vector**

The volume fraction of monomer, solvent, concentration of initiator and reactor temperature define the state vector as

\[
x = \begin{bmatrix} v_m & v_s & c_i & T \end{bmatrix}^T
\]  \hspace{1cm} (53)

**State transition matrix**

The elements \(f_{ij}\) of the state transition matrix, \(F\) are computed by taking the partial derivatives of \(f(x)\) defined by Eqs. (4)-(7) with respect to the state vector:

\[
F = \begin{bmatrix}
f_{11} & f_{12} & f_{13} & f_{14} \\
f_{21} & f_{22} & f_{23} & f_{24} \\
f_{31} & f_{32} & f_{33} & f_{34} \\
f_{41} & f_{42} & f_{43} & f_{44}
\end{bmatrix}
\]  \hspace{1cm} (54)

**Measurement matrix**

The measurement relation for temperature is

\[
H = \begin{bmatrix} 0 & 0 & 0 & 1 \end{bmatrix}
\]  \hspace{1cm} (55)

The temperature state equation, Eq. (7) in its discrete form is used as the nonlinear measurement equation, \(h(x)\). The elements of the measurement transition matrix, \(H_x\) are computed by taking the partial derivatives of \(h(x)\) with respect to the state vector

\[
H_x = \begin{bmatrix} h_{11} & h_{12} & h_{13} & h_{14} \end{bmatrix}
\]  \hspace{1cm} (56)

All these components are evaluated for homopolymerization reactor and used with the EKF estimator to obtain measured and unmeasured states of the reactor. The soft sensor uses the temperature data of every sampling time as measurements and provides the estimates of temperature as well as reactor species concentrations.
6. Analysis of state estimation results

6.1 Chemical reactor

The reactor system represented by eqs. (1)-(3) exhibits multi-stationary behavior, oscillations and chaos for parameter values given in Table 1. For parameter set I, the system shows unstable steady state. For parameter sets II and III, the system exhibits limit cycle oscillations and chaotic behavior, respectively. The temperature data used for state estimation are obtained through numerical integration of model equations using Gear’s method with a sampling time of 0.0001 units. The temperature measurement of every 1 sec is considered for state estimation. The EKF is designed and applied in conjunction with the known temperature measurements to estimate the process states. These estimated states include the reacting species concentrations as well as temperature. The diagonal elements of the EKF design parameters such as the initial state covariance matrix $P_o$, the process noise covariance matrix, $Q$ and the observation noise covariance matrix, $R$ are selected as 0.000256, 0.000424, 0.53407, respectively, and diagonal elements of the observation noise covariance are set be 100. The performance of the EKF estimator is evaluated for different cases of process parameter values shown in Table 1. The results in Figs. 9 and 10 represent the actual and estimated concentration profiles, and the phase plane plots corresponding to the parameter sets II and III of Table 1, respectively.

![Fig. 9 - Concentration profiles and phase plots for set-II: actual ($x_1, x_2$); estimated ($\hat{x}_1, \hat{x}_2$)](image-url)
In order to represent realistic situation, temperature state is corrupted with random Gaussian noise having a mean zero and standard deviation 0.25. Fig. 11 shows the actual and estimated concentration profiles corresponding to set III in the presence of stochastic noise in temperature obeying Gaussian distribution. In all the cases, the estimated states are in close resemblance with the actual states.
6.2 Polymerization Reactor

The mathematical model of homopolymerization reactor is solved by numerical integration using Gear’s method with a sampling time of 0.0001 units. The diagonal elements of the EKF design parameters such as the initial state covariance matrix $P_0$, the process noise covariance matrix, $Q$ and the observation noise covariance matrix, $R$ are selected as 0.00157, 0.00745, 0.00345 and 3.476, respectively, and diagonal elements of the observation noise covariance are set be 100. From the results of Fig. 7, it can be observed that for the given set of operating conditions ($T_c = 318$ K, $T_f = 315$ K, $v_{mf} = 0.3$, $c_{if} = 0.03203$ gmol/lt), at residence time $\theta = 27.0$ min, the system exhibits limit cycle behavior with sustained period oscillations. As $\theta$ is increased by 0.2 min from 27.0 min, there exist two minimum and maximum temperatures showing double periodic limit cycles. The actual and estimated double periodic oscillatory limit cycles and the phase plane plots that are generated at $\theta = 27.2$ min are shown in Fig. 12. With the further increase of $\theta$ by another 0.08 min, the system exhibits period doubling.
characteristic with four minimum temperatures and four maximum temperatures. This actual and estimated sustained quadruple periodic oscillatory behavior in temperature responses and the corresponding phase plane plots for the same operating conditions at $\theta = 27.28$ min are shown in Fig. 13. As $\theta$ is increased further, there exist multiple minimum temperatures and multiple maximum temperatures. This leads to huge temperature oscillations leading to chaotic behavior. The actual and estimated chaotic responses in temperature and the corresponding phase plane plots for the same operating conditions at $\theta = 27.37$ min are shown in Fig. 14. These results confirm the effectiveness of the method of EKF as a state estimator for polymerization reactor.

![Fig. 12. Actual and estimated double periodic limit cycle and corresponding phaseplane plots at $\theta = 27.2$ min.](image)

The performance of the estimator is also evaluated in terms of integral squared error (ISE) which is computed based on the actual and estimated results for different conditions. The ISE results indicate the sensitivity of the estimator towards the influence of different levels of the estimator design parameters, $P_o$, $Q$, and $R$. The ISE values shown in Table 3 correspond to the conditions for which the results are depicted in figures referred in the same table. The values of $P_o$, $Q$, and $R$ that are selected to yield optimal performance of the estimator are referred to base case values. While studying the influence of any one of these parameters,
the other parameters are kept at their base case level. A marginal variation of about two to three times from the base case level of these parameters is considered, because higher variations in them can lead to adverse affect on the performance of the process due to its complex nature. From the ISE results of Table 3, it is observed that the effect of $P_o$, $Q$ and $R$ on the performance of the process is very much dependent on the dynamic behavior of the process caused by its characteristic parameters. These results show that increasing or decreasing the $P_o$, and $Q$ by two to three times has only a mild influence on the performance of the chemical and polymerization reactors. It is also observed that the performance of the polymerization reactor is more affected by the measurement covariance matrix, $R$ than the chemical reactor. The small variations in process performance for the changes considered in the estimator design parameters indicate the robustness of the scheme for state estimation in nonlinear dynamical systems. The results evaluated for both the chemical and polymerization reactors thus confirm the better suitability of the method of EKF for state estimation in chemical processes that exhibit complicated dynamic behavior.

Figure 13 - Actual and Estimated quadruple periodic limit cycle responses and corresponding phase plane plots at $\theta = 27.28$ min.
Fig. 14. Actual and estimated chaotic responses and corresponding phase plane plot at $\theta = 27.37$ min.

7. Conclusions

Successful operation and control of nonlinear processes heavily rely on the availability of a fast and accurate evaluation of the system performance. The measurement problems and the delays associated with the complex dynamic systems require the development of on-line state estimators as alternative measurement tools. The knowledge obtained by understanding the dynamical behavior of the chemical processes can be effectively utilized to develop state estimators for such systems. In this work, a state estimation method based on extended Kalman filter is presented for nonlinear dynamical systems that are characterized by complex dynamic phenomena such as multiple steady state behavior, limit cycle oscillations and chaos. The design and implementation of the state estimator is studied by considering two typical continuous non-isothermal nonlinear processes, a chemical reactor and a polymerization reactor, which show rich dynamical behavior ranging from stable situations to chaos. In order to understand the dynamic phenomena and to analyze the conditions that lead to an improved operation, these processes are also thoroughly analyzed for multiplicity, stability and bifurcation studies. The results demonstrate the better performance of the model based state estimation method for nonlinear chemical processes that exhibit complex dynamic behavior.
Table 3 – Effect of estimator design parameters – ISE results.

<table>
<thead>
<tr>
<th>Design parameter</th>
<th>Chemical reactor</th>
<th>Homopolymerization reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fig. 9</td>
<td>Fig. 10</td>
</tr>
<tr>
<td>Initial state covariance matrix</td>
<td></td>
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</tr>
<tr>
<td>P0</td>
<td>3.50E-02</td>
<td>5.18E-02</td>
</tr>
<tr>
<td>P0/2</td>
<td>3.35E-02</td>
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<tr>
<td>P0/3</td>
<td>3.09E-02</td>
<td>3.69E-02</td>
</tr>
<tr>
<td>2P0</td>
<td>3.55E-02</td>
<td>5.34E-02</td>
</tr>
<tr>
<td>3P0</td>
<td>3.54E-02</td>
<td>5.34E-02</td>
</tr>
<tr>
<td>Process noise covariance matrix</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>3.50E-02</td>
<td>5.18E-02</td>
</tr>
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<td>Q/2</td>
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<td>3.50E-02</td>
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<tr>
<td>Measurement noise covariance matrix</td>
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<td></td>
</tr>
<tr>
<td>R</td>
<td>3.50E-02</td>
<td>5.18E-02</td>
</tr>
<tr>
<td>R/2</td>
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<tr>
<td>3R</td>
<td>3.09E-02</td>
<td>3.69E-02</td>
</tr>
</tbody>
</table>

Appendix A – Elements of state transition matrix

\[ a_{11} = -1 - Da \exp(x_3), \quad a_{12} = 0, \quad a_{13} = -Dax_1 \exp(x_3), \]
\[ a_{21} = Da \exp(x_3), \quad a_{22} = -1 - DaS \exp(x_3), \quad a_{23} = Dax_1 \exp(x_3) - DaS \exp(x_3), \]
\[ a_{31} = BDa \exp(x_3), \quad a_{32} = -DaB\alpha S \exp(x_3) \]
\[ a_{33} = -1 + BDax_1 \exp(x_3) - DaB\alpha Sx_2 \exp(x_3) - \beta. \]

Appendix B – Elements of state transition matrix

\[ a_{11} = -\frac{\left(\frac{d(q_i, q_i)}{dv_m}\right) v_m + (q_i, q_i)}{\theta} - \frac{MWm}{\rho_m} \frac{dR_m}{dv_m} + \frac{1}{\rho_m} \left( - \frac{d\rho_m}{dT} v_m \frac{d}{dv_m} \left( \frac{dT}{dt} + \frac{dv_m}{dt} \right) \right) \]
\[
a_{12} = \frac{v_m}{\theta} \frac{d(q,q_i)}{dv_i} + \left( \frac{-d\rho_m}{dT} \frac{v_m}{\rho_n} \frac{d}{dv_i} \left( \frac{dT}{dt} \right) \right),
\]
\[
a_{13} = \frac{v_m}{\theta} \frac{d(q,q_i)}{dc_i} + \left( \frac{-d\rho_m}{dT} \frac{v_m}{\rho_n} \frac{d}{dc_i} \left( \frac{dT}{dt} \right) \right) - \frac{MW_m}{\rho_n} \frac{d}{dc_i} \left( \frac{R_m}{\rho_n} \right),
\]
\[
a_{14} = \frac{\phi_n \rho_m}{\rho_n} \frac{d\rho_m}{dT} \frac{v_m}{\theta} \frac{d}{dv_i} \left( \frac{1}{\rho_n} \frac{d}{dt} \right) \frac{v_m}{\rho_n} \frac{MW_m}{\rho_n} \frac{d}{dv_i} \left( \frac{R_m}{\rho_n} \right) + \frac{d}{dt} \left( \frac{R_m}{\rho_n} \right)\frac{d}{dv_i} \left( \frac{R_m}{\rho_n} \right),
\]
\[
a_{21} = \frac{v_i}{\theta} \frac{d(q,q_i)}{dv_m} - \frac{v_i}{\rho_s} \frac{d}{dv_m} \frac{dv_i}{dv_m} \frac{d}{dt} \left( \frac{dT}{dt} \right) a_{22} = \left( \frac{d(q,q_i)}{dv_m} v_i + (q(q_i)) \right) - \frac{d\rho_m}{dT} \frac{v_m}{\rho_n} \frac{d}{dv_i} \left( \frac{dT}{dt} \right) + \frac{d}{dt} \left( \frac{R_m}{\rho_n} \right)\frac{d}{dv_i} \left( \frac{R_m}{\rho_n} \right),
\]
\[
a_{23} = \frac{v_i}{\theta} \frac{d(q,q_i)}{dc_i} - \frac{v_i}{\rho_s} \frac{d}{dc_i} \frac{dv_i}{dv_m} \frac{d}{dt} \left( \frac{dT}{dt} \right) a_{24} = \left( \frac{d(q,q_i)}{dc_i} v_i - (q(q_i)) \right) - \frac{v_i}{\theta} \frac{d}{dv_m} \frac{dv_i}{dv_m} \frac{d}{dc_i} \left( \frac{dT}{dt} \right) + \frac{d}{dt} \left( \frac{R_m}{\rho_n} \right)\frac{d}{dv_m} \left( \frac{R_m}{\rho_n} \right),
\]
\[
a_{31} = \frac{c_i}{\theta} \frac{d(q,q_i)}{dv_m} a_{32} = \frac{c_i}{\theta} \frac{d(q,q_i)}{dv_m} a_{33} = \frac{-1}{\theta} \frac{d(q,q_i)}{dc_i} (q(q_i) - k_d),
\]
\[
a_{34} = \frac{c_i}{\theta} \frac{d(q,q_i)}{dv_i} - c_i \frac{dk_d}{dT},
\]
\[
a_{41} = \frac{d}{dv_m} \left( \frac{d}{dT} \right) a_{42} = \frac{d}{dv_i} \left( \frac{d}{dT} \right) a_{43} = \frac{d}{dc_i} \left( \frac{d}{dT} \right) a_{44} = \frac{d}{dt} \left( \frac{d}{dT} \right)
\]

**Notation**

- \(c_i\) initiator concentration in reactor, \(\text{gmol/l}\)
- \(c_{if}\) initiator feed concentration, \(\text{gmol/l}\)
- \(d_1, d_2, d_3\) Load disturbance in \(x_1, x_2, x_3\)
- \(Da\) Damkohler number
- \(\varepsilon_A\) activation number
- \(f\) initiator dissociation efficiency
- \(-\Delta H_R\) heat of polymerization, \(\text{cal/gmol}\)
- \(k\) Ratio of the activation energies for the series reaction
- \(k_d\) rate constant for initiator decomposition, \(\text{l/s}\)
- \(k_p\) rate constant for propagation, \(\text{l/gmol s}\)
- \(k_t\) rate constant for termination, \(\text{l/gmol s}\)
- \((MW)_m\) molecular weight of monomer, \(\text{g/gmol}\)
- \(P\) live radical concentration, \(\text{gmol/l}\)
- \(q/q_i\) ratio of outlet to inlet volumetric flow rate
- \(R_m\) rate of consumption of monomer, \(\text{gmol/l min}\)
- \(S\) Ratio of the rate constants for the series reaction
- \(t\) Time, min


\( T \) reactor temperature, \( K \)  
\( UA \) Overall heat transfer coefficient, \( cal/min K \)  
\( V \) Volume of the reactor, \( l \)  
\( v_m \) Volume fraction of monomer in reactor  
\( v_{mf} \) Volume fraction of monomer in feed  
\( x_t \) mole fraction of polymer  
\( x_1, x_2 \) Dimensionless concentration of species A, B  
\( x_3 \) Dimensionless temperature  
\( x_{3c} \) Dimensionless coolant temperature  
\( x_{1s}, x_{2s}, x_{3s} \) Steady state values of \( x_1, x_2 \) and \( x_3 \)  
\( y_i \) weight fraction of respective components (\( i=m,s,p \))

Greek symbols

\( \alpha \) Ratio of heat effects for the series reaction  
\( \beta \) Heat transfer coefficient  
\( \theta \) Residence time, \( min \)  
\( \tau \) Dimensionless time (\( =t/\theta \))  
\( \rho \) Density of reaction mixture, \( g/l \)

Subscripts

\( m \) monomer  
\( s \) solvent  
\( p \) polymer  
\( f \) feed  
\( c \) coolant

References


Venkateswarlu, Ch., and Kumar, B.J., “Composition estimation of multicomponent reactive batch distillation with optimal sensor configuration”, Chemical Engineering Science, 2006, 61, 17, 5560–5574.