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Optimization of the pre-polymerization step of polyethylene terephthalate (PET) production in a semi-batch reactor

Joonho Shin[1,a], Yunghyo Lee[b], Sunwon Park[a,*]

[a]Department of Chemical Engineering, KAIST, Teajon, 305-701, South Korea
[b]SKC Co., Ltd., Suwon, South Korea

Abstract

The time minimization (free-end-time problem) of the transesterification reaction in a semi-batch reactor was performed using successive quadratic programming (SQP) and the cubic spline interpolation method, and the numerical optimization result was verified by experiment. The process constraints of the semi-batch reactor are the rate of temperature increase, the amount of ethylene glycol (EG) in the vapour phase (as an indicator of the flooding of dimethyl terephthalate (DMT) and the concentration of side products (especially diethylene glycol (DEG)). The proposed optimal temperature trajectory was applied to the industrial process and reduced the reaction time of the transesterification from 150 to 110 min (about a 25% reduction), while satisfying the process constraints, such as the upper limit of the by-product concentration, the rate of temperature increase and the flooding. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Prepolymerization; Polyethylene terephthalate (PET); Successive quadratic programming (SQP)

1. Introduction

Polyethylene terephthalate (PET) is the raw material for the production of synthetic fibres, films, filaments and plastic objects. PET is one of the most important polymers from a commercial point of view. Fibre-grade PET is mainly used in textiles, and its contribution to the world synthetic fibre demand is around 40%. In addition to this, it has many industrial application; for example, it can be used as a raw material for the production of a base for photographic film, and for moulding material [8]. The production of PET proceeds via two stages: (1) a transesterification stage or esterification stage; (2) a polycondensation stage. In the first stage, prepolymer (monomer for the polycondensation stage) containing mainly bis(2-hydroxyethyl)terephthalate (BHET) is synthesized either through the transesterification of dimethyl terephthalate (DMT) and ethylene glycol (EG) or through the direct esterification of terephthalic acid (TPA). In the second stage, the polycondensation stage, the prepolymer produced in the first stage is polymerized at high temperature (260–290°C) using a high vacuum (0.5–1 Torr), and EG is removed continuously. Generally, antimony compounds (such as antimony trioxide) are used to catalyse the polycondensation reaction. The equilibrium constant for the polycondensation reaction is very low (approximately 0.5), and the rate of EG removal becomes the rate-controlling factor.

Some of the by-products formed have an important influence of the fibre properties. Thus, even though the amount of diethylene glycol (DEG) formed is very small (1–2 wt.%), it has an effect on the physical and chemical properties of PET. Indeed, the melting point of PET decreases by 5°C for each weight per cent increase of DEG incorporated, and the presence of small amounts of DEG has a substantial influence on dyeing. It was therefore thought to be desirable to study the effects of the process and operational variables (EG-to-DMT ratio, temperature, etc.) on the rate of formation of DEG, acid end groups and other side products [12].

Several investigators have performed optimization studies. A fixed-end-time optimization study of the transesterification reaction was performed by Kumar et al. [7,8] with control vector iteration (CVI) based on Pontryagin's maximum principle. The objective was to attain the desired degree of polymerization and to minimize the side products. The proposed optimal temperature profile suggests the use of a high temperature initially to obtain a high conversion of E_m, the methyl ester functional group, followed by lower temperatures in the final phases of the reaction to minimize

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*Corresponding author. Tel.: +82-42-869-3920; fax: +82-42-869-3910; e-mail: swpark@convex.kaist.ac.kr

[1] Present address: SK Engineering & Construction, 192–18, Kwanhun-dong, Chongro-gu, Seoul 110–300, Korea.

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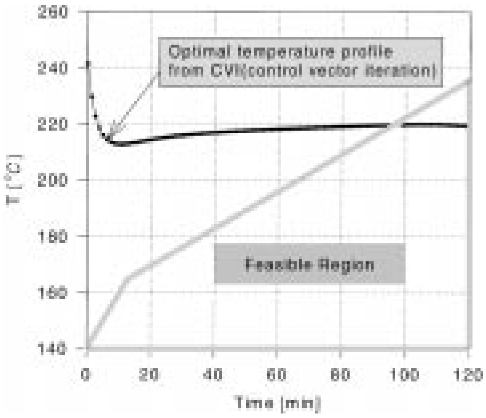


Fig. 1. Feasibility of reactor temperature trajectory.

side product formation [7]. However, the proposed optimal temperature trajectory requires a high pressure or inert compounds having high boiling points to achieve a high initial temperature. The optimal temperature trajectory obtained by CVI cannot be practically applied to conventional industrial processes. A condensation reaction occurs in the prepolymerization step, and the product of the condensation reaction, methanol, should be removed in order to accelerate the forward reaction and shift the equilibrium. An inert compound having a high boiling point is also undesirable, because additional equipment may be required in order to separate it.

Usually, the optimal temperature trajectories obtained by CVI are not feasible, as shown in Fig. 1, and cannot be applied to industrial processes, because the process constraints cannot be handled. It is therefore very important to consider the process constraints in the optimization. The main aim of this study was to determine a feasible optimal temperature trajectory of the transesterification reaction that reduces the batch reaction time whilst handling the process constraints.

2. Industrial process

A typical industrial process [10] is shown in Fig. 2. The transesterification stage is performed by the following procedures. Solid DMT is melted and mixed with EG in a mixer before charging it to the reactor at about 140°C. As the condensation reaction proceeds, methanol is produced and evaporates together with some EG. EG is separated in the distillation column and recycled to the reactor. In this stage, the molar ratio of DMT to EG in the feed is usually about 1 : 2, and the condensation reaction occurs mostly in the temperature range 140–240°C at atmospheric pressure. A typical temperature trajectory of the transesterification reaction in industrial processes shows a constant increase in temperature ($140 + 30°\mathrm{C}\ \mathrm{h}^{-1}$). The reaction takes 2.5 h up to 95% conversion. A catalyst is commonly used so that the reaction can be completed in a reasonable reactor residence time. The transesterification reaction has been proposed to occur through the nucleophilic attack of the hydroxyl groups of EG on the carbon of the ester carbonyl groups of DMT. Zinc acetate is the most effective catalyst and is commonly used in industry.

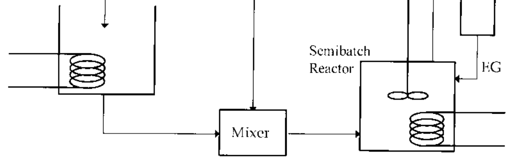


Fig. 2. Flow sheet of transesterification stage.

3. Mathematical model of the transesterification stage

Kinetic and mathematical models of the transesterification reaction have been proposed by Ravindranath and Mashelkar [12]. They reported that there was a fair agreement between the model predictions and plant data. These kinetic and mathematical models have been used in order to evaluate the objective function and process constraints considered in this work. The various reactions occurring in the transesterification stage are given in Table 1. The kinetic rate and equilibrium constants of these reactions are shown in Table 2. In addition to the kinetic model, the mathematical model for a semi-batch reactor is shown in Table 3. As shown in Table 3, the concentration of diethylene species is defined by the sum of DEG and E_{DEG}. These kinetic and mathematical models are the same as those of Kumar and Sukthandar [7]. It is assumed that the species with a high molecular weight (such as E_m, E_g, E_c, Z, E_v and D, defined in Table 1) are not vaporized. It is also assumed that the species with a low molecular weight (such as M, W and A, defined in Table 1) are instantaneously vaporized and removed from the semi-batch reactor after being produced under the operating temperature (140–240°C). Therefore there is no accumulation of M, W and A in the semi-batch reactor. In addition, it is assumed that EG is totally returned to the reactor from the distillation column. As the transesterification reaction progresses, there is a shrinkage in the volume of the reaction mass as the condensation product flashes out [4]. The volume of the reaction mass is calculated from the formula given in Table 3, where V_{DMT}, V_{EG}, V_M, and V_W are the molar volumes of DMT, EG, methanol and water respectively, as reported by Fontana [4]. DMT_0 and EG_0 are the numbers of moles of DMT and EG loaded initially. M_{tot} and W_{tot} denote the moles of methanol and water removed up to time t.

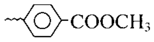
Table 1
Reactions of functional group in the transesterification stage of PET formation from the DMT route

Main reactions	
Ester interchange reaction	$E_m + EG \underset{k_1/K_1}{\overset{k_1}{\rightleftarrows}} E_g + M$
Transesterification reaction	$E_m + E_g \underset{k_2/K_2}{\overset{k_2}{\rightleftarrows}} Z + EG$
Polycondensation reaction	$2E_g \underset{k_3/K_3}{\overset{k_3}{\rightleftarrows}} Z + EG$
Important side reactions	
Acetaldehyde formation	$E_g \xrightarrow{k_4} E_c + A$
Diethylene glycol formation	$E_g + EG \xrightarrow{k_5} E_c + DEG$ $2E_g \xrightarrow{k_6} E_c + E_{DEG}$
Water formation	$E_c + EG \underset{k_7/K_4}{\overset{k_7}{\rightleftarrows}} E_g + W$ $E_c + E_g \underset{k_8/K_5}{\overset{k_8}{\rightleftarrows}} Z + W$
Vinyl group formation	$Z \xrightarrow{k_9} E_c + E_v$ $E_g + E_v \xrightarrow{k_3} Z + A$

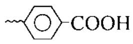
Symbols:

A : CH_3CHO

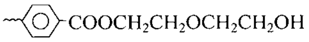
DEG : $HOCH_2CH_2OCH_2CH_2OH$

E_m : 

E_g : 

E_c : 

E_v : 

E_{DEG} : 

M : CH_3OH

W : H_2O

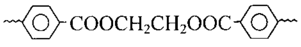
Z : 

Table 2
Rate and equilibrium constants, k_i and k_i defined in Table 1

Kinetic constant ($K_i = A_i\,e^{-E_iRT}$)	Activation energy, E_i (kcal mol^{-1})	Frequency factor, A_i (l mol^{-1} min^{-1})	Equilibrium constant, K_i
k_1	15.0	4.00×10^4	$K_1 = 0.30$
k_2	15.0	2.00×10^4	$K_2 = 0.15$
k_3	18.5	6.80×10^5	$K_3 = 0.50$
k_4	29.8	2.17×10^{9a}	$K_4 = 2.50$
k_5	29.8	2.17×10^9	$K_5 = 1.25$
k_6	29.8	2.17×10^9	
k_7	17.6	1.00×10^6	
k_8	17.6	1.00×10^6	
k_9	37.8	3.60×10^9	

[a] All units are in min^{-1}.

Table 3
Mole balance equation for transesterification reaction in a semi-batch reactor

$$dE_m/dt = V(-R_1 - R_2) = F_1$$
$$dE_g/dt = V(R_1 - R_2 - 2R_3 - R_4 - R_5 - R_6 + R_7 - R_8 - R_{10}) = f_2$$
$$dEG/dt = v(-R_1 + R_3 - R_7) = f_3$$
$$dZ/dt = V(R_2 + R_3 + R_8 - R_9 + R_{10}) = f_4$$
$$dE_c/dt = V(R_4 + R_5 + R_6 - R_7 - R_8 + R_9) = f_5$$
$$dD/dt = V(R_5 + R_6) = f_6$$
$$dE_v/dt = V(R_9 - R_{10}) = f_7$$
$$dM/dt = V(R_1 + R_2) = f_8$$
$$dW/dt = V(R_7 + R_8) = f_9$$
$$dA/dt = V(R_4 + R_{10}) = f_{10}$$

where

$[D] = [DEG] + [E_{DEG}]$

$R_1 = k_1(2[E_m][EG] - [E_g][M]/K_1)$, $R_2 = k_2([E_m][E_g] - 2[Z][M]/K_2)$

$R_3 = k_3([E_m]^2 - 4[Z][EG]/K_3)$, $R_4 = k_4[E_g]$

$R_5 = 2k_5[E_m][EG]$, $R_6 = k_6[E_g]^2$

$R_7 = k_7(2[E_c][EG] - [E_g][W]/K_4)$, $R_8 = k_8([E_c][E_g] - 2[Z][W]/K_5)$

$R_4 = k9[Z]$, $R_{10} = k_3[E_v][E_g]$

$m_{tot} = \int_0^t f_8\,dt$, $w_{tot} = \int_0^t f_9\,dt$,

$V = V_{DMT}\,DMT_0 + V_{EG}\,EG_0 - m_t V_M - w_t V_W$, and $[M] = [W] = [A] \cong 0$

4. Flash distillation model

As mentioned above, the transesterification reaction occurs in the temperature range 140–240°C at atmospheric pressure. The boiling point of EG is 197.6°C, and a considerable amount of EG vapour is present in the reactor and the distillation column in this temperature range. In addition, the reaction rate in the initial step is very fast although the temperature range is low in the initial step, the concentration of the reactants is high). Therefore, the evaporation rate of the volatile products (such as methanol, water and acetaldehyde) is fast. If the reaction rate is fast, the volatile components may entrain the relatively high molecular weight molecules, such as DMT, MHET and BHET, in the reacting mixture. If DMT (the melting point of DMT is 140.65°C and the boiling point is 243°C) excited the reactor, it would solidify in the packed column or condenser. The solidified DMT may block up the column and condenser, resulting in an unsuccessful batch operation. In this case, the product quality could not be guaranteed, and a cleaning operation would be required. This phenomenon is known as *flooding* in the industry.

Flooding of the reactants (especially DMT) causes serious problems to the column and condenser. Because the vapour pressure of DMT is low in the temperature range 140–240°C, the escape of DMT is not caused by vaporization. Thus, the flooding phenomenon cannot be explained by the vaporization of DMT. No theoretical approach has been proposed in order to describe the flooding phenomenon. However, it has been observed from many experiments that the rate of vaporization of the methanol formed and the concentration of EG in the vapour phase are related to flooding. The concentration of EG in the vapour phase can be used as an indicator of flooding. The flash distillation model was studied to calculate the concentration of EG in the vapour phase. Ravindranath and Mashelkar [12] made a quasi-steady-state assumption for small increments of time, and considered a flash distillation process. They calculated the concentration of volatile species by Raoult's law and the rate of outflow of volatile species by the material balance equations written for a flash tank. The same approach is taken in this work, and two assumptions are added in order to reduce the computational burden. The first assumption is that the volatile components, methanol, water and acetaldehyde, are flashed our through the distillation column, and the second is that the liquid mass fraction of the volatile components produced in Δt is negligible and only EG is in equilibrium.

The concentration of EG in the vapour phase can be calculated by a simple algebraic equation based on these assumptions,

$$P_{\mathrm{T}}\left(1-\frac{a+m+w}{N_{\mathrm{V}}}\right)=\frac{P^{*}_{\mathrm{EG}}\mathrm{EG}}{(N_{\mathrm{T}}-N_{\mathrm{V}})+(P^{*}_{\mathrm{EG}}/P_{\mathrm{T}})N_{\mathrm{V}}} \tag{1}$$

where

$$\log P^{*}_{\mathrm{EG}}(\mathrm{mm\ Hg})=21.61-\frac{3729}{T}-4.042\log(T) \tag{2}$$

In the above equation, N_{V} and N_{T} are the total number of moles in the vapour phase and the reactor, respectively.

5. Process constraints

As mentioned in Section 1, the process constraints should be considered to obtain a feasible operating condition. In this work, therefore, three constraints of the transesterification reaction have been considered, and the free-end-time optimization problem has been formulated and solved. The first constraint is the rate of temperature increase or decrease, which is constrained by the heat flux from or through the reactor jacket: for example, the heat duty of the electric heater has a finite capacity and the heat transfer may be limited by the overall heat transfer coefficient. The constraint can be formulated by the following equation

$$\frac{\mathrm{d}T}{\mathrm{d}t}\Big|_{\mathrm{L}}\leq\frac{\mathrm{d}T}{\mathrm{d}t}\leq\frac{\mathrm{d}T}{\mathrm{d}t}\Big|_{\mathrm{U}} \tag{3}$$

The second constraint is the extent of reaction and the concentration of the undesired side products (especially the concentration of DEG). The extent of reaction should be achieved up to the desired conversion, 95%, and the undesired side product should be within a limiting concentration at the end of the reaction. These constraints have been formulated as follows

$$X_{\mathrm{f,L}}\leq X_{\mathrm{f}} \tag{4}$$

$$[\mathrm{D}]_{\mathrm{f}}\leq[\mathrm{D}]_{\mathrm{U}} \tag{5}$$

In the above equations, the subscript f denotes the end time of the reaction. Finally, the constraint concerning flooding has been formulated by limiting the amount of EG in the vapour phase, N_{V}. As mentioned previously, the safe operation of transesterification is achieved by controlling flooding, and N_{V} can be used as an indicator of flooding. The following formulation is adopted is adopted to prevent flooding

$$N_{\mathrm{V}}(t)\leq N_{\mathrm{V},U} \tag{6}$$

The amount of EG in the vapour phase N_{V} is taken as the constraint for flooding. It is clear that smaller $N_{\mathrm{V,U}}$ may make the operation of the transesterification reaction safer.

6. Formulation of the optimization problem and solution method

The general constrained variational problem, which should be considered in the batch reactor optimization, is stated as follows

$$\mathrm{MIN}\,J[u(t)]=G[x(x_{\mathrm{f}}),t_{\mathrm{f}}]+\int_{f_0}^{t_{\mathrm{f}}}F(x,u,t)\mathrm{d}t \tag{7}$$

subject to

$$\dot{x}=f(x,u,t) \tag{8}$$

$$g(x,u,\dot{u},t)=0 \tag{9}$$

$$h(x,u,\dot{u},t)\geq 0 \tag{10}$$

$$x_{\mathrm{L}}\leq x(t)\leq x_{\mathrm{U}} \tag{11}$$

$$u_{\mathrm{L}}\leq u(t)\leq u_{\mathrm{U}} \tag{12}$$

Many researchers have studied different methods to solve the optimization problem [1,2,6,9]. In the above formulation, the system dynamic equation should be treated. Therefore, the problem is called a dynamic optimization problem. The various solution methods of the dynamic optimization problem have been studied by many workers and have their own merits and demerits. The solution method based on the mixed integration collocation (MICO) method proposed by

Jang and Yang [6], is used to find the optimal trajectory. The cubic spline interpolation method [18] instead of the orthogonal polynomial.

In this work, the following optimization problems has been formulated

$$\underset{u}{\mathrm{MIN}}\,\Phi = t_\mathrm{f} \tag{13}$$

subject to

$$\dot{x} = f(x, u, t) \tag{14}$$

(system equations described in Table 3)

$$\frac{\mathrm{d}T}{\mathrm{d}t}\Big|_\mathrm{L} \le \frac{\mathrm{d}T(t)}{\mathrm{d}t} \le \frac{\mathrm{d}T}{\mathrm{d}t}\Big|_\mathrm{U} \tag{15}$$

$$X_\mathrm{f,L} \le X_\mathrm{f} \tag{16}$$

$$[\mathrm{D}]_\mathrm{f} \le [\mathrm{D}]_\mathrm{U} \tag{17}$$

$$N_\mathrm{V}(t) \le N_\mathrm{V,U} \tag{18}$$

Note that the objective function of the problem is the reaction time of the transesterification reaction, and the process constraints are incorporated in the above formulation. It is assumed that neither a singular arc nor a discontinuous point exists in the optimal control profile.

Successive quadratic programming (SQP) is used as the non-linear programming (NLP) solver, and the cubic spline interpolation method is also used in order to parametrize the control vector in this work. The temperature profile, which is discretized by the number of elements specified, is taken as the decision variable in the optimization. The cubic spline points are equally spaced between 0 and t_f and used as the characterization points of the control vector, $\boldsymbol{u}$. The discretized control vector, $\boldsymbol{u} \in R^N(u_i, i = 1, 2, \ldots, N)$, is employed to build the continuous curve of the temperature trajectory using the cubic spline. Then, the continuous temperature trajectory is applied to solve the batch reactor model and to evaluate the objective function and constraints as mentioned above. The ordinary differential equation (ODE) solver (Ranger–Kutta fourth-order method) returns the system information to the non-linear solver, SQP. The end-time of the reaction t_f is determined when the reaction reaches the specified conversion (for example, $[\mathrm{EG}]_\mathrm{L} = 0.05[\mathrm{EG}]_0$) by integrating the process model. The constant temperature profile, 180°C, 190°C, and so on, is used as the initial estimate of the control vector.

7. Optimization results

The optimal temperature trajectories, which minimize the reaction time t_f under the process constraints, have been obtained. Fig. 3 shows the results under the constraints: $[\mathrm{D}]_\mathrm{U} = 0.15$, 0.19 and 0.23 mol l^{-1} and $N_\mathrm{V,U} = 0.006$ mol with $X_\mathrm{f,L} = 0.97$. The temperature profiles are bounded up to the conversion, 80% by the rate of temperature increase and the amount of vaporized EG (N_V) As $[\mathrm{D}]_\mathrm{U}$ decreases, the reaction time that satisfies the conversion increases. The profiles of the conversion are presented in Fig. 4. The reaction time for a conversion of 97% is about 100 min. For $[\mathrm{D}]_\mathrm{U} = 0.15$ mol l^{-1}, the temperature profile is bounded by the constraints over the entire reaction time region. As shown in Fig. 5, the concentration of DEG is within the constraint $[\mathrm{D}]_\mathrm{U}$. The amount of vaporized EG satisfies the constraint $N_\mathrm{V,U}$ as shown in Fig. 6. Thus the optimal temperature trajectories minimize the reaction time while satisfying the process constraints considered in the problem formulation. In this optimization study, the optimal temperature trajectory reduces the reaction time of the transesterification stage by about 40 min (from 150 to 110 min), while satisfying the process constraints. The analysis of the these results is discussed in detail and the experimental

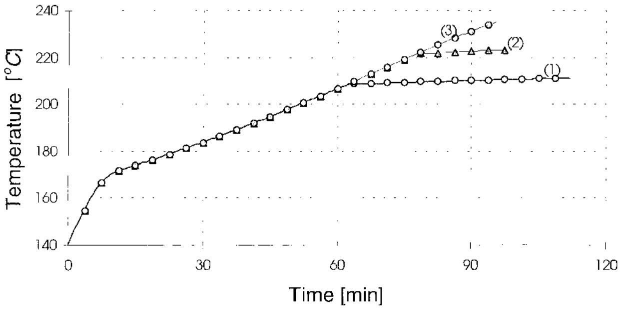


Fig. 3. Optimal temperature profiles achieved under the minimum reaction time policy when $N_\mathrm{V,U} = 0.006$, $-1 \le \mathrm{d}T/\mathrm{d}t \le 4$ and $X_\mathrm{f,L} = 0.97$ with (1) $[\mathrm{D}]_\mathrm{U} = 0.15$, (2) $[\mathrm{D}]_\mathrm{U} = 0.19$ and (3) $[\mathrm{D}]_\mathrm{U} = 0.23$.

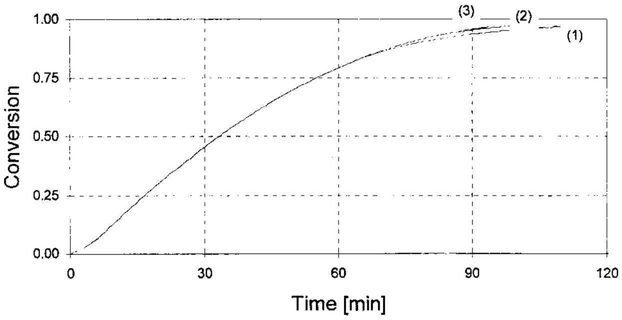


Fig. 4. Conversion profiles under the minimum reaction time policy when $N_\mathrm{V,U} = 0.006$, $-1 \le \mathrm{d}T/\mathrm{d}t \le 4$ and $X_\mathrm{f,L} = 0.97$ with (1) $[\mathrm{D}]_\mathrm{U} = 0.15$, (2) $[\mathrm{D}]_\mathrm{U} = 0.19$ and (3) $[\mathrm{D}]_\mathrm{U} = 0.23$.

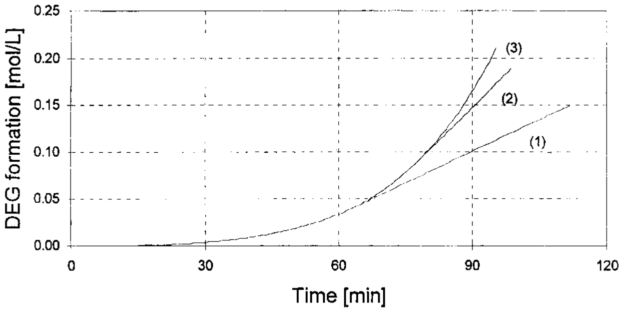


Fig. 5. DEG formation profiles under the minimum reaction time policy when $N_\mathrm{V,U} = 0.006$, $-1 \le \mathrm{d}T/\mathrm{d}t \le 4$, and $X_\mathrm{f,L} = 0.97$ with (1) $[\mathrm{D}]_\mathrm{U} = 0.19$, (2) $[\mathrm{D}]_\mathrm{U} = 0.19$ and (3) $[\mathrm{D}]_\mathrm{U} = 0.23$.

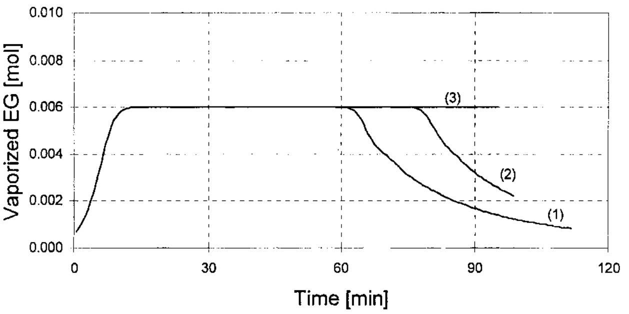


Fig. 6. N_V profiles under the minimum reaction time policy when $N_{V,U} = 0.006$, $-1 \le dT/dt \le 4$ and $X_{f,L} = 0.97$ with (1) $[D]_U = 0.15$, (2) $[D]_U = 0.19$ and (3) $[D]_U = 0.23$.

results with this optimal temperature trajectory are presented (see below). The experimental results agree well with the simulation results. Additional simulation studies have been performed (e.g. different constraints: minimum/maximum rate of temperature increase, allowable DEG concentration, final conversion, etc), and similar results to those in Fig. 3 were obtained.

8. Analysis and minimization of the reaction time

As mentioned previously, the minimum time optimization problem of the transesterification reaction has many constraints: maximum rate of temperature increase, flooding (EG and DMT can escape form the distillation column with the methanol condensate), maximum allowable by-product concentration (especially the concentration of DEG), and minimum allowable conversion.

In the experimental study, the following analyses and experimental observations were used to explain the free-end-time optimization result which was obtained by solving the free-end-time optimization problem.

The mechanism of the transesterification reaction is complex, and reliable kinetic data are difficult to obtain. The main reaction of transesterification is relatively well known [3,4,14–16]. In this work, this mechanism [3,16] has been used to the main reaction kinetics (see the details in Ref. [13]). The total-mass-based kinetic equations of the main reactions are obtained as follows. for $N_{B,0}/N_{A,0} \neq 2$

$$C_1 N_M + C_2 \ln\left|\frac{N_{B,0}}{N_{B0} - N_M}\right| + 2C_3 \ln\left|\frac{N_{A,0}}{N_{A,0} - 0.5N_M}\right| = \int_0^{t'} k_a \mathrm{d}t \qquad (19)$$

For $N_{B,0}/N_{A,0} = 2$

$$C_1 N_M + C_2 \ln\left|\frac{N_{B,0}}{N_{B0} - N_M}\right| + C_3\left(\frac{1}{(N_{B,0} - N_M)} - \frac{1}{N_{B,0}}\right) = \int_0^{t'} k_a \mathrm{d}t \qquad (20)$$

where C_1, C_2 and C_3 are the integration constants.

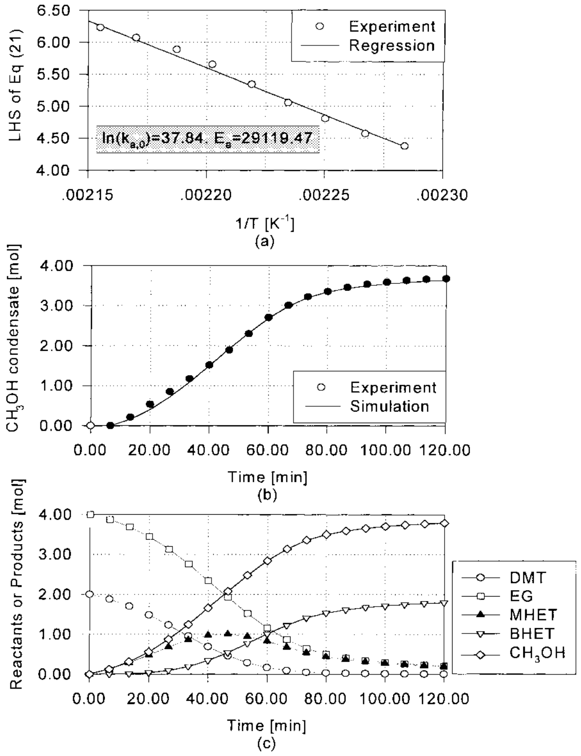


Fig. 7. Typical non-isothermal experiment: (a) kinetic analysis result, (b) comparison of simulation and experiment and (c) product distribution.

For the non-isothermal reaction, we can obtain the rate constants of the main reaction by

$$\ln\left[\frac{(M_0 - N_M M_{W,M})^2}{(N_{B,0} - N_M)(N_{A,0} - 0.5N_M)}\frac{\mathrm{d}N_M}{dt}\right] = \ln(k_{a,0}) - \left(\frac{E_a}{R}\right)\frac{1}{T} \qquad (21)$$

The results of the non-isothermal kinetic data analyses provide the following Arrhenius equation

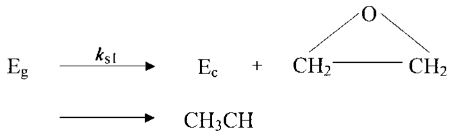
$$\ln(k_a) = 35.01428 - \frac{26620.19}{RT} \qquad (22)$$

Even though the *irreversible* reaction is induced by the removal of methanol, the kinetic model presented by very accurate as shown in Fig. 7. It is clear that the reaction temperature must be at its highest allowable value in order to minimize the reaction time for the irreversible reaction. Note that the left-hand side of Eq. (19) or Eq. (20) monotonically increases with N_M

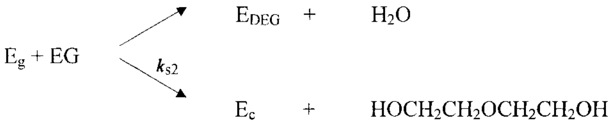
$$\frac{\mathrm{d(LHS)}}{\mathrm{d}M_M} = \frac{(M_0 - N_M M_{W,M})^2}{(N_{B,0} - N_M)(N_{A,0} - 0.5N_M)} > 0, N_M \in [0, \min(2N_{A,0}, N_{B,0})] \qquad (23)$$

Therefore, the reaction temperature must be at its highest allowable value in order to maximize the conversion at any given time. However, the highest allowable temperature at any given time will be constrained by the duty of the heater, flooding and the by-product concentration as shown in the numerical optimization results.

So far, we have discussed the main reaction only; the side reaction of transesterification (especially DEG formation [5]) should also be considered. Some side products (such as DEG) have an effect on the quality of the product. Ravindranath and Mashelkar [12] have reviewed the mechanism of DEG formation. The formation of DEG due to the dehydration of EG is low even at 280°C, and DEG is formed via a different mechanism. The degradation of the 2-hydroxyethyl ester and group (E_g) is likely to proceed via a five-membered orthoester-type intermediate, and the formation of acetaldehyde via the intermediate formation of ethylene oxide



The formation of DEG is caused by the interaction of EG with E_g as shown below



DEG is also formed by the following mechanism

$$E_g + E_g \xrightarrow{k_{s3}} E_c + E_{DEG}$$

Ravindranath and Mashelkar [12] noted that, although there is controversy about the reaction mechanism of DEG formation the above equations probably represent the correct routes for the formation of DEG and acetaldehyde. These side reactions, the formation of acetaldehyde and DEG, have larger activation energies than that of the main reaction (see Table 2). A high temperature favours reactions with a high activation energy, and vice versa [11]. From a consideration of the kinetics of the main reaction and side reaction, it is clear that the transesterification reaction should be performed in the low temperature range as rapidly as possible in order to minimize the reaction time and to reduce the side reaction products.

The initial reaction rate is low because of the low temperature (about 140–160°C). Therefore, the initial reaction rate is constrained by the duty of the heater. The maximum rate of temperature increase of the laboratory-scale semi-batch reactor is about 2.5°C min^{-1}. A higher initial temperature is desirable to reduce the induction time and to remove methanol efficiently. The initial heat-up stage is the key to optimization, because a faster reaction at a lower temperature will produce less side product and reduce the reaction time.

Flooding of the reactants (especially DMT) causes serious problems to the column and condenser as mentioned previously. When the reactor temperature reached about 160–165°C from an initial 140°C with maximum heating, the maximum allowable temperature was constrained by flooding. The maximum allowable rate of temperature increase, which does not cause flooding of the reactants, was about 0.6°C min^{-1} in the middle of the reaction.

The transesterification stage is followed by the polycondensation stage. In the polymerization stage, the rate-determining step is the removal of EG, so a high temperature (260–290°C) and a low pressure (0.5–1.0 Torr) are required. The EG concentration of the product in the transesterification stage should be as low as possible. Therefore, at the end of the transesterification stage, the reactor temperature is required to be over 220–240°C.

Consequently, the realistic optimal temperature trajectory of the transesterification reaction can be summarized in the following two stages.

1. The temperature is increased from 140°C to 160–165°C in 10 min with maximum heating ($dT/dt \approx 2.5$°C min^{-1}).
2. The temperature is increased from 160–165°C to 210–220°C for 80–100 min ($dT/dt \approx 2.5$°C min^{-1}).

The first stage ensures a reduction in the induction time (faster removal of methanol from the reactor) and the side reactions. The second stage ensures that there is no flooding and allows safe batch operation.

9. Experimental system

DMT and EG were prepared in the molar ratio of 1 : 2. In this experiment, 388.4 g of DMT (2 mol) and 248.3 g of EG (4 mol) were used. A mixture of zinc acetate and calcium acetate was used as a catalyst [17]. The catalyst concentration was fixed at an allowable level, used in industry. The reactor was a 1.0 l flask with four necks, and the reacting mixture was mixed by a two-paddle agitator connected to a variable RPM motor. Stirring was executed throughout the batch operation with constant RPM. Stirring is not important because mass transfer is not the rate-determining step in the transesterification stage. An electrical heater was used to heat the laboratory-scale semi-batch rector. Four resistance temperature detectors (RTDs) were used. One RTD measured the jacket temperature, and the remaining three RTDs measured the reactor temperature, and the top and bottom temperatures of the distillation column. The distillation column was packed with glass beads to separate the volatile EG from methanol. The top temperature of the column was maintained between 70°C and 100°C. This temperature range of the distillation column ensures the condensation of volatile EG and the vaporization of methanol. The vaporized methanol was continuously condensed by the water-cooled condenser, which was attached to the packed column. The condensed methanol was weighed automatically at each sampling time (5 s) by an electrical balance, which provided information on the extent of reaction and the kinetics. The computer (IBM PC 486DX) was connected to

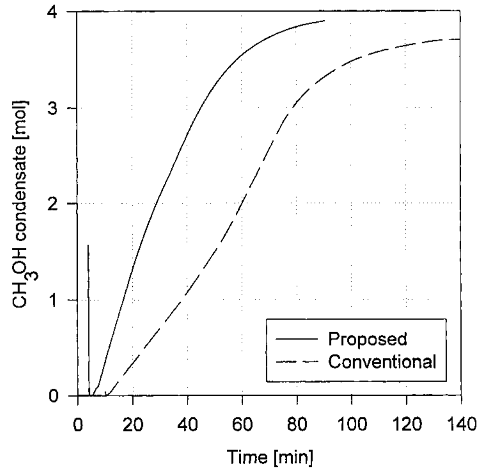


Fig. 8. Comparison of optimal and conventional trajectories (experimental result with 95% conversion).

analogue–digital (A/D) and digital–analogue (D/A) input–output (I/O) boards with a 12-bit converter. The data acquisition and control system were programmed in C language. The reactor temperature was controlled by a conventional PID controller. The mixture of DMT and EG was heated to 140°C, the melting temperature of DMT. After the melting of DMT , the prepared catalyst was injected into the batch reactor.

10. Experiment with optimal temperature trajectory

The experimental result for the proposed optimal temperature trajectory is compared with that for the conventional trajectory in Fig. 8. As expected, the initial heat-up reduced the induction time of methanol and increased the initial reaction rate. In the middle of the batch, in order to prevent flooding, the heat-up rate was slowed down using the proposed strategy. The entrainment of DMT and high molecular weight oligomers was negligible and flooding did not occur, and the reaction rate reacted the desired value. At the end of the reaction, the remaining EG was vaporized as expected. The undesired side product (DEG) concentration, analysed by gas chromatography (GC) and mass spectroscopy, was within the allowable level. The batch time of the prepolymerization step was reduced by 30–40 min (from 150 to 110 min).

11. Conclusions

An optimization study of the transesterification stage in the production of PET was performed, and the optimal temperature trajectory was obtained using the NLP technique combined with the cubic spline interpolation method. The process constraints (rate of temperature increase, concentration of DEG and flooding) were considered and treated in the numerical study. An analysis of a simple kinetic model of the main reaction, qualitative considerations and experimental observations were presented, and an experimental study using the proposed optimal temperature profile was performed. The process constraints (maximum allowable rate of temperature increase and flooding) were determined by experiment. The proposed optimal temperature trajectory reduces the induction time and side product concentration, and allows rapid vaporization of methanol in the reactor. The proposed optimal temperature trajectory reduces the batch reaction time from 150 to 110 min while satisfying the process constraints. It is expected that the proposed optimal temperature trajectory will improve the productivity of the batch reactor and the quality of the product, resulting in a significant economic benefit.

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Appendix

Nomenclature

C	integration constant
k_a	third-order rate constant of the main reaction [g^2 mol^{-2} s^{-1}]
N	number of moles
$\mathbf{x}$	state vector
$\mathbf{u}$	control vector
X	conversion

Subscripts

0	initial condition
A	DMT
B	EG
M	methanol
f	the end time of the reaction
L	lower bound
U	upper bound

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