

EXPERIMENTAL STUDY OF BATCH ESTERIFICATION CONVERSION CONTROL USING CONDUCTANCE MEASUREMENT

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In batch reactor operation, a reliable method of knowing the reaction state on-line is an important requirement for quality regulation between batches and minimum batch cycle time. An on-line quality control scheme using conductance measurement of the reaction mixture is presented for a pre-defined optimized operation of a batch esterification reactor. Through a series of experimental studies, a semi-empirical equation for the conductance-conversion correlation is derived. Using this conductance measurement together with a reaction model, a cascade nonlinear control scheme for the batch esterification reactor is designed. Additionally, to solve the problem of model inaccuracies and uncertainties, the extended Kalman filter is applied for the reaction state estimation. Experimental studies have been conducted to illustrate the performance of the control scheme. The proposed approach shows better control performance than the commonly used temperature control approach in controlling the batch esterification reactor.

Introduction

Batch esterification reaction is an essential part of the manufacturing process for commercially important polyester resins. The success of this reaction depends mainly on the chosen profile of reaction temperature. Of course, the purity of raw materials, the type and quantity of catalyst, and the arrangement of the process equipment also play a part. For reaction control, temperature control is the prevailing industrial method. In production by batch reactors, tracking a pre-defined reaction temperature trajectory is the method mainly used. However, with this method the inter-batch product quality is often unsatisfactory and/or batch cycle time cannot be maintained consistently even under exactly the same operating conditions, because of unknown disturbances. Therefore, if measuring the reaction state during the esterification reaction is possible, it should be a helpful means of enhancing product quality.

Available methods for measurement that have direct correlation with the composition or conversion of the reaction mixture have been rarely reported. Although rarely used, infrared spectroscopy¹³⁾, conductance measurement⁶⁾ and ultrasonic absorption⁹⁾ have been suggested as helpful tools. Among these methods, conductance measurement has been regarded as the simplest. However, it has been reported to be very difficult to eliminate the coupled noise from the measured signal and to correlate the measured conductance with the reaction state. Thus, its usage has been restricted to the detection of reaction end-time and/or unwanted contamination⁴⁾. However, these limitations are no longer serious if precise and high-speed electronic measuring devices and computers are utilized.

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The purpose of this paper is twofold. The first objective is to verify the usefulness of on-line conductance measurements for batch esterification reactors.

The second is to propose a new control scheme for direct conversion control of batch esterification reactors. In other words, if an optimized conversion trajectory is given and the tracking is performed satisfactorily, the regulation of both the batch production time cycle and inter-batch product quality can be simultaneously realized.

1. System Description

The chemistry of esterification and polyesterification has received considerable attention in the literature^{2, 7)}. Esterification of a glycol with a diacid (carboxylic acid or anhydride) is a common method of synthesizing polyester resins.

The reaction system to be considered in this paper is a batch esterification reaction of dimethyl terephthalate (DMT) with ethylene glycol (EG). The product is a monomer, bis-hydroxyethyl terephthalate (BHET), which is a reactant for a polyethylene terephthalate (PET) product³⁾. The reaction is carried out in a jacketed stirred-tank batch reactor.

1.1 Experimental setup

Laboratory-scale experiments are conducted in a 1-L electrically heated glass reactor equipped with a distillation column unit and a ceramic-coated conductance measuring cell, as shown in **Fig. 1**. The heating system of the reactor consists of an electric heater of which the power is regulated by a SCR unit. Reactor cooling depends only on the heat of vaporization of volatile components and the recycle unit on the distillation column. Temperature sensors (four 0-400°C Pt 100 Ω

Lab-scale Batch Reactor System

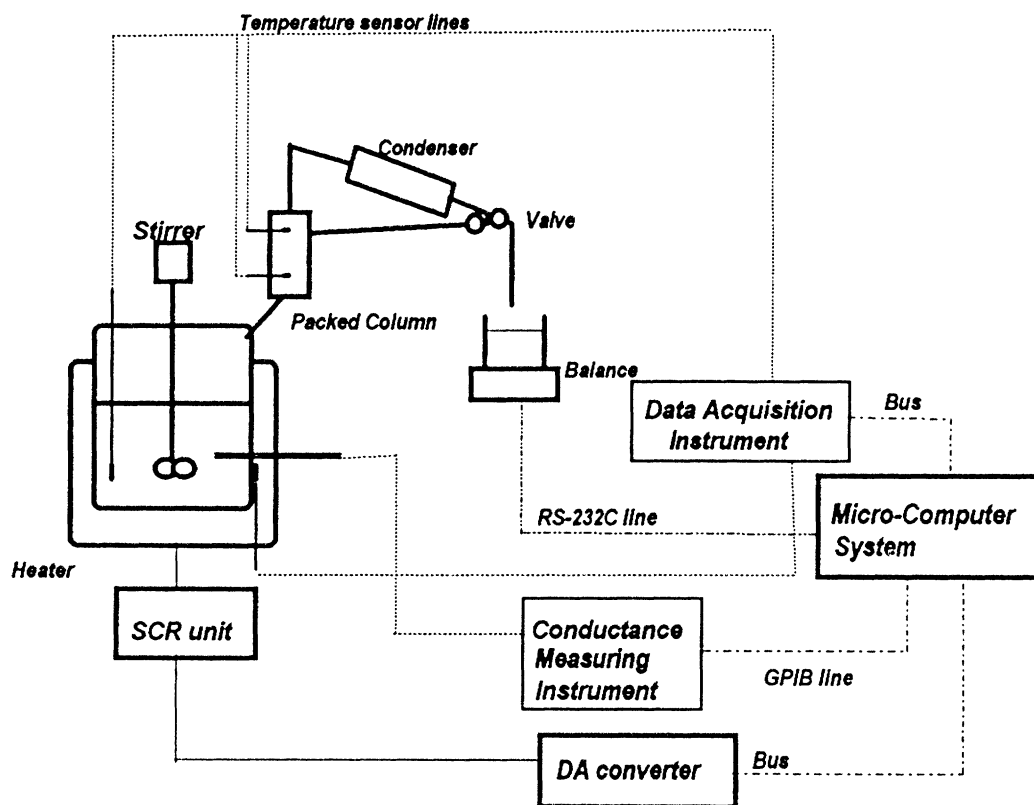


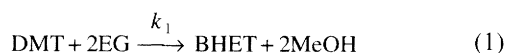
Fig. 1 Schematic diagram of experimental system

RTD, accuracy: $\pm 0.2^\circ\text{C}$) are attached to the reactor, the heating jacket, and the bottom and the top of the column. The weight of condensate outputs is measured by an electronic balance that is connected to a micro-computer system. We use a resistance measuring instrument to determine the conductance of the reaction mixture. This is connected to the computer system and data gathered at a rate of 50 data a second are averaged to reduce the effect of noise. Input source voltage to the cell is AC 1V (frequency: 1 kHz). The sampling period is 5 seconds.

1.2 Reaction kinetic model

There have been many studies about the modeling of the esterification reaction¹⁰⁾. However, the reaction models used are so complex that they are not suitable for control purposes. Therefore, we use only one main reaction kinetics and do not include the internal sub-reactions and the formation of side products.

Reactions take place in a homogeneous liquid phase. Assuming that no oligomerization occurs in this stage, the main reaction is



Since the reaction occurs in the high-temperature range (140–220°C), volatile components evaporate and the mass of the liquid reaction mixture changes while the reaction proceeds. Under this condition, it can be assumed that volatile component MeOH vaporizes easily

and thus reversible reaction is negligible. From the mole balance of this reaction and the experimental determination of the reaction order (which was 2), we can obtain a kinetic model expressed in DMT conversion X_{DMT} as follows:

$$\frac{dX_{\text{DMT}}}{dt} k_0 \exp\left(-\frac{E}{RT_r}\right) \frac{C_0(1-X_{\text{DMT}})^2}{(1-0.032C_0)} \quad (2)$$

where C_0 is the concentration of carboxyl group in mol kg^{-1} (two carboxyl groups exist in the DMT molecule) at time 0, and 0.032 is the molecular weight of MeOH in kg mol^{-1} . For this reaction-rate equation to be valid, initial reactants are assumed to be used in stoichiometric ratio. The reaction rate constant includes the effect of the catalyst quantity on the reaction rate and is expressed in the classical Arrhenius form. k_0 is the frequency factor, E is the activation energy, and T_r is the reactor temperature. The catalyst used in this work is zinc acetate, and its injected quantity is $4.7 \times 10^{-5} \text{ kg/DMT-mol}$.

For evaluating the actual kinetic constant to fit Eq. (2), we regarded k_0 as a time-varying parameter and E as a constant for the determined catalyst type. According to this approach, first, we can obtain the fixed value of E by regressing analysis of the experimental data in the prevailing temperature range. The results are shown in Table 1. Determining the defined time-varying fre-

Table 1. Experimentally estimated parameters of the system model

Estimated parameter	Value	Unit
α_1	62.5	k Ω
α_2	2.98	
α_3	1.2×10^8	K ³
n	2	
E	7.344×10^4	J mol ⁻¹ K ⁻¹ (a)
$k_0^{(b)}$	1.90×10^4	kg ² mol ⁻² sec ⁻¹

(a) based on the mol of carboxy group in DMT

(b) This is a fixed value used only for simulation study

quency factor in on-line fashion will be explained in section 2.2.

1.3 Conversion-conductance correlation

According to the theory of conductance of solution⁸, when two electrodes are placed in a solution containing ions and an electrostatic potential is impressed across these electrodes, the ions are accelerated instantaneously to the point at which the viscous drag of the solvent limits their speed.

In the reaction mixture, it is believed that the reaction mass causes the frictional force for the movement of ions through it. Ions are mainly formed by added catalysts that are metal derivatives. As the reaction goes on, the composition of the reaction mixture changes. Therefore, the apparent conductance alters as reaction advances. Assuming that the frictional force is proportional to the mole fraction of each component, the following equation can be easily derived:

$$\frac{1}{A} = \frac{\left(\frac{3}{A^*}\right)(1 - X_{DMT}) + \alpha_1 X_{DMT}}{(3 - \alpha_2 X_{DMT})} \exp\left[\alpha_3 \left(\left(\frac{1}{T}\right)^3 - \left(\frac{1}{T^*}\right)^3\right)\right], \quad (3)$$

where A is the conductance (in siemens, S)—that is, the inverse of the resistance (in ohms, Ω). The asterisk represents the initial state of reaction and parameters α_1 , α_2 and α_3 , are to be evaluated using a nonlinear regression of experimental data.

The estimated values of parameters in the given esterification reaction system are shown in Table 1. Regarding the temperature dependency of the conductance of the reaction mixture, experimental investigations were made into the reactant EG and the product BHET respectively. For all these materials, $\ln(1/A)$ is proportional to T^3 and the evaluated parameter α_3 was in the range of $1.0 \times 10^8 \sim 1.4 \times 10^8$. It is noticeable that the conductance values are not very sensitive to the parameter α_3 in the operating temperature range of the reactor. Thus the proposed model, consisting of the product of a conversion-dependent term and a temperature-dependent term is valid in form.

Figure 2 compares the conversion profile estimated by the conductance measurement with that calculated by MeOH condensate measurement, which is compensated by the column-resident MeOH.

2. Control Scheme

In most industrial batch reactions, due to distur-

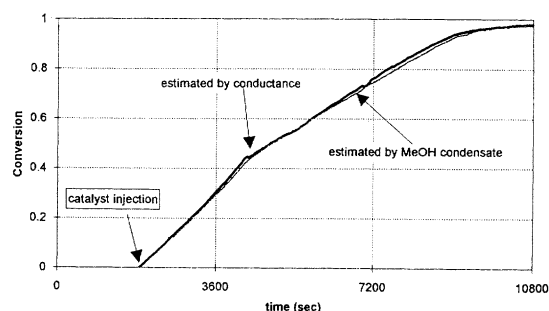


Fig. 2 Comparison of conversion profiles estimated by measurements of conductance and MeOH condensate

bances of unknown cause such as impurities or perturbed initial reactants and catalyst concentrations, the regulation of cycle time and inter-batch quality cannot be accomplished by temperature control alone.

As a solution to this problem, we propose a method using conductance measurement to predict the conversion during the reaction and a new conversion control scheme using measured data. In this study, from our experimental experience we fixed the reference trajectory in the following form:

$$X_{ref}(t) = X_f \left(1 - \exp\left(-\beta \frac{t - t_s}{t_f - t_s}\right) \right) / (1 - \exp(-\beta)), \quad (4)$$

where X_f is the desired final conversion, t_s is the catalyst injection time, that is, the reaction start time, t_f is the reaction end time, and β is the adjustment parameter. As the parameter β increases, the reaction rate in the first period of the reaction becomes more rapid.

To develop a control scheme to track the trajectory established already as closely as possible, we first applied a PID controller tuned by IMC tuning guideline^{11, 12}) but could not satisfy the requirements. Particularly, in the last range of the reaction the temperature and conversion often oscillate, and the control action fluctuates greatly due to the noise in conductance measurement. Therefore, we decided to try a new nonlinear conversion control scheme.

2.1 Conversion control scheme using cascade nonlinear controller

Recently, an application of nonlinear control theory to the control of highly nonlinear batch processes was proposed by Kravaris *et al.*⁵) Their work was based on differential geometric nonlinear systems theory. By applying their idea, we have derived a control algorithm using only ordinary differential equations of the system model.

In batch reactor operations, the time constant of the reaction temperature is much smaller than that of the conversion, and the rate of conversion is a function of the conversion and reactor temperature at a given time. Defining $G(X_k, T_{rk})$ as the right-hand side of Eq. (2), we can convert the reaction model to this approximate discrete form:

$$\frac{dX}{dt}\bigg|_{k+1} = G(X_k, T_{rk}) + \left(\frac{\partial G}{\partial T_r}\right)_k \Delta T_{rk+1}, \quad (5)$$

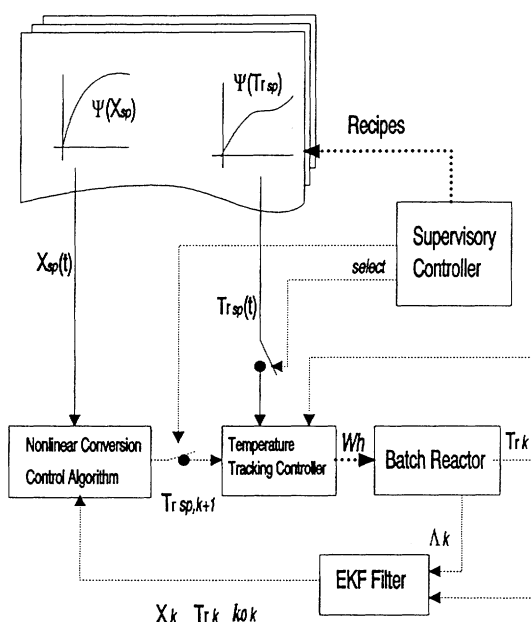


Fig. 3 Block diagram of cascade nonlinear conversion control scheme

where ΔT_{rk+1} is the variation of the reaction temperature during the k^{th} sampling interval from time t_k to t_{k+1} . Considering the above formulation, we can design a model-based open-loop nonlinear conversion controller. Setting the reaction temperature in the next time step, T_{rk+1} , to the value of the temperature setpoint, $T_{rsp,k+1}$, and considering a PID-type feedback controller to reject unknown disturbances and model uncertainty, we can arrive at the following control law:

$$T_{rsp,k+1} = T_{rk} + \frac{PID + \frac{dX}{dt} \Big|_{sp,k+1} - G(X_k, T_{rk})}{\left(\frac{\partial G}{\partial T_r}\right)_k}, \quad (6)$$

where T_{rk} is the measured temperature, and X_k is the conversion estimated from the measured conductance at time t_k . $T_{rsp,k+1}$ evaluated at each sampling time becomes the reaction temperature setpoint that will be tracked by an inner PD-type temperature controller. *PID* indicates the **PID** feedback⁷⁾ having the following form:

$$PID = K_p^{rcc} \left[e_k + \sum_{i=1}^k \frac{\Delta t}{\tau_i^{rcc}} e_i + \frac{\tau_d^{rcc}}{\Delta t} (e_k - e_{k-1}) \right], \quad (7)$$

where e_k is $(X_k - X_{k-1})$ and superscript *rcc* denotes reaction conversion controller.

In this control scheme, the reference trajectories should be used as setpoint trajectories of a cascade-type controller. The reason for using the cascade-type control strategy is its flexibility for switching from conversion control mode using conductance measurements to single temperature tracking control mode in the case of losing confidence in the conversion estimates obtained from conductance measurements (see **Fig. 3**). Therefore, we think that good features of this control structure are its simplicity and operability.

For the overall batch reactor operation, two PID-

Table 2. Tuning parameters of three PID controllers used for conversion control

Controller	Tuning parameter	Value	Unit
Temperature controller as an inner controller of the nonlinear cascade controller	K_c^{rtc}	7.168	J sec ⁻¹ K ⁻¹
	τ_i^{rtc}	4577	sec
	τ_d^{rtc}	53.43	sec
Part of the nonlinear controller (Eq. (6))	K_c^{rcc}	0.004	K
	τ_i^{rcc}	1000	sec
	τ_d^{rcc}	0.0	sec

type controllers are used. The tuning parameters are shown in **Table 2**. The first PID controller is the reactor temperature controller, used to track the temperature trajectory as the inner-loop controller of the cascade control scheme. The tuning parameters K_c^{rtc} , τ_i^{rtc} , τ_d^{rtc} (superscript *rtc* denotes reaction temperature control) were determined based on the rules proposed by Rotstein and Lewin¹²⁾, and they show good performance across the full range of the temperature trajectory. For the second PID controller, the parameters K_c^{rcc} , τ_i^{rcc} , τ_d^{rcc} (superscript *rcc* denotes reaction conversion control) in Eq. (7) can be obtained easily by trial and error.

Through a series of experimental and simulation studies, we knew that the kinetic model/plant mismatch and conductance measurement noise affected the conversion control performance. To eliminate the model/plant mismatch, we chose the extended Kalman filter as an estimator, because it conveniently handles nonlinear state space models directly.

2.2 On-line parameter estimator

In this application, the conductance measurement is used as a correction variable. Therefore, if we accept the reaction temperature measurement as a model input, the difference between the model predicted and the measured conductance is a measure of the correction that has to be applied to the predicted conversion. With this idea, we designed the following estimator.

Estimator design: If we assume that the conversion model structure is accurately known (which was experimentally evaluated), the system and observation models for the simultaneous estimation of conversion and time-variant parameter $k_0(t)$ are given by

$$\dot{X}_{DMT}(t) = k_0(t) \exp\left(-\frac{E}{RT_r}\right) \frac{C_0(1 - X_{DMT}(t))^2}{1 - 0.032 C_0} + w_1(t) \quad (8)$$

$$\dot{k}_0(t) = w_2(t) \quad (9)$$

$$\frac{1}{\Lambda_m(t)} = \frac{\left(\frac{3}{\Lambda^*}\right)[1 - X_{DMT}(t)] + \alpha_1 X_{DMT}(t)}{[3 - \alpha_2 X_{DMT}(t)] \exp\left[\alpha_3 \left(\left(\frac{1}{T}\right)^3 - \left(\frac{1}{T^*}\right)^3\right)\right] + v(t)} \quad (10)$$

where w_1 , w_2 and v are independent white-noise sequences with covariances Q_{11} , Q_{22} and R_{11} , respectively. Because of the high accuracy of the initial estimate in this system, the term P_{011} can be relatively small.

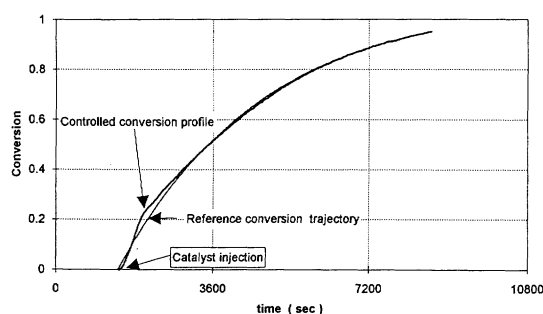


Fig. 4a Trajectory tracking performance of cascade nonlinear conversion controller with well-tuned EKF estimator

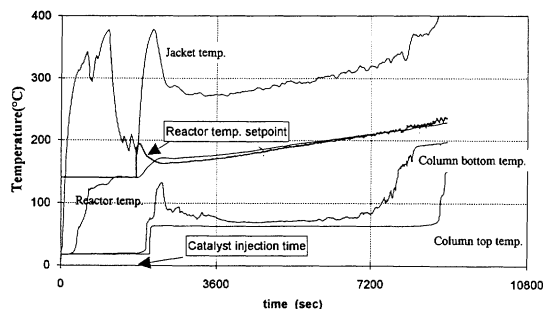


Fig. 4b Temperature profiles when cascade nonlinear conversion controller with well-tuned EKF estimator is used

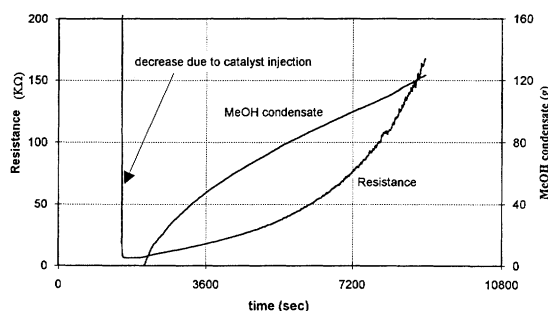


Fig. 4c Profiles of resistance (inverse of conductance) and MeOH condensate when cascade nonlinear conversion controller with well-tuned EKF estimator is used

Therefore, we choose $P_{011} = 10^{-5}$. The uncertainty in the initial value of k_0 is very high. The analysis of the experimental data indicates that the k_0 value is within the range $1.5 \times 10^4 \sim 2.0 \times 10^4$. Considering $P_{022} = E \{ (k_0(0) - \hat{k}(0))^2 \}$, we set the value to be 1.0×10^8 . Based on these factors, \hat{x}_0 and P_0 take the following values:

$$\hat{x}_0 = \begin{pmatrix} 0.0 \\ 2 \times 10^4 \end{pmatrix}, P_0 = \begin{pmatrix} 10^{-5} & 0 \\ 0 & 10^8 \end{pmatrix}. \quad (11)$$

The Q matrix, containing modeling error covariances, should be large for systems that have dynamics that are not well understood; this has the effect of increasing the steady-state error. Considering the confidence of the kinetic model structure relative to the time-varying kinetic parameter k_0 , Q_{11} should have a small value compared with Q_{22} . Therefore, we set the values of the model error covariance Q as follows:

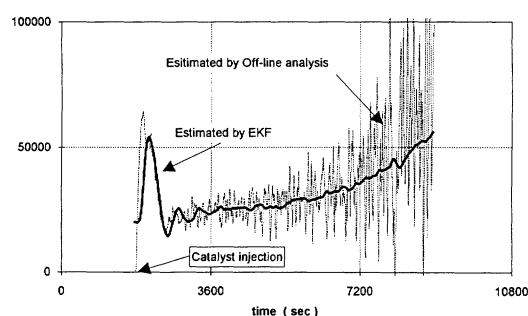


Fig. 4d Performance of well-tuned EKF estimator (solid line; online estimated by the EKF, dotted line; off-line estimated by Eq. (14) after the reaction)

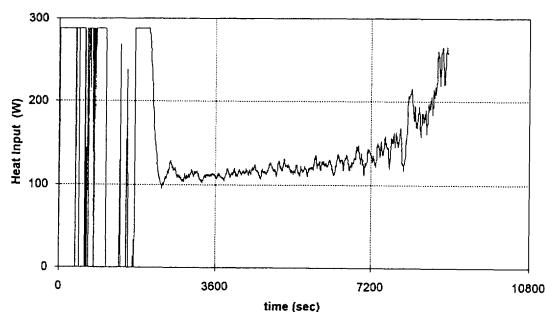


Fig. 4e Actual manipulated heat input profile generated by cascade nonlinear conversion controller with well-tuned EKF estimator

$$Q = \begin{pmatrix} 10^{-5} & 0 \\ 0 & 10^8 \end{pmatrix} \quad (12)$$

The measurement error covariance R is set by measuring devices⁹. In the present system, the coupled noise of the conductance measurement becomes larger in the later part of the reaction. The reason is that as the conversion increases, the viscosity of the reaction mixture becomes higher and the size of bubbles generated by the boiling of the reactant EG becomes larger¹, and then the rising bubbles more strongly affect the electric current flow between cells. Considering this time-varying measurement noise, we have determined the value of the covariance matrix R (i.e., the variance of the conductance measurement), of which the choice has a substantial impact on filter performance, as the following function of the conversion:

$$R = (10^{(-0.2 + 4 * \hat{x}_{DMT}(t))}), \quad (13)$$

where the constant parameters were determined by several simulation and experimental studies.

3. Experimental Results and Discussion

A series of experiments in batch esterification incorporating proposed cascade nonlinear conversion control schemes were carried out.

Figure 4 shows representative experimental results of well-tuned conversion control. This experiment was performed so that the conversion control followed the reference trajectory expressed by Eq. (4), of which the parameters were set to 0.95 for X_p , 2.2 for β and 2.0

hours for $(t_f - t_s)$, respectively. Values of the tuning parameters for the controllers were the same as those in Table 2. For the parameters of the kinetic estimator EKF, the values in Eqs. (11)-(13) were used.

Figure 4a shows the performance of the proposed control scheme. Good agreement between the reference trajectory and the controlled values can be seen except in the initial part of the reaction. The reason for the initial disagreement is that at the start of reaction control, the setpoint of the reaction temperature T_{rs} generated by the nonlinear conversion control scheme is very high compared with the current reaction temperature T_r ; that is, T_{rs} cannot be instantaneously tracked by the inner loop controller due to the slow heating dynamics as depicted in Fig. 4b.

Figure 4c shows the trends of conductance measurement and MeOH condensate output. In this figure, note that the coupled noise of the conductance measurement becomes larger in the later part of the reaction. In Fig. 4d, the estimated frequency factor using EKF is plotted together with that calculated off-line using the following equation:

$$k_0(t)_f = \frac{((dX)_m / dt)_f (1 - 0.032 C_0)}{\exp(-E / RT_r) C_0 (1 - X_m)^2}, \quad (14)$$

where subscript f denotes the filtered value, X_m is the conversion directly calculated using both Eq. (3) and the conductance measurements, and T_r is the measured reaction temperature. The recursive moving-average filter was used for eliminating high-frequency noise¹⁴⁾. The figure shows that the trend of the estimated frequency factor by the EKF is in accord with that of the noise-corrupted real values; that is, it illustrates the validity of the form of Eq. (13). Figure 4e depicts the corresponding profile of the actual manipulated variable. The performance of the nonlinear control scheme can be seen in its smooth variation.

Conclusion

This work is the first experimental study of a conversion control scheme using conductance measurements for a batch esterification reactor.

Firstly, through experimental studies, the possibility of conversion control of practical batch esterification reactors using on-line conductance measurements was investigated. The accuracy of the conversion information derived from the conductance measurements is sufficient for it to be applied to the conversion control of the batch esterification reaction and reaction-quality monitoring.

Secondly, a cascade nonlinear control scheme was formulated and successfully implemented in a bench-scale batch reactor system. This control scheme was designed to perform two functions concurrently: nonlinear control of a reaction conversion and on-line reaction kinetic parameter estimation. The proposed control scheme shows desirable control performance and ease of

tuning. The extended Kalman filter (EKF) was introduced for reaction kinetic parameter estimation to achieve further improvement of control performance.

Finally, we believe that this proposed conversion control scheme using conductance measurement can be used for on-line quality control of batch (esterification) reactors.

Nomenclature

E	= activation energy for reaction	[J·mol ⁻¹]
G	= reaction conversion rate equation	[sec ⁻¹]
k_0	= frequency factor of reaction	[kg ² ·mol ⁻² ·sec]
P_0	= covariance matrix of initial-state errors	[-]
Q	= covariance matrix of measurement noise	[-]
R	= covariance matrix of plant noise state transition matrix	[-]
R	= gas constant	[J·mol ⁻¹ ·K ⁻¹]
t	= time	[sec]
T_r	= reaction temperature	[K]
X_i	= conversion of reactant i	[-]
\hat{x}_0	= vector of initial state estimates	[-]
Λ	= conductance at the time t	[kΩ ⁻¹]
β	= adjustment parameter for the reference trajectory	[-]
τ_i	= response time constant of i	[sec]

<Subscripts and superscripts>

d	= derivative action
f	= filtered value or reaction end time
I	= integral action
k	= current time step
m	= measured value
sp	= setpoint

<Abbreviations>

AC	= alternating current
BHET	= bis-hydroxyethyl terephthalate
DMT	= dimethyl terephthalate
EG	= ethylene glycol
EKF	= extended Kalman filter
IMC	= internal model control
MeOH	= methanol
RTD	= resistance temperature detector

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