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Abstract

This paper describes an application of the extended Kalman filter algorithm to the state estimation of the melt transesterification stage of a continuous polyethylene terephthalate condensation polymerization process. When only two on-line measurements of reaction variables are used for state estimation, the prediction of reaction rates and product concentrations are unsatisfactory. When such limited on-line measurements are supplemented by five additional off-line measurements of various functional group concentrations, the system is completely observable and the overall performance of the state estimator is greatly improved. It has been shown that the analysis delay of 24 hours is quite adequate for accurate state estimation of the process. In particular, the concentration of unwanted side product such as diethylene glycol (DEG) was predicted precisely. The simulation results indicate that the extended Kalman filter can be used successfully with a dynamic transesterification process model for precise control of reaction product quality.
INTRODUCTION

Polyethylene terephthalate (PET) is one of the fastest growing thermoplastic polyesters used extensively for fibers, films, bottles, injection molded parts and other products. PET is manufactured by a step growth melt polymerization process which comprises three reaction steps: (i) melt transesterification of dimethyl terephthalate (DMT) with ethylene glycol (EG), (ii) prepolymerization at 250-300°C and \(~30 \text{ mmHg,}\) (iii) finishing polymerization at 280 \(~300°C\) and \(~1 \text{ mmHg.}\)

Biaxially oriented PET films contain a high degree of molecular orientation which improves its tensile strength, clarity, stiffness, chemical resistance and barrier properties. Such PET films have found commercial application not only in the traditional areas of magnetic tape media and photographic film coating, but also in such diversified areas as food packaging and electrical appliance insulation. PET resins may also be crystallizable or reinforced with glass fibers and minerals for many additional engineering applications.

Due to the stringent industrial product specifications that today's polymers and engineering plastics must meet, the need for fine tuning the base polymer properties through more effective reactor operation is now more acute than ever. For instance, in order to produce PET resins offering a combination of high strength, stiffness, dimensional stability, chemical and heat resistance, and good electrical properties, the polymer molecular weight and undesirable side product concentrations must be controlled within limits that would not damage industrial end requirements. The presence of diethylene glycol (DEG), even in
small concentrations (1~2 wt %), in final polymer products causes decreased polymer crystallinity, resulting in lowered melting points, reduced heat resistance, and decreased thermal oxidative and UV light stability. Such polymer property variables, in most instances, are very difficult or impossible to measure on-line. Thus, it is very difficult to control polymer product quality when all that is available are only infrequent and delayed off-line laboratory measurements. For this reason, much current research interest in the area of polymerization process control is devoted to a study of estimation theory and subsequent real time application.

Optimal state estimation, the process of extracting information concerning a parameter or function from noise-corrupted observations, has recently found extensive application in many areas such as chemical processes, telecommunication and satellite orbit determination [Wells (1971), Sage and Melsa (1971), Nahi (1976), Schuler and Suzhen (1985), Papadopoulou and Gilles (1986), Taylor et al. (1986)]. In order to apply the techniques of estimation theory to a particular engineering problem, an appropriate mathematical model must be constructed for the system of concern. Most chemical processes, due to their highly nonlinear nature, cannot be readily modeled and thus defining control strategies becomes cumbersome. Since the implementation of estimation algorithms is based primarily on system state observations or some function thereof, the use of the extended Kalman filter can aid in parameter estimation and model development given that a measure of the inaccuracy of the
model is directly obtainable.

The objective of this paper is to model the first stage of a PET condensation polymerization process and to develop an optimal state estimator. DMT conversion and product composition distribution will be estimated using the extended Kalman filter. The performance of the state estimator will be illustrated through numerical simulation of the dynamic model.
MODEL DEVELOPMENT

Consider the process flow diagram for a continuous transesterification process shown in Figure 1. Molten DMT is fed to the ester interchange reactor which is kept under an inert atmosphere within the temperature range 180-200°C. Ethylene glycol is passed in a similar fashion to the reactor from an EG storage tank. The metal acetate catalyst (e.g., zinc acetate) is injected into the EG feed stream from a catalyst storage vessel. The resultant vapors (mostly methanol, EG and trace amounts of other volatile side products) from the combination of DMT and EG to produce BHET are rectified in the distillation column; thus, EG is refluxed back into the reactor. The more volatile components in the vapor phase are condensed in a condenser and their amounts are used to gauge the extent of reaction in the liquid phase. The transesterification product is transferred to the prepolycondensation reactor which is maintained between 10-30 mmHg and 280-300°C. The polymer melt is pumped to the finishing polymerization reactor, usually an extruder type or a wiped film reactor.

Of the large number of possible chemical reactions postulated for the transesterification stage, we shall consider four of the most important ones. For an exhaustive evaluation of the transesterification reaction chemistry, the works of Ravindranath and Mashelkar (1981, 1982(a), (b)) should prove to be very instructive. The motivation concerning the choice and number of reactions is to reduce the complexity posed by considering every possible reactions but also to maintain a
Figure 1. Schematic diagram of continuous melt PET polymerization process.
realistic workable model which can be used for process control purposes. Assuming that no oligomerization occurs in this stage, the main transesterification reactions are

\[
\begin{align*}
D + G & \xrightleftharpoons[k_2]{k_1} R_1 + M & (1) \\
R_1 + G & \xrightleftharpoons[k_2']{k_2} P_1 + M & (2)
\end{align*}
\]

The chemical formulae for the symbols are shown in Table 1. When the continuous removal of liberated methanol (M) is efficiently performed, the two reactions above may be conveniently approximated as irreversible reactions. In addition to main the reactions (1) and (2), important side reactions lead to the formation of diethylene glycol (DEG), which often deteriorates the properties of the final PET produced (e.g. the melting point of PET decreases by 5°C for each weight percent of DEG incorporated, and the presence of small amounts of DEG causes undesirable coloring problems [Ravindranath and Mashelkar, 1981]). Therefore, the side reactions considered in this work deal directly with the formation of DEG,

\[
\begin{align*}
R_1 + G & \xrightarrow[k_3]{k_3} T_1 + G_D & (3) \\
P_1 + G & \xrightarrow[k_4]{k_4} Q_1 + G_d & (4)
\end{align*}
\]

Note that the reactivities of reactions (3) and (4) have been assumed to be the same according to Ravindranath and Mashelkar (1981). The temperature dependence of the rate constants is accounted for in the standard Arrhenius rate expression (i.e. \(k_i = A_i e^{-E_i / RT}\)).
Table 1: Chemical formulae for the transesterification model.

Dimethyl terephthalate (DMT or D)

\[
\text{H}_2\text{COOC} \-
\text{O} \-
\text{COOCH}_3
\]

Ethylene glycol (EG or G)

\[
\text{HOCH}_2\text{CH}_2\text{OH}
\]

Diethylene glycol (DEG or GD)

\[
\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}
\]

Methanol (M)

\[
\text{CH}_3\text{OH}
\]

Bis-hydroxyethyl terephthalate (BHET or P\text{,})

\[
\text{HOCH}_2\text{CH}_2\text{OOC} \-
\text{O} \-
\text{COOCH}_2\text{CH}_2\text{OH}
\]

Hydroxyethyl terephthalic acid (HTPA or Q\text{,})

\[
\text{HOCH}_2\text{CH}_2\text{OOC} \-
\text{O} \-
\text{COOH}
\]

Methyl-hydroxyethyl terephthalate (MHET or R\text{,})

\[
\text{H}_3\text{COOC} \-
\text{O} \-
\text{COOCH}_2\text{CH}_2\text{OH}
\]

Methyl terephthalic acid (MTPA or T\text{,})

\[
\text{H}_3\text{COOC} \-
\text{O} \-
\text{COOH}
\]
Modeling Equations

Unlike most of the other works on the modeling of the transesterification stage [Ravindranath and Mashelkar (1981, 1982(a), 1982(b))], the catalyst concentration in the reactor has not been incorporated into the frequency factor of the rate constant and its effect on the reactor states will be considered independently. The material balances for each species and the energy balance take the following form:

Material balances:

\[ V \frac{dD}{dt'} = D_{o}q_{o} - D_{q_{1}} - k_{1}VC_{cat}DG \]  \hspace{2cm} (5)

\[ V \frac{dG}{dt'} = G_{o}q_{o} - G_{q_{1}} - k_{1}VC_{cat}G - (k_{2} + k_{3})VC_{cat}R_{1}G - k_{3}VC_{cat}P_{1}G \]  \hspace{2cm} (6)

\[ V \frac{dG_{D}}{dt'} = G_{D_{o}}q_{o} - G_{D_{q_{1}}} + k_{3}VC_{cat}G(R_{1} + P_{1}) \]  \hspace{2cm} (7)

\[ V \frac{dR_{1}}{dt'} = R_{1_{o}}q_{o} + k_{1}VC_{cat}DG - (k_{2} + k_{3})VC_{cat}R_{1}G \]  \hspace{2cm} (8)

\[ V \frac{dP_{1}}{dt'} = P_{1_{o}}q_{o} - P_{1_{q_{1}}} + k_{2}VC_{cat}R_{1}G - k_{3}VC_{cat}P_{1}G \]  \hspace{2cm} (9)

\[ V \frac{dQ_{1}}{dt'} = Q_{1_{o}}q_{o} - Q_{1_{q_{1}}} + k_{3}VC_{cat}P_{1}G \]  \hspace{2cm} (10)

\[ V \frac{dT_{1}}{dt'} = T_{1_{o}}q_{o} - T_{1_{q_{1}}} + k_{3}VC_{cat}R_{1}G \]  \hspace{2cm} (11)

\[ V \frac{dC_{cat}}{dt'} = C_{cat_{o}}q_{o} - C_{cat_{q_{1}}} \]  \hspace{2cm} (12)

Energy balance:

\[ \rho C_{p}V \frac{dT}{dt'} = \rho_{o}C_{p_{o}}(T_{o} - T_{r}) - \rho_{1}C_{p_{q_{1}}}(T - T_{r}) - U_{o}A_{e}(T - T_{h}) \]
\[ - V [k_{1}C_{cat}DG\Delta H_{1} + k_{2}C_{cat}R_{1}G\Delta H_{2} + k_{3}C_{cat}R_{1}G\Delta H_{3} + k_{3}C_{cat}P_{1}G\Delta H_{4}] \]
\[ - V [\Delta H_{v}(T_{r}) + C_{p_{m_{r}}}(T - T_{r})][k_{1}C_{cat}DG + k_{2}C_{cat}R_{1}G] \]
Since the reactor is operated at constant reactor volume, the following equation is valid for the effluent stream flow rate which is subject to vary according to the methanol vapor removal rate:

\[
q_1 = q_0 - \hat{V}_M (k_1 VC_{cat} DG + k_2 VC_{cat} R_1 C) \tag{14}
\]

where \(\hat{V}_M\) denotes the molar volume of methanol.

It is convenient to put the transesterification modeling equations (5)-(14) into dimensionless form. For this purpose, the dimensionless variables and parameters defined in Table 2 were substituted into the material and energy balances, resulting in the following dimensionless dynamic modeling equations:

\[
\frac{dx_1}{dt} = -1 + q(1 - x_1) + x_2 Dar_1(1 - x_1)(1 - x_2)(1 - x_8) \exp \left[ \frac{R x_9}{1 + x_9/T} \right] \tag{15}
\]

\[
\frac{dx_2}{dt} = -1 + q(1 - x_2) + Dar_1(1 - x_1)(1 - x_2)(1 - x_8) \exp \left[ \frac{R x_9}{1 + x_9/T} \right] + Dar_2(1 - x_2)x_4(1 - x_8) \exp \left[ \frac{R x_9}{1 + x_9/T} \right] + Da(1 - x_2)x_5(1 - x_8) \exp \left[ \frac{R x_9}{1 + x_9/T} \right] \tag{16}
\]

\[
\frac{dx_3}{dt} = z_3 - qx_3 + x_2 Da(1 - x_2)(x_4 + x_5)(1 - x_8) \exp \left[ \frac{R x_9}{1 + x_9/T} \right] \tag{17}
\]

\[
\frac{dx_4}{dt} = z_4 - qx_4 + x_2 Dar_1(1 - x_1)(1 - x_2)(1 - x_8) \exp \left[ \frac{R x_9}{1 + x_9/T} \right] - x_2 Dar_2(1 - x_2)x_4(1 - x_8) \exp \left[ \frac{R x_9}{1 + x_9/T} \right] - x_2 Da(1 - x_2)x_4(1 - x_8) \exp \left[ \frac{R x_9}{1 + x_9/T} \right] \tag{18}
\]
\[
\frac{dx_5}{dt} = z_5 - qx_5 + z_2 Da(1 - x_2) x_4 (1 - x_8) \exp \left[ \frac{E_2 x_9}{1 + x_9 / \Gamma} \right] \\
- z_2 Da(1 - x_2) x_5 (1 - x_8) \exp \left[ \frac{x_9}{1 + x_9 / \Gamma} \right]
\] (19)

\[
\frac{dx_6}{dt} = z_6 - qx_6 + z_2 Da(1 - x_2) x_5 (1 - x_8) \exp \left[ \frac{x_9}{1 + x_9 / \Gamma} \right]
\] (20)

\[
\frac{dx_7}{dt} = z_7 - qx_7 + z_2 Da(1 - x_2) x_4 (1 - x_8) \exp \left[ \frac{x_9}{1 + x_9 / \Gamma} \right]
\] (21)

\[
\frac{dx_8}{dt} = -1 + q (1 - x_8)
\] (22)

\[
\frac{dx_9}{dt} = y_4 (y_1 + y_7) - y_6 q (x_9 + y_7) - B_1 Da r_1 (1 - z_1)(1 - x_2)(1 - x_8) \exp \left[ \frac{E_1 x_9}{1 + x_9 / \Gamma} \right] \\
- B_2 Da r_2 (1 - x_2) x_4 (1 - x_8) \exp \left[ \frac{E_2 x_9}{1 + x_9 / \Gamma} \right] - B_3 Da (1 - x_2) x_4 (1 - x_8) \exp \left[ \frac{x_9}{1 + x_9 / \Gamma} \right]
- B_4 Da (1 - x_2) x_5 (1 - x_8) \exp \left[ \frac{x_9}{1 + x_9 / \Gamma} \right] - \beta (x_9 - y_2)
- \left( B_6 + y_6 (x_9 + y_2) \left( Da r_1 (1 - z_1)(1 - x_2)(1 - x_8) \exp \left[ \frac{E_1 x_9}{1 + x_9 / \Gamma} \right] \right. \\
+ Da r_2 (1 - x_2) x_4 (1 - x_8) \exp \left[ \frac{E_2 x_9}{1 + x_9 / \Gamma} \right] \right)
\] (23)

where

\[
q = 1 - y_3 Da r_1 (1 - z_1)(1 - x_2)(1 - x_8) \exp \left[ \frac{E_1 x_9}{1 + x_9 / \Gamma} \right] \\
- y_3 Da r_2 (1 - x_2) x_4 (1 - x_8) \exp \left[ \frac{E_2 x_9}{1 + x_9 / \Gamma} \right]
\] (24)
Table 2: Dimensionless parameters.

\[ x_1 = \frac{D_o - D}{D_o} \quad x_2 = \frac{G_o - G}{G_o} \quad x_3 = \frac{G_o}{D_o} \]
\[ x_4 = \frac{\eta_x}{D_o} \quad x_5 = \frac{\eta_x}{D_o} \quad x_6 = \frac{G_1}{G_o} \]
\[ x_7 = \frac{T_k}{D_o} \quad x_8 = \frac{C_{cat} - C_{cat}}{C_{cat}} \quad x_9 = \frac{(T - T_k)\Gamma}{T_k} \]
\[ y_1 = \frac{(T_o - T_k)\Gamma}{T_k} \quad y_2 = \frac{(T_k - T_o)\Gamma}{T_k} \quad y_3 = G_o \hat{V}_M \]
\[ y_4 = \frac{\rho_o}{\rho} \quad y_5 = \frac{\rho_1}{\rho} \quad y_6 = \frac{C_{pM2}G_o}{\rho G_p} \]
\[ y_7 = \frac{(T_k - T_o)\Gamma}{T_k} \]

\[ z_2 = \frac{G_o}{D_o} \quad z_3 = \frac{G_{D_o}}{D_o} \quad z_4 = \frac{R_{1e}}{D_o} \]
\[ z_5 = \frac{P_{1e}}{D_o} \quad z_6 = \frac{Q_{1e}}{D_o} \quad z_7 = \frac{T_{1e}}{D_o} \]

\[ B_1 = \frac{\Delta H_1 G_o \Gamma}{\rho C_p T_k} \quad B_2 = \frac{\Delta H_2 G_o \Gamma}{\rho C_p T_k} \quad B_3 = \frac{\Delta H_3 G_o \Gamma}{\rho C_p T_k} \]
\[ B_4 = \frac{\Delta H_4 G_o \Gamma}{\rho C_p T_k} \quad B_6 = \frac{\Delta H_5 (T_k) G_o \Gamma}{\rho C_p T_k} \quad D_a = k_o (T_k) \theta D_o C_{cat} \]

\[ r_1 = \frac{k_1(T_k)}{k_1(T_k)} \quad r_2 = \frac{k_2(T_k)}{k_2(T_k)} \quad t = t' \theta \]

Greek letters:

\[ \Gamma = \frac{E_2}{E_3} \quad \Gamma = \frac{E_1}{E_3} \quad \Gamma = \frac{E_2}{E_3} \]
\[ \theta = \frac{\varphi}{\varphi_o} \quad \beta = \frac{U_g \Delta x}{\rho C_p \varphi_o} \]
Implicit assumptions in the model include perfect backmixing and constant physical properties within the temperature range of interest.

All the measurements whether on-line or off-line are assumed to contain random noise (i.e., zero mean and uncorrelated in time). If on-line measurements are made, then the measured quantities will be the amount of methanol produced per unit time and the reactor temperature. In dimensionless form these take the following form ($y_{mi}$ signifies a measured variable),

\begin{equation}
    y_{m1} = y_3 D \alpha_1 (1-x_1)(1-x_2)(1-x_8) \exp \left[ \frac{\pi z_0}{1 + \frac{z_0}{r}} \right] + y_3 D \alpha_2 (1-x_2) z_4 (1-x_8) \exp \left[ \frac{\beta z_0}{1 + \frac{z_0}{r}} \right]
\end{equation}

\begin{equation}
    \text{Reaction temperature: } y_{m2} = z_0 + 1
\end{equation}

Note that the methanol flow rate ($y_{m1}$) reflects the variations in five state variables. If, in addition, the on-line measurements are supplemented with off-line analysis (i.e., delayed laboratory analysis), then more information about the actual reactor states may be ascertained. The experimental procedures required for determining the concentrations of the various species involved in the transesterification reactions are well described by Yamada et al. (1986). A mathematical adaption of these off-line measurements in dimensionless form is

\begin{equation}
    y_{m3} = 1 - x_2
\end{equation}

\begin{equation}
    y_{m4} = x_3
\end{equation}

\begin{equation}
    y_{m5} = x_6 + x_7
\end{equation}

\begin{equation}
    y_{m6} = x_4 + 2x_5 + x_6
\end{equation}

\begin{equation}
    y_{m7} = 2(1-x_1) + 2x_4 + 2x_5 + x_6 + x_7
\end{equation}
where \( y_{m3} \) = free EG concentration in the reaction mixture, \( y_{m4} \) = DEG concentration, \( y_{m5} \) = carboxyl end group concentration, \( y_{m6} \) = hydroxyl end group concentration, and \( y_{m7} \) = saponification value. Note that we can have up to seven process variable measurements (i.e. two on-line measurements and five off-line measurements) for nine state variables.

The system of modeling equations described above may then be condensed down to the following form in compact vector notation

\[
\begin{align*}
\mathbf{x} &= \mathbf{f}(\mathbf{x},t) \quad (32) \\
y_m &= \mathbf{h}(\mathbf{x},t) \quad (33)
\end{align*}
\]

where \( \mathbf{x} \) is the nine state vector, \( \mathbf{f} \) the system state model, \( y_m \) the measurement vector (largest dimension is seven) and \( \mathbf{h} \) the system measurement model given by eqs. (25) and (26) on a semi-continuous basis and by eqs. (27)-(31) on a discrete basis.

The Extended Kalman Filter

Although the use of optimal or suboptimal state estimation techniques to reconstruct the unknown system states has become standard practice, especially in the fields of electrical and aeronautical engineering, Kalman and Bucy laid the theoretical groundwork for finite-time optimal filtering for linear systems with random white noise not more than thirty years ago [Kalman (1960), Kalman and Bucy (1961)]. Their research was subsequently extended to nonlinear systems and is now contained in pertinent references [Jazwinski (1970), Sage and Melsa (1971), Gelb (1974), Ray (1981)]. Since most chemical processes are nonlinear in nature, this section concerns the development of the discrete
extended Kalman filter.

In general, the filter equations specify an optimal estimate of the states of a dynamic system observed sequentially in the presence of white noise (zero-mean and uncorrelated in time). The estimate obtained at each time is the least square estimate of each state. The system and observation models are given by

$$ \dot{x}(t) = f[x(t), t] + w(t) $$
$$ y_m(t) = h[x(t), t] + y(t) $$

with initial state estimates

$$ x(0) = x_0 + w_0 $$

where $x(t)$ is the $n$-dimensional state vector, $f(x, t)$ is the $n$-dimensional vector-valued function, $y_m(t)$ is the $m$-dimensional observation vector, $w(t)$ is the $n$-dimensional plant-noise vector, and $y(t)$ is the $m$-dimensional observation-noise vector. The vectors $w$ and $y$ are zero-mean white Gaussian noise processes assumed to be independent of each other. The discrete formulation of the process model is given by

$$\begin{align*}
x(t_{k+1}) &= F[x(t_k), t_k] + w(t_k) 
y_m(t_k) &= h[x(t_k), t_k] + y(t_k)
\end{align*} \tag{37.a,b}
$$

where $F[x(t_k), t_k] = x(t_k) + \int_{t_k}^{t_{k+1}} f[x(t), t] \, dt$ \tag{38}

The extended Kalman filter determines the state estimate that minimizes the following least square objective function,

$$ I = \frac{1}{2} x^T P_0^{-1} x + \frac{1}{2} \Delta t \sum_{j=0}^{k} (y^T P^{-1} y + y^T Q^{-1} y) $$ \tag{39}
where $\Delta t$ is the sampling interval and the following deviation variables are used:

$$
\mathbf{X} = [x(0) - \mathbf{x}_o]
$$

$$
\mathbf{Y} = [y(t_j) - h(x(t_j), t_j)]
$$

$$
\mathbf{W} = [x(t_{j+1}) - \mathbf{F}(x(t_j), t_j)]
$$

The weighting matrices $\mathbf{P}_{x_o}^{-1}$, $\mathbf{R}^{-1}$ and $\mathbf{Q}^{-1}$ are chosen to reflect the errors in the initial state estimate, the plant model, and the measuring device. Thus the expected value relations are

$$
\mathcal{E}[w(t_k)] = 0 \\
\mathcal{E}[y(t_k)] = 0 \\
\mathcal{E}[x(0)] = \mathbf{x}_o \\
\mathcal{E}[w(t_k)x^T(0)] = \mathbf{0} \\
\mathcal{E}[v(t_k)x^T(0)] = \mathbf{0} \\
\mathcal{E}[w(t_k)v^T(t_k)] = \mathbf{0} \\
\mathcal{E}[(x_o - \mathbf{x}(0))(x_o - \mathbf{x}(0))^T] = \mathbf{P}_{x_o} \\
\mathcal{E}[w(t_k)w^T(t_j)] = \mathbf{R}(t_k)\delta_{jk} \\
\mathcal{E}[v(t_k)v^T(t_j)] = \mathbf{Q}(t_k)\delta_{jk}
$$

where $\delta_{jk}$ is the Kronecker delta function, $\mathbf{P}_{x_o}$ is the covariance matrix of the initial state errors, $\mathbf{R}$ is the covariance matrix of the plant noise, and $\mathbf{Q}$ is the covariance matrix of the measurement noise. The extended Kalman filter is then represented, according to Jazwinski (1970), by the recursive relations as follows:
Filter:

\[
\mathbf{\tilde{x}}(t_{k+1}|t_{k+1}) = \mathbf{\tilde{x}}(t_{k+1}|t_k) + \mathbf{K} [t_{k+1}, \mathbf{\tilde{x}}(t_{k+1}|t_k)] \left[ \mathbf{y}_m(t_{k+1}) - \mathbf{h}[t_{k+1}, \mathbf{\tilde{x}}(t_{k+1}|t_k)] \right]
\]

(42)

One-stage prediction:

\[
\mathbf{\tilde{x}}(t_{k+1}|t_k) = \mathbf{\tilde{x}}(t_k|t_k) + \int_{t_k}^{t_{k+1}} \mathbf{f}[\mathbf{\tilde{x}}(t|t_k), t] \, dt
\]

(43)

Kalman filter gain:

\[
\mathbf{K}[t_{k+1}, \mathbf{\tilde{x}}(t_{k+1}|t_k)] = \mathbf{P}(t_{k+1}|t_k) \mathbf{M}^T [t_{k+1}, \mathbf{\tilde{x}}(t_{k+1}|t_k)] \left[ \mathbf{M}[t_{k+1}, \mathbf{\tilde{x}}(t_{k+1}|t_k)] \mathbf{P}(t_{k+1}|t_k) \right]^{-1}
\]

(44)

Prior error-variance:

\[
\mathbf{P}(t_{k+1}|t_k) = \mathbf{Q}[t_{k+1}, t_k; \mathbf{\tilde{x}}(t_k|t_k)] \mathbf{P}(t_k|t_k) \mathbf{P}^T [t_{k+1}, t_k; \mathbf{\tilde{x}}(t_k|t_k)] + \mathbf{R}(t_{k+1})
\]

(45)

Error-variance:

\[
\mathbf{P}(t_{k+1}|t_k) = \left[ \mathbf{I} - \mathbf{K}[t_{k+1}, \mathbf{\tilde{x}}(t_{k+1}|t_k)] \mathbf{M}[t_{k+1}, \mathbf{\tilde{x}}(t_{k+1}|t_k)] \right] \mathbf{P}(t_{k+1}|t_k)
\]

\[
\times \left[ \mathbf{I} - \mathbf{K}[t_{k+1}, \mathbf{\tilde{x}}(t_{k+1}|t_k)] \mathbf{M}[t_{k+1}, \mathbf{\tilde{x}}(t_{k+1}|t_k)] \right]^T
\]

\[
+ \mathbf{K}[t_{k+1}, \mathbf{\tilde{x}}(t_{k+1}|t_k)] \mathbf{Q}(t_{k+1}) \mathbf{K}^T [t_{k+1}, \mathbf{\tilde{x}}(t_{k+1}|t_k)]
\]

(46)

Initial conditions:

\[
\mathbf{\tilde{x}}(t_0|t_0) = \mathbf{\tilde{x}}_0 \quad \mathbf{P}(t_0|t_0) = \mathbf{P}_0
\]

(47)

where

\[
\mathbf{Q} = \mathbf{J}_f(t_{k+1} - t_k) + \mathbf{I}
\]

\[
\mathbf{M} = \mathbf{J}_h
\]

(48)
The "a priori" estimate, \( x(t_k | t_k) \), and initial state error covariance, \( P_{x_0} \), are used as initial conditions for these recursive equations. Note that the integral in eq. (43) may be evaluated by a number of methods. In this paper, Euler's method is used. \( J_f \) and \( J_h \) denote Jacobian matrices for the state and measurement model equations, respectively.

Wells (1971) and Sage and Melsa (1971) have discussed the impact of filter tuning parameters on the dynamic response of the filter. The initial state estimate and the initial covariance, \( x(t_0 | t_0) \) and \( P_{x_0} \), respectively determine the speed of response of the filter. Depending on how much \( x(t_0 | t_0) \) deviates from \( x_0 \) and how large \( P_{x_0} \) is, the time required to reach steady state estimates will increase. The \( R \) matrix, containing modeling error covariances, should be large for systems which have dynamics that are not well understood; this has the effect of increasing the steady state error. The measurement error covariance, \( Q \), is set by the measuring devices; however, in cases where \( Q \) is time dependent, it has the opposite effect of \( R \). The Jacobian matrices \( J_f \) and \( J_h \) are obtained from the first terms of linearized functions \( f \) and \( h \) using a Taylor series expansion about the current state estimate. Thus, the Jacobian \( J_f \) is given by

\[
J_f = \begin{pmatrix}
  f_{11} & f_{12} & 0 & f_{14} & 0 & 0 & 0 & f_{18} & f_{19} \\
  f_{21} & f_{22} & 0 & f_{24} & f_{25} & 0 & 0 & f_{28} & f_{29} \\
  f_{31} & f_{32} & f_{33} & f_{34} & f_{35} & 0 & 0 & f_{38} & f_{39} \\
  f_{41} & f_{42} & 0 & f_{44} & 0 & 0 & 0 & f_{48} & f_{49} \\
  f_{51} & f_{52} & 0 & f_{54} & f_{55} & 0 & 0 & f_{58} & f_{59} \\
  f_{61} & f_{62} & 0 & f_{64} & f_{65} & f_{66} & 0 & f_{68} & f_{69} \\
  f_{71} & f_{72} & 0 & f_{74} & 0 & 0 & f_{77} & f_{78} & f_{79} \\
  f_{81} & f_{82} & 0 & f_{84} & 0 & 0 & 0 & f_{88} & f_{89} \\
  f_{91} & f_{92} & 0 & f_{94} & f_{95} & 0 & 0 & f_{98} & f_{99}
\end{pmatrix}
\]
When only two on-line measurements (methanol evolution rate and temperature) are made, the Jacobian of the measurements equations \( J_h \) is

\[
J_h = \begin{pmatrix}
  h_{11} & h_{12} & 0 & h_{14} & 0 & 0 & 0 & h_{18} & h_{19} \\
  0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1
\end{pmatrix}
\] (50)

Note that the methanol evolution rate measurement \( y_{m1} \) is a function of five state variables. In the case where five off-line measurements are also included, the measurement Jacobian takes on a very simple form

\[
J_h = \begin{pmatrix}
  h_{11} & h_{12} & 0 & h_{14} & 0 & 0 & 0 & h_{18} & h_{19} \\
  0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \\
  0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
  0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \\
  0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
  -2 & 0 & 0 & 2 & 2 & 1 & 1 & 0 & 0
\end{pmatrix}
\] (51)

The \( f_{ij} \) and \( h_{ij} \) for \( J_f \) and \( J_h \) are given in Khan (1986).

**Observability**

In any state estimation scheme, the question of observability must be answered first. According to Ray (1981), a system is completely observable if it is possible to determine all the state variables at some time \( t_o \) based on a knowledge of the system output \( y_m(t) \) and control \( u(t) \) over some finite interval. It is impossible to design a state estimation algorithm for a system which is not observable. It can be shown that a discrete system is completely observable on \([t_o, t_f]\) if the symmetric Gramian matrix, defined by

\[
\mathcal{M}(k_o, k_f) = \sum_{k=k_o}^{k_f} \mathcal{C}^T(k, k_o) \mathcal{M}^T(k) \mathcal{M}(k) \mathcal{C}(k, k_o)
\] (52)
is positive definite or nonsingular. For constant-coefficient systems, it can be shown [Kalman (1960)] that a discrete constant system is completely observable if and only if the rank of the observability matrix $L_0$ is $n$ ($n$ is the number of states),

$$L_0 = \left[ M^T (\Phi M)^T (\Phi M) M^T \ldots (\Phi M)^{n-1} M^T \right]$$

(53)

where $M$ and $\Phi$ have been defined in eq. (48). For a continuous stirred tank reactor (CSTR), $\Phi$ and $M$ are both constant at steady state; thus it is possible to use the observability matrix as it is defined above. In the present case, $n = 9$, and the rank of $L_0$ for the transesterification reactor model as proposed is indeed 9 when two on-line measurements and five off-line measurements are available (the determination of the rank of $L_0$ is given in more detail in Khan (1986)). Note that five off-line measurements are EG concentration, DEG concentration and three functional end group concentrations. With those five additional measurements, the dynamic system consisting of nine state variables is completely observable. Without those five off-line measurements and with only two on-line measurements of methanol evolution rate and temperature, the system is clearly not observable.

**Process Parameters**

In order to simulate the transesterification reactor model here as closely as possible to industrial reactors, the parameters listed in Table 3 have been chosen to reflect actual operating and physical conditions. The main operating variables
Table 3: Numerical values of physical constants and parameters.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>$8.8513 \times 10^9$</td>
<td>$\frac{L^2}{mol^2\text{hr}}$</td>
<td>[1]*</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$6.0531 \times 10^9$</td>
<td>$\frac{L^2}{mol^2\text{hr}}$</td>
<td>[1]</td>
</tr>
<tr>
<td>$A_3$</td>
<td>$1.3020 \times 10^{11}$</td>
<td>$\frac{L^2}{mol^2\text{hr}}$</td>
<td>[2]</td>
</tr>
<tr>
<td>$A_c$</td>
<td>$574.0$</td>
<td>$\text{cm}^2$</td>
<td></td>
</tr>
<tr>
<td>$C_p$</td>
<td>$0.245$</td>
<td>$\frac{\text{cal}}{g\cdot K}$</td>
<td>[3]</td>
</tr>
<tr>
<td>$C_{pMv}$</td>
<td>$12.60$</td>
<td>$\frac{\text{cal}}{\text{mol} \cdot K}$</td>
<td>[3]</td>
</tr>
<tr>
<td>$E_1$</td>
<td>$14340.0$</td>
<td>$\frac{\text{cal}}{\text{mol}}$</td>
<td>[1]</td>
</tr>
<tr>
<td>$E_2$</td>
<td>$14784.0$</td>
<td>$\frac{\text{cal}}{\text{mol}}$</td>
<td>[1]</td>
</tr>
<tr>
<td>$E_3$</td>
<td>$29800.0$</td>
<td>$\frac{\text{cal}}{\text{mol}}$</td>
<td>[2]</td>
</tr>
<tr>
<td>$\Delta H_1$</td>
<td>$1400.0$</td>
<td>$\frac{\text{cal}}{\text{mol}}$</td>
<td>[4]</td>
</tr>
<tr>
<td>$\Delta H_2$</td>
<td>$1400.0$</td>
<td>$\frac{\text{cal}}{\text{mol}}$</td>
<td>[4]</td>
</tr>
<tr>
<td>$\Delta H_3$</td>
<td>$0.0$</td>
<td>$\frac{\text{cal}}{\text{mol}}$</td>
<td>[4]</td>
</tr>
<tr>
<td>$\Delta H_4$</td>
<td>$0.0$</td>
<td>$\frac{\text{cal}}{\text{mol}}$</td>
<td>[4]</td>
</tr>
<tr>
<td>$\Delta H_v$</td>
<td>$8936.0$</td>
<td>$\frac{\text{cal}}{\text{mol}}$</td>
<td>[3]</td>
</tr>
<tr>
<td>$T_k$</td>
<td>$450.0$</td>
<td>$^\circ \text{K}$</td>
<td></td>
</tr>
<tr>
<td>$T_r$</td>
<td>$298.15$</td>
<td>$^\circ \text{K}$</td>
<td></td>
</tr>
<tr>
<td>$U_o$</td>
<td>$10.0$</td>
<td>$\frac{\text{cal}}{\text{cm}^2 \text{hr} \cdot \text{K}}$</td>
<td>[3]</td>
</tr>
<tr>
<td>$V_M$</td>
<td>$0.05363$</td>
<td>$\frac{L}{\text{mol}}$</td>
<td>[3]</td>
</tr>
<tr>
<td>$\rho$</td>
<td>$1.11$</td>
<td>$\frac{g}{\text{cm}^3}$</td>
<td></td>
</tr>
<tr>
<td>$\rho_1$</td>
<td>$1.11$</td>
<td>$\frac{g}{\text{cm}^3}$</td>
<td></td>
</tr>
<tr>
<td>$\rho_D$</td>
<td>$1.088$</td>
<td>$\frac{g}{\text{cm}^3}$</td>
<td>[5]</td>
</tr>
</tbody>
</table>

would include the inlet EG/DMT ratio, residence time (or inlet flow rate), inlet catalyst concentration, and heating medium temperature. With respect to these four variables, the base case chosen is

Reactor Volume: 1.0 L
EG/DMT Mole Ratio: 1.6
Residence Time: 3 hr
Inlet Catalyst Concentration: $1.08 \times 10^{-3}$ mol/L
Heating Medium Temperature: 180°C

Variations thereof shall be introduced to ascertain the effect of each variable on the reactor states. For the purpose of simulating measurement noise, the standard deviation of the measurement devices are required. For a type J thermocouple (iron-constantan) a 1.2°C deviation in the temperature range of interest here (160-240°C) is typical [Omega Handbook, 1984]. The standard deviation of the condensate measurement was taken to be approximately 10mL/hr. For the off-line measurements, the measured concentrations were assumed to fall within five percent of the actual concentrations. In dimensionless form, the standard deviations for all the measurements (two on-line measurements and five off-line measurements) become

\[
\begin{align*}
\sigma_1 &= 0.03 \\
\sigma_2 &= 0.09 \\
\sigma_3 &= 0.02 \\
\sigma_4 &= 0.0004 \\
\sigma_5 &= 0.0004 \\
\sigma_6 &= 0.043 \\
\sigma_7 &= 0.06
\end{align*}
\]
The dynamic modeling equations were solved deterministically using the fourth order Runge-Kutta method to generate the true process state trajectory. The initial conditions for all the state variables came from the appropriate steady state profiles. On-line measurements (methanol flow rate and temperature) were made at a rate of once every 0.005 dimensionless time increments (about 1 minute in real time for the base case; more frequently for cases involving shorter residence times). The initial conditions of the estimator were deliberately chosen as poor initial state estimates of the actual system states. When five off-line measurements were incorporated, it was assumed that laboratory sample analysis results were returned 24 hours after the sampling. When the results of the off-line product analysis were made available, the filtering estimates were recomputed starting at the time the sample was actually taken. In order to model white noise in the measurements, a pseudo-random number generator was used to corrupt the actual measured value (obtained from the solution to the dynamic state equations) with a small perturbation. The perturbation was assumed to fall within three standard deviations of the actual measurement. Therefore, the noise-corrupted trajectory then modeled the real process. As a final precaution the error covariance matrix was made symmetric at every time step according to the recommendation of Nahi (1976):

\[
P_k = \frac{1}{2} (P_k^T + P_k)
\]

(55)

Note that \( P(t_k \) should always be symmetric but computer round-off error prevents it from being exactly so all the time.
In addition to the measurement covariance matrix \( Q \) and the initial values of the state estimates, \( \hat{x}(t_0 | t_0) \), the extended Kalman filter requires certain tuning parameters in the form of the initial error covariance matrix \( P_{\equiv 0} \) and the covariance matrix of the process noise \( R \). The measurement covariance matrix simply contains the variances of the measuring instruments along the diagonal. For the case of semicontinuous on-line measurements of methanol evolution rate and temperature, it takes on the form

\[
Q = \begin{pmatrix}
0.0009 & 0 \\
0 & 0.0081
\end{pmatrix}
\]  

(56)

When additional off-line measurements are also made the measurement covariance matrix takes the following form:

\[
Q = \begin{pmatrix}
0.0009 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0.0081 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0.0004 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1.6 \times 10^{-7} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1.6 \times 10^{-7} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0.0018 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0.0924
\end{pmatrix}
\]  

(57)

The values for the diagonal covariance matrices \( P_{\equiv 0} \) and \( R \) were found more or less by trial and error; choices for these two matricies had a substantial impact on the results generated. Note that \( R \) and \( Q \) may both be variable with time [Wells (1971)], but in this study, they were assumed constant.
DMT) in the transesterification product has an enormous impact on the molecular weight of polyesters to be produced in the second stage (e.g. the presence of methylester groups in the prepolycondensation stage decreases the polymer molecular weight significantly [Ault and Mellichamp, 1972]). The initial covariances (P_ii and R_{ii}) used in this simulation correspond to the case with relatively large modeling error. As expected the prediction of concentration parameters as shown in Figure 2 is not quite satisfactory. In particular, the estimation of DEG and MHET concentrations are very poor. This is because those state variables are only detectable when two on-line measurements (temperature and methanol flow rate) are all that is available.

**Case 2.** When the two on-line measurements (temperature and methanol flow rate) are supplemented by five additional off-line measurements of functional group concentrations, the system is completely observable and the filter performance is significantly improved. Figure 3 shows the filter response to the same step disturbance as in Figure 2. Although 24 hours of measurement delay (indicated by the solid black dots) exists, fast filter convergence is observed and the estimation of the reactor states is excellent [Such a measurement delay (i.e. 24 hrs) is quite realistic from a practical point of view (Yamada et al., 1986)].

Similar simulations were conducted for a step disturbance in the feed EG/DMT mole ratio from 1.6 to 2.0. Figures 4 and 5 show the reactor transients without and with five additional off-line measurements, respectively. Again, excellent filter performance
RESULTS

The simulation of the melt transesterification reactor model incorporating the extended Kalman filter was carried out for the following cases in which step changes in the operating conditions were introduced:

Case 1: With two on-line measurements only.

\[ P_{ii}(0) = 10^{-8} \text{ for } i = 1, 2, \ldots, 9 \]

\[ R_{ii} = 10^{-4} \text{ for } i = 1, 2, \ldots, 9 \]

Case 2: Same as Case 1 but with 5 additional off-line measurements (delay time = 24 hrs).

The filter starting point in all cases was

DMT Conversion: 0.5

EG Conversion: 0.5

\[ \text{[DEC]} = 0.0 \text{ mol/L, [MHET]} = 0.5 \text{ mol/L,} \]

\[ \text{[BHET]} = 0.5 \text{ mol/L, [HTPA]} = 0.0 \text{ mol/L,} \]

\[ \text{[MTPA]} = 0.0 \text{ mol/L, [C_{cat}]} = 1.08 \times 10^{-3} \text{ mol/L} \]

Reactor temperature = 180°C

Case 1. Figure 2 shows the transient response along with the nonlinear state estimate of the transesterification reactor to a step change in heating medium temperature with only two on-line measurements \((y_{m1} \text{ and } y_{m2})\) and no off-line concentration measurements. The reactor is operated at steady state prior to the step change. Here the solid lines represent the true states and the dotted lines the filter response. Of the nine state variables, DMT conversion, EG conversion, DEG concentration, and MHET concentration are the most important and their transients are shown in Figure 2. The concentration of MHET (half-esterfied
Figure 2: (Case 1) Filter response to step change in heating medium temperature from 180°C to 200°C with only two on-line measurements.
Figure 3: (Case 2) Filter response to step change in heating medium temperature from 180°C to 200°C with two on-line measurements and five off-line measurements.
Figure 4: (Case 1) Filter response to step change in feed EG/DMT mole ratio from 1.6 to 2.0 with only two on-line measurements.
Figure 5: (Case 2) Filter response to step change in feed EG/DMT mole ratio from 1.6 to 2.0 with two on-line measurements and five off-line measurements.
is observed with five additional delayed off-line measurements. It is also interesting to note that increasing the EG/DMT ratio resulted in a significant increase in DEG concentration.

The extended Kalman filter is further capable of accommodating pulse disturbances in reactor operating conditions. Figures 6 and 7 illustrate the filter response to a six hour pulse in the feed EG/DMT molar ratio with only two on-line measurements and with five additional off-line measurements, respectively. Note that the filter estimates rapidly converge to true values with initial filter parameters chosen and that once the state estimator converges to the true solution, variations in the state variables afterward can be predicted satisfactorily for pulse disturbance when the system is completely observable. In other words, the extended Kalman filter indeed provides accurate estimates of unmeasured variables between the off-line measurements.
Figure 6: Filter response to a six hour pulse in feed EG/DMT mole ratio with only on-line measurements.
Figure 7: Filter response to a six hour pulse in feed EG/DMT mole ratio with two on-line measurements and five off-line measurements.
CONCLUDING REMARKS

A nonisothermal dynamic model for the melt transesterification of DMT with EG has been developed. The model accounts for the variable reactor effluent flow due to the continuous removal of transesterification condensate (methanol) and further incorporates the formation of diethylene glycol which is the major unwanted reaction side product. The extended Kalman filter was used to reconstruct the state variables with a limited number of on-line measurements and delayed laboratory off-line analysis. The reactor system consisting of nine state variables is completely observable when two on-line measurements (methanol flow rate and temperature) and five off-line measurements including EG concentration, DEG concentration and various functional end group concentrations are made. Although relatively large modeling errors were introduced in the simulation runs, the performance of the filter was greatly improved when on-line measurements were supplemented with infrequent off-line analysis. This indicates that the control of side product formation may be effectively achieved by integrating a state estimation algorithm with an appropriate reactor control strategy.
Acknowledgement

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Literature Cited


**NOTATION**

A<sub>1</sub> frequency factor for reaction 1, \(L^2\text{mol}^2/\text{hr}\)

A<sub>2</sub> frequency factor for reaction 2, \(L^2\text{mol}^2/\text{hr}\)

A<sub>3</sub> frequency factor for reactions 3 and 4, \(L^2\text{mol}^2/\text{hr}\)

A<sub>c</sub> heat transfer area, \(\text{cm}^2\)

B<sub>i</sub> dimensionless adiabatic temperature rise for reaction \(i\)

B<sub>v</sub> dimensionless heat of vaporization for methanol

C<sub>cat</sub> reactor catalyst concentration, \(\text{mol/L}\)

C<sub>cato</sub> feed catalyst concentration, \(\text{mol/L}\)

C<sub>p</sub> heat capacity of reaction mixture, \(\text{cal/g}^\circ\text{K}\)

C<sub>PMg</sub> molar heat capacity of methanol gas, \(\text{cal/gmol}^\circ\text{K}\)

D reactor DMT concentration, \(\text{mol/L}\)

D<sub>f</sub> feed DMT concentration, \(\text{mol/L}\)

D<sub>a</sub> Damkohler number

E<sub>1</sub> activation energy for reaction 1, \(\text{cal/gmol}\)

E<sub>2</sub> activation energy for reaction 2, \(\text{cal/gmol}\)

E<sub>3</sub> activation energy for reactions 3 and 4, \(\text{cal/gmol}\)

G reactor ethylene glycol concentration, \(\text{mol/L}\)

G<sub>f</sub> feed ethylene glycol concentration, \(\text{mol/L}\)

G<sub>D</sub> reactor diethylene glycol concentration, \(\text{mol/L}\)

G<sub>Df</sub> feed diethylene glycol concentration, \(\text{mol/L}\)

\(\Delta H_1\) heat of reaction 1 at \(T_r\), \(\text{cal/gmol}\)

\(\Delta H_2\) heat of reaction 2 at \(T_r\), \(\text{cal/gmol}\)

\(\Delta H_3\) heat of reaction 3 at \(T_r\), \(\text{cal/gmol}\)

\(\Delta H_4\) heat of reaction 4 at \(T_r\), \(\text{cal/gmol}\)

\(\Delta H_v\) heat of vaporization for methanol at \(T_r\), \(\text{cal/gmol}\)

k<sub>1</sub> reaction rate constant for reaction 1, \(L^2\text{mol}^2/\text{hr}\)

k<sub>2</sub> reaction rate constant for reaction 2, \(L^2\text{nk}^2/\text{hr}\)
\( k_3 \) reaction rate constant for reactions 3 and 4, \( L^2 \text{mol}^2/\text{hr} \)

\( M \) methanol concentration, \( \text{mol/L} \)

\( P_1 \) reactor BHET concentration, \( \text{mol/L} \)

\( P_{10} \) feed BHET concentration, \( \text{mol/L} \)

\( Q_1 \) reactor HTPA concentration, \( \text{mol/L} \)

\( Q_{10} \) feed HTPA concentration, \( \text{mol/L} \)

\( q \) dimensionless liquid exit flow

\( q_o \) feed flow rate, \( \text{L/hr} \)

\( q_1 \) exit liquid flow rate, \( \text{L/hr} \)

\( R \) gas constant, \( \text{cal/gmol/}^\circ\text{K} \)

\( R_1 \) reactor MHET concentration, \( \text{mol/L} \)

\( R_{10} \) feed MHET concentration, \( \text{mol/L} \)

\( r_1 \) ratio of reaction rate constants \( k_1 \) and \( k_3 \) at \( T_k \)

\( r_2 \) ratio of reaction rate constants \( k_2 \) and \( k_3 \) at \( T_k \)

\( T \) reactor temperature, \( ^\circ\text{K} \)

\( T_o \) feed temperature, \( ^\circ\text{K} \)

\( T_1 \) reactor MTPA concentration, \( \text{mol/L} \)

\( T_{10} \) feed MTPA concentration, \( \text{mol/L} \)

\( T_h \) heating medium temperature, \( ^\circ\text{K} \)

\( T_k \) non-dimensionalizing base temperature, \( ^\circ\text{K} \)

\( T_r \) reference temperature, \( ^\circ\text{K} \)

\( t^- \) time, hr

\( t \) dimensionless time

\( U_o \) overall heat transfer coefficient, \( \text{cal/cm}^2/\text{}^\circ\text{K/hr} \)

\( V \) reactor working volume, \( \text{L} \)

\( V_M \) molar volume of methanol in desired temperature range, \( \text{L/mol} \)

\( W_D \) molecular weight of DMT, \( \text{g/mol} \)
$W_c$  
molecular weight of EG, g/gmol  

$W_m$  
molecular weight of methanol, g/gmol  

$x_1$  
DMT conversion  

$x_2$  
EG conversion  

$x_3$  
dimensionless DEG concentration  

$x_4$  
dimensionless MHET concentration  

$x_5$  
dimensionless BHET concentration  

$x_6$  
dimensionless HTPA concentration  

$x_7$  
dimensionless MTPA concentration  

$x_8$  
catalyst conversion  

$x_9$  
dimensionless reactor temperature  

$y_1$  
dimensionless feed temperature  

$y_2$  
dimensionless heating medium temperature  

$y_3$  
dimensionless methanol molar volume  

$y_4$  
ratio of inlet to reactor densities  

$y_5$  
ratio of outlet to reactor densities  

$y_6$  
dimensionless methanol heat capacity  

$y_7$  
dimensionless reference temperature  

$z_2$  
feed EG/DMT ratio  

$z_3$  
dimensionless feed DEG concentration  

$z_4$  
dimensionless feed MHET concentration  

$z_5$  
dimensionless feed BHET concentration  

$z_6$  
dimensionless feed HTPA concentration  

$z_7$  
dimensionless feed MTPA concentration
Greek Letters

\( \beta \)  dimensionless heat transfer capability

\( \gamma \)  feed catalyst/DMT mole ratio

\( \rho \)  reaction mass density, g/L

\( \rho_0 \)  feed density, g/L

\( \rho_i \)  exit flow density, g/L

\( \Gamma \)  dimensionless activation energy

\( \Gamma_1 \)  ratio of activation energies \( E_1 \) and \( E_3 \)

\( \Gamma_2 \)  ratio of activation energies \( E_2 \) and \( E_3 \)

\( \sigma_i \)  standard deviation of measurement \( i \)

\( \theta \)  residence time, hr

Matrices and Vectors

\( f \)  n-dimensional state vector-valued function

\( h \)  m-dimensional observation vector

\( v \)  m-dimensional observation-noise vector

\( w \)  n-dimensional plant-noise vector

\( x \)  state vector

\( x_0 \)  initial value of state vector

\( \hat{x} \)  vector of state estimates

\( \hat{x}_0 \)  initial value vector for state estimates

\( y \)  m-dimensional observation vector

\( I \)  identity matrix

\( J_f \)  Jacobian matrix of state equations

\( J_h \)  Jacobian matrix of measurement equations

\( K \)  Kalman gain

\( L \)  observability matrix

\( M \)  Jacobian matrix of measurement equations

symmetric Gramian matrix
\[ P \]

covariance matrix

\[ P_0 \]

covariance matrix of initial state errors

\[ Q \]

covariance matrix of measurement noise

\[ R \]

covariance matrix of plant noise

state transition matrix
Figure Captions

Figure 1  Schematic diagram of continuous melt PET polymerization process.

Figure 2  (Case 1) Filter response to step change in heating medium temperature from 180°C to 200°C with only two on-line measurements (solid line; true state, dotted line; filter estimate).

Figure 3  (Case 2) Filter response to step change in heating medium temperature from 180°C to 200°C with two on-line measurements and five off-line measurements (solid line; true state, dotted line; filter estimate).

Figure 4  (Case 1) Filter response to step change in feed EG/DMT mole ratio from 1.6 to 2.0 with only two on-line measurements (solid line; true state, dotted line; filter estimate).

Figure 5  (Case 2) Filter response to step change in feed EG/DMT mole ratio from 1.6 to 2.0 with two on-line measurements and five off-line measurements (solid line; true state, dotted line; filter estimate).

Figure 6  Filter response to a six hour pulse in feed EG/DMT mole ratio from 1.6 to 2.0 with only two on-line measurements (solid line; true state, dotted line; filter estimate).

Figure 7  Filter response to a six hour pulse in feed EG/DMT mole ratio from 1.6 to 2.0 with two on-line measurements and five off-line measurements (solid line; true state, dotted line; filter estimate).