OPTIMIZATION FOR THE MINIMUM REACTION TIME OF PET ESTERIFICATION

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Abstract – We have investigated the direct esterification reaction between terephthalic acid (TPA) and ethylene glycol (EG) in semi-batch reactors, the first stage process for making polyethylene terephthalate (PET), to get optimum conditions for the minimum reaction time. An independent-variable-minimization problem, i.e., a free-end-time/fixed-end-point problem, has been formulated for the system, and then converted to a dependent-variable-minimization (fixed-end-time/free-end-point) problem by a coordinate transformation, for the latter problem readily yields to established solution methods. We have solved this reformulated problem to obtain the optimal temperature profiles in the reactor required for the minimum reaction time, by iteratively improving the temperature (manipulating variable) profile using the Pontryagin's minimum principle. The results prove that the method employed here successfully finds an optimal solution for the PET esterification process. The reduction of the reaction time realized following this optimal temperature profile in the reactor was, however, found to be smaller than expected, due to the approximating assumptions of neglecting the solubility equation of TPA in the model. The results obtained using a more improved model of the system will be reported in the future.

Key words: Coordinate Transformation, Minimum Reaction Time, Optimal Temperature Profile, PET Esterification, Pontryagin's Principle

INTRODUCTION

Polyethylene terephthalate (PET) is an industrially important major polymer material which is widely used for the production of synthetic fibers, films and bottles. The still-growing demand for these products continually warrants the production costs reduced and the product quality improved. The research along this line has been conducted in two ways: one is to develop more efficient catalysts for the involved reactions and the other is to increase the reaction productivity employing various process optimization techniques. This paper is about the latter route.

The synthesis of PET requires four distinct reaction stages: (1) transesterification or direct esterification, (2) prepolymerization, (3) melt polycondensation, and (4) solid-state polycondensation. The last step is required only for the production of bottles. In this study, we deal with the first reaction step, i.e., the direct esterification reaction between terephthalic acid (TPA) and ethylene glycol (EG) with water removed from the reaction system to produce BHET (Bis-hydroxyethyl terephthalate) and its oligomers which become the starting material for the final PET product in subsequent reaction steps. Until high purity TPA has become available recently on the industrial scale, the transesterification reaction between dimethyl terephthalate (DMT) and EG used to be carried out in the presence of one or more metal catalysts with methanol removed continuously from the reaction system. But now thanks to the technological advance-

ments made in this industry, TPA is replacing DMT as the raw material, since with the acid end groups of TPA playing the role of the catalysts, we don't need any catalyst in the TPA and EG esterification reaction.

In this paper, we study this direct esterification reaction of TPA and EG in semi-batch reactors as to whether the reaction time can be reduced by the optimal control of the system variables. The examples of these system variables which can be adjusted in this optimum-seeking problem are the initial composition of the reactants, the residence times of the materials in the reactor, the reactor temperature and pressure, the recycle ratio of the oligomers produced, etc. Few attempts have been made to solve this time-optimal problem of the direct esterification of TPA and EG as compared with those for the transesterification of DMT and EG (e.g., Kumar et al. [1984] and Lee [1993]). The most apparent reason for this is believed to lie with the modeling difficulties in the direct esterification reaction arising from the fact that the low solubility of TPA in EG renders the reaction medium of multi-phase. Here we, however, have assumed that the reacting system is homogeneous by neglecting the vapor phase and the equilibrium solubility question of the system, to simplify the problem formulation yet to retain the main features in order to prove the methodology adopted in this study.

The formulated problem is then of free-end-time/fixed-end-point form, i.e., an independent-variable-minimization problem, for which rigorous proof has not been established for the existence of solutions. So we have converted this problem to a fixed-end-time/free-end-point form, i.e., a dependent-variable-

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minimization problem, which is readily solvable by standard methods. The coordinate transformation by Kwon and Evans [1975] has been employed for this conversion and the control vector iteration (CVI) procedure [with the reaction temperature having been chosen as the control (manipulating) variable] based on the Pontryagin's minimum principle was followed. The kinetic model together with the appropriate parameters for the system has been adopted from the papers by Yamada et al. [1985, 1986]. In order to be able to obtain the optimal solution, we need some constraints, since as the reactor temperature is raised, the reaction time gets short monotonically. We have chosen the constraint on the diethyl glycol (DEG) content in the final product because of its known detrimental effects on the product quality.

This two-point-boundary-value problem (see Denn [1969] for detailed analysis) is then solved yielding the optimal temperature profile of the reactor which would result in the shortest reaction time. The results by this optimal temperature profile have been compared with the results by other profiles including those generated simply maintaining industrially preferable isothermal conditions in the reactor. The reduction of reaction time realized by the control of the temperature according to thus-obtained optimal temperature profile was, however, smaller than expected. The reason for this can be ascribed to the oversimplified model neglecting the solubility equation of TPA. When a more detailed model is employed, however, more improved results are expected, and we will report them in the future.

MODELING OF THE DIRECT ESTERIFICATION REACTION

The various reactions occurring in this esterification process are given in Table 1 [Yamada et al., 1985]. The reacting mass is thus composed of many different compounds such as carboxyl end groups, ethylene glycol, hydroxyl end groups, diester groups, and water as the reactants, intermediates and products, and also free and bound diethyl glycols as the side products. Table 2 shows the values of the reaction rate constants for these reactions [Yamada, 1986]. It is assumed that all the species except ethylene glycol and water are nonvolatile, since the controlled reactor temperature is generally higher than 200°C, i.e., above the boiling temperatures of both ethylene glycol and water but below those of other species of the system.

Ravindranath and Mashelkar [1982, 1986] were the first to have developed a mathematical model for the continuous direct esterification system and then Yamada et al. [1985] followed by introducing a refined model for the same continuous system. Obtaining a reliable model for the esterification reaction in batch reactors is more difficult than these continuous cases, mainly because the transient concentrations of the compounds in the system cannot be easily measured, which makes the direct on-line comparison between simulations and experiments impossible. Yet solving the time-optimal problem of this batch esterification reaction by using a model is a worthy endeavor because potential economic savings in the industry through shorter reaction times is enormous.

Table 1. The reactions occurring in the esterification

Table 2. Rate constants for the reactions occurring in the esterification

Frequency factor A_i	$\dfrac{kg}{(g\text{-mol})\ (hr)}$	Activation energy E_i	$\dfrac{cal}{g\text{-mol}}$
k_1	1.8006×10^9		19640
k_2	1.8463×10^8		18140
k_3	4.5715×10^9		22310
k_4	7.9816×10^7		18380
k_5	9.0941		2810
k_6	6.8229×10^6		14960
k_7	2.4905×10^{15}		42520
k_8	4.9810×10^{15}		42520
k_9	9.9620×10^{15}		42520

We now model the batch esterification reaction system by adopting the following assumptions.

1. TPA is completely dissolved in EG before the reactions start.

2. The moles of the vapor phase in the system are negligible compared with those of the liquid phase. With these assumptions 1 and 2, the system is regarded as homogeneous having the liquid phase only.

3. All acidic functions are performed by carboxyl end groups.

4. The reactivity of the functional groups does not depend on the polymer chain length, since the degree of polymerization is not very high in this esterification step.

5. In the DEG formation reactions, the reactivity of each hydroxyl end group is assumed the same, i.e., $k_8 = 2k_7$ and $k_9 = 4k_7$.

6. The sum of the free and bound DEG's represents the total moles of the DEG produced in the system.

Incorporating the above assumptions into our model, we have the reaction system as shown in Table 3 where C's represent the concentrations of the components and R's the reaction rates. This system is then solved yielding the optimal temperature profile of the reactor which results in the shortest reaction time. The existence of the solution is guaranteed because whereas the higher temperature shortens the reaction time in general, the maximum-allowed-level of DEG's in the final product limits this high temperature profile.

FORMULATION OF THE OPTIMIZATION PROBLEM FOR THE MINIMUM REACTION TIME

Now we proceed to formulate our optimization problem, i.e., finding the optimal temperature profile of the batch reactor which minimizes the reaction time while satisfying the constraints of the system. That is, we minimize the objective function

$$J = t_f \text{ when } N_{1,f} \text{ and } W_{DEG,f} \text{ are given a priori.} \quad (1)$$

Here t_f=time at the completion of the reaction, $N_{1,f}$=moles of the carboxyl end groups on TPA at t_f, $W_{DEG,f}$=the level of DEG content at t_f. In other words, we seek the minimum reaction time when the desired conversion of TPA and the desired level

Table 3. The mole balance equations of the components in the reactions

$$\frac{dC_1}{dt} = -R_1 - R_2 - R_7$$

$$\frac{dC_2}{dt} = -R_1 + R_3 - R_2 - 2R_6$$

$$\frac{dC_3}{dt} = R_1 - R_2 - 2R_3 - 2R_4 - R_5$$

$$\frac{dC_4}{dt} = R_2 + R_3$$

$$\frac{dC_5}{dt} = R_1 + R_2 + R_4 + R_5 + R_6 + R_7 - \dot{Q}_4$$

$$\frac{dC_6}{dt} = R_4$$

$$\frac{dC_7}{dt} = R_5 + R_7$$

$$\frac{dC_8}{dt} = R_6 - R_7$$

where

$$R_1 = k_1 C_1 C_2 - k_2 C_3 C_5$$

$$R_2 = k_3 C_2 C_3 - k_4 C_4 C_5$$

$$R_3 = k_5 C_3^2 - k_6 C_2 C_4$$

$$R_4 = k_7 C_3^2$$

$$R_5 = k_8 C_2 C_3$$

$$R_6 = k_9 C_2^2$$

$$R_7 = k_1 C_1 C_8 - k_2 C_5 C_7$$

$\dot{Q}_4$=the moles of the water which leaves the reactor by evaporation per unit time.

$$= R_1 + R_2 + R_4 + R_5 + R_6 + R_7$$

of DEG in the product are given.

Thus here we have a free-end-time/fixed-end-point problem with nonlinear constraints. For linear systems solution methods to the minimum-time problems are available, but for this type of nonlinear minimum-time optimization problems the standard general method has not been fully established yet. There are two ways to solve this problem: either to convert the problem into the one of fixed-end-time/free-end-point type or to follow the scheme presented by Jang and Yang [1989]. The latter method requires the checking of the final constraints at each time step and also requires a substantially large number of iterations for finding the final time where the final constraints are exactly satisfied. In this study we have chosen the former because it is more straightforward and simple for our example. For converting the problem, a coordinate transformation similar to the one by Kwon and Evans [1975] has been introduced to the system so that the established standard solution method (e. g., Bryson and Ho [1975]) can be easily utilized.

In other words, instead of the free-end-time/fixed-end-point (independent-variable-minimization) problem we have a fixed-end-time/free-end-point (dependent-variable-minimization) problem for which the solution is proved to exist. This transformation is possible when we can find at least one dependent variable which monotonically increases as the reaction proceeds. Then we make this dependent variable become the new independent variable (new time coordinate) and the previous independent variable (old time coordinate) is made one of the new dependent variables while the other old dependent variables remain unchanged. In most polymerization reactions including the present esterification reaction, the conversion always monotonically increases with time and thus by adopting this conversion as our new independent variable we can make the said transformation work. We illustrate the procedure below.

The original variables consist of one independent variable, i. e., t (time) and eight dependent variables, i.e., x_1 through x_8, defined as

$$x_1 = 1 - N_1/N_{1,0}$$
$$x_i = N_i/N_{1,0} \quad (i = 2-8) \quad (2)$$

where $N_{1,0}$ and N_1 are the moles of the carboxyl end groups on TPA at time zero and time t, respectively, and N_i denotes the moles of the i-component at time t in the reaction medium. Here time is a dimensional variable whereas all x_i's are dimensionless.

Table 4 shows thus-derived state equations. Here we can easily notice that x_1 defined above is a monotone increasing variable with time because of N_1 decreasing with time, and thus denotes the conversion of the reaction. So this x_1 becomes our new independent variable. The coordinate transformation of the system equations is then performed by changing the variables as shown below.

$$x_1 \rightarrow \tau$$
$$t \rightarrow y_1$$
$$x_i \rightarrow y_i \quad (i = 2-8)$$
$$1/f_1 \rightarrow g_1$$

Table 4. The dimensionless mole balance equations of the components in the reactions

$$\frac{dx_1}{dt} = (r_1 + r_2 + r_7)N_{1,0}/m_L \equiv f_1$$

$$\frac{dx_2}{dt} = (-r_1 + r_3 - r_5 - 2r_6)N_{1,0}/m_L \equiv f_2$$

$$\frac{dx_3}{dt} = (r_1 - r_2 - 2r_3 - 2r_4 - r_5)N_{1,0}/m_L \equiv f_3$$

$$\frac{dx_4}{dt} = (r_2 + r_3)N_{1,0}/m_L \equiv f_4$$

$$\frac{dx_5}{dt} = (r_1 + r_2 + r_4 + r_5 + r_6 + r_7)N_{1,0}/m_L - \dot{q}_w \equiv f_5$$

$$\frac{dx_6}{dt} = r_4 N_{1,0}/m_L \equiv f_6$$

$$\frac{dx_7}{dt} = (r_5 + r_7)N_{1,0}/m_L \equiv f_7$$

$$\frac{dx_8}{dt} = (r_6 - r_7)N_{1,0}/m_L \equiv f_8$$

where

$r_1 = k_1(1-x_1)x_2 - k_2 x_3 x_5$

$r_2 = k_3(1-x_1)x_3 - k_4 x_4 x_5$

$r_3 = k_5 x_3^2 - k_6 x_2 x_4$

$r_4 = k_7 x_3^2$

$r_5 = k_8 x_2 x_3$

$r_6 = k_9 x_2^2$

$r_7 = k_1 x_1 x_8 - k_2 x_5 x_7$

m_L = the mass of the reaction medium

$\dot{q}_w$ = the dimensionless moles of the water which leaves the reactor by evaporation per unit time.

$= (r_1 + r_2 + r_4 + r_5 + r_6 + r_7)N_{1,0}/m_L$

$$f_i/f_1 \rightarrow g_i \quad (i = 2\text{-}8) \tag{3}$$

where τ represents the new dimensionless independent variable (new time=the conversion of the reaction) and y_i's the new dimensionless dependent variables except y_1 which is dimensional.

The final state equations resulting from the above coordinate transformation are then as follows.

$$\dot{y}(\tau) \equiv \frac{dy(\tau)}{d\tau} = g(y, u, \tau) \tag{4}$$

where y and u denote the new state variable vector and the manipulating (control) variable vector, respectively. In our problem here, the reactor temperature, $T(\tau)$, is chosen as $u(\tau)$.

The optimization problem then comprises this state equation of Eq. (4) with the boundary conditions of time, i.e.,

$\tau_0 = 0$, and $\tau_f = $ fixed

(final conversion, τ_f, is assumed given a priori.) (5)

and the objective function,

$$J = y_1(\tau_f) \tag{6}$$

which should be minimized with the given constraints at $\tau = \tau_f$,

$$h[y(\tau_f)] = 0 \tag{7}$$

The specification of the DEG content in the final product is an example of the constraints of Eq. (7).

We have combined Eq. (6) and Eq. (7) in this study to have a new objective function to be minimized as shown in Eq. (8).

$$J = \frac{y_1(\tau_f)}{y_3(\tau_f)} \bigg/ \left[\frac{y_1(\tau_f)}{y_3(\tau_f)}\right]_0 + p\frac{W_{DEG,f}}{[W_{DEG,f}]_0} \tag{8}$$

where $W_{DEG,f} = m_{DEG,f}/[y_3(\tau_f)M_3]$, $m_{DEG,f}$ = the total mass of DEG in the product, M_3 = molecular weight of BHET.

Here we minimize the reaction time $(y_{1,f})$ per unit dimensionless mole of BHET produced and the DEG level $(m_{DEG,f})$ per unit mass of BHET produced at the given final conversion (τ_f), since we always want to maximize the production of BHET also. The parameter p represents the relative weight of the DEG content level $(W_{DEG,f})$ as compared to the reaction time per unit dimensionless mole of BHET produced in the objective function J which is minimized. We use for both terms in Eq. (8) the values normalized by their pre-iteration values to maintain comparable dimensionless magnitude between them.

The set of Eqs. (4), (5) and (8) is solved using the Pontryagin's minimum principle with the Hamiltonian, H, defined as

$$H(y, u, \tau) = \lambda^T g(y, u, \tau) \tag{9}$$

where λ denotes the adjoint (or costate) variable vector.

The detailed standard procedure of solving this optimization (fixed-end-time/free-end-point) problem, is described in the Appendix.

NUMERICAL ALGORITHM FOR OBTAINING THE OPTIMUM TEMPERATURE PROFILES

The optimal temperature profile of the batch reactor is obtained solving the above two-point-boundary-value problem with the iteration of the temperature profile in the direction of the gradient of the Hamiltonian with respect to temperature. Some of such numerical examples are illustrated in Ray and Szekely [1973] and Ray [1981]. The procedure adopted in this study is as follows.

(a) Guess a temperature profile, $T(\tau)$, over the entire time domain, $0 \leq \tau \leq \tau_f$ (A simplest starting guess is an isothermal condition.).

(b) Integrate Eq. (4) forward in τ to get $y(\tau)$ over $0 \leq \tau \leq \tau_f$.

(c) The differential equation of the adjoint variable, λ (shown in Appendix), is integrated backward in τ to get $\lambda(\tau)$.

(d) The gradient, $\partial H(\tau)/\partial T$, is computed over the entire time domain, from which the new temperature profile is then obtained as follows.

$$T_{j+1}(\tau_k) = T_j(\tau_k) - \varepsilon_{opt,j}\left(\left.\frac{\partial H}{\partial T}\right|_{\tau_k}\right)_j \tag{10}$$

where $\varepsilon_{opt,j}$ is the constant which is optimally chosen at j-th iteration step to keep the objective function decreasing.

(e) The iteration is repeated until convergence on $T(\tau)$ is attained.

RESULTS AND DISCUSSION

Before we try to obtain the optimal temperature profile minimizing the reaction time per unit dimensionless mole of BHET produced and the DEG content level in the product at the given conversion, we first get the results of the reaction time and the DEG content level when we maintain the industrially preferable isothermal conditions in the batch reactor. As shown in Fig. 1, the reaction time per unit dimensionless mole of BHET produced gets smaller as the reactor temperature is increased, whereas the DEG content level in the product gets larger. This is not surprising because as Table 2 shows, all the reactions including the DEG production reactions proceed faster as temperature rises.

Here, as mentioned before, we notice an important result: unless we minimize or impose a certain limit to the final DEG content level, we have a trivial optimization problem, i.e., the higher the reactor temperature, the shorter the reaction time. This is the reason why we need a nonzero value for the parameter p in Eq. (8).

Fig. 2 shows an example of the numerical scheme finding the optimal temperature profile which, at the given conversion of 0.98, gives the shortest reaction time per unit dimensionless mole of BHET to be 0.0723 hr, and the target DEG content level per unit mass of BHET in the product to be 0.01. Starting with the initial guess of the isothermal condition of 520 K, we have obtained the final result after 17 iterations. Some of the temperature profiles at the intermediate iteration steps are also shown. The value of the parameter p in Eq. (8) has been adjusted to meet the final DEG content level which has been imposed a priori. Fig. 3 clearly reveals the effect of this parameter p in the optimization program, by exhibiting the different optimal temperature profiles when we use different p values to meet different final DEG content levels imposed on the system.

Fig. 4 shows how much better the above-obtained optimal temperature profile performs as compared with other temperature profiles, i.e., the isothermal condition, a decreasing

temperature profile, and increasing temperature profiles, all of which produce the same final DEG content level. Although the optimal solution exhibits the best result in the reaction time per unit dimensionless mole of BHET (the yield of the reaction), the differences are surprisingly small, which are attributable to our earlier assumption of neglecting the multi-phase nature of the reacting system. The conclusions are, therefore, that our scheme successfully generates the optimal temperature profile in the batch reactor leading to minimum reaction time, but due to the overly-simplified reaction model the reduction of the reaction time is not much. With an enhanced model including the solubility equation, however, we can accomplish much larger reduction of the reaction time.

Finally two more graphs are reported here. Fig. 5 and Fig. 6 show the results when different final conversion constraints and different initial mole ratios of the reactants of EG/TPA,
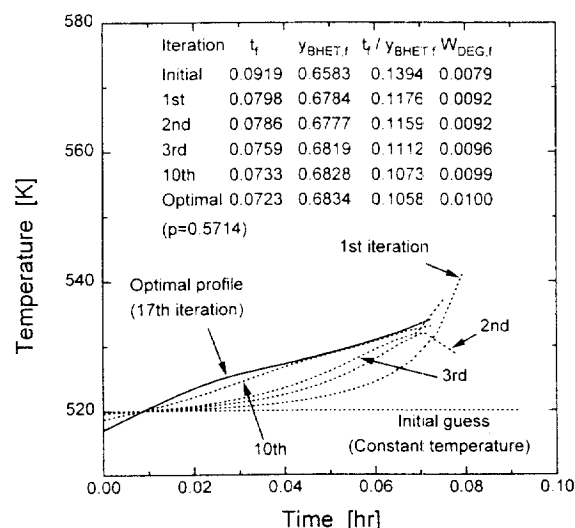

Fig. 2. An example showing how the reactor temperature profile can be improved by the iteration based on the gradient of the Hamiltonian.
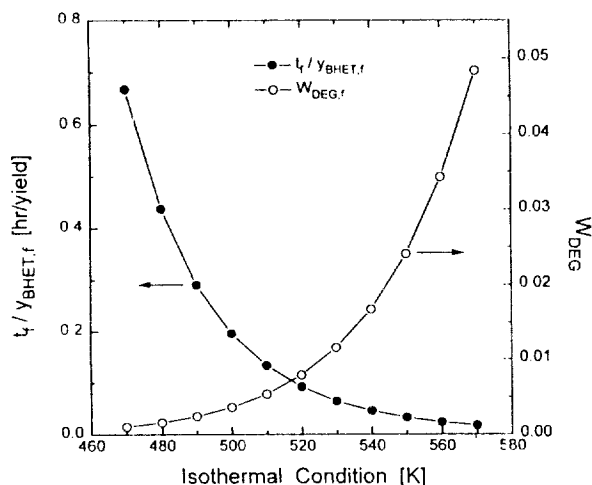

Fig. 1. The reaction time per unit dimensionless mole of BHET and the total mass of EG per unit mass of BHET at the end of reaction plotted against the imposed isothermal conditions in the reactor.
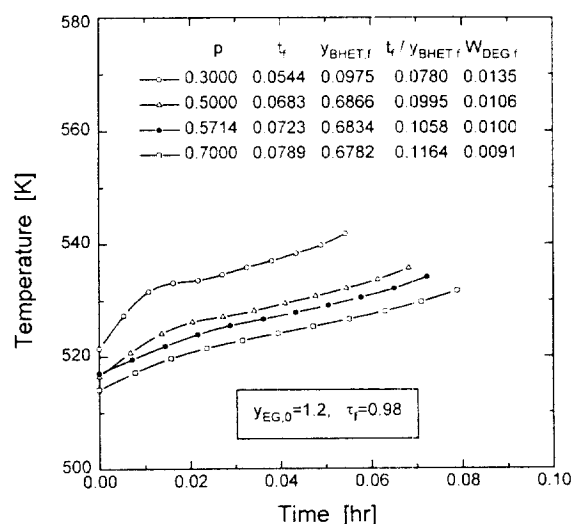

Fig. 3. An example showing how different values of the parameter p in the objective function produce different final DEG levels.
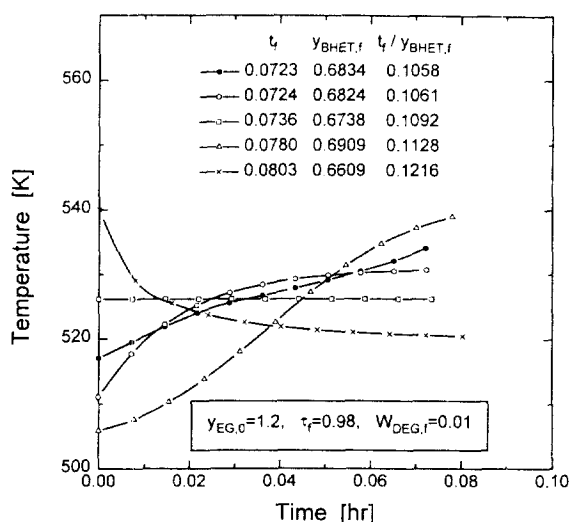
Fig. 4. Comparison of the reaction times produced by the optimal temperature profile and other temperature profiles.
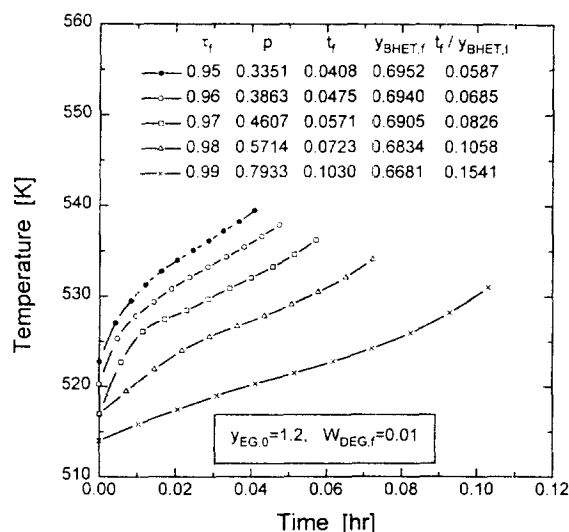

Fig. 5. The effect of different imposed final conversions on the reaction results.
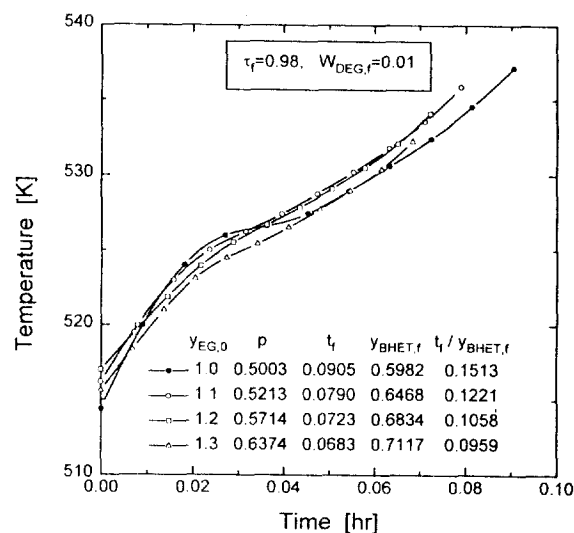

Fig. 6. The effect of different initial mole ratios of EG/TPA on the reaction results.

The imposed optimal level of the final conversion of the esterification is thus determined by considering the optimization of the polycondensation together with the present problem. Since in this study we are only concerned with the esterification optimization, we assume the final conversion to be given a priori.

Fig. 6 reveals that the larger initial mole ratio of EG/TPA, the smaller reaction time and the larger yield. In other words, the effect of larger initial mole ratio of EG/TPA is the same as that of smaller final conversion explained above in Fig. 5. Again, there is an upper limit to large mole ratio of EG/TPA in real industrial situations (normally 1.3 is the limit), because too large mole ratio results in too much unreacted EG at the end of reaction which hurts the downstream processes. Just like in the cases of Fig. 5, we can see that the optimal initial mole ratio of EG/TPA can only be determined considering the polycondensation together with the present problem. So in this study we assume this initial mole ratio to be given a priori.

CONCLUSIONS

The direct esterification reaction between terephthalic acid (TPA) and ethylene glycol (EG) in semi-batch reactors, which is the first stage process for making polyethylene terephthalate (PET), has been investigated generating optimum reactor temperature profile for the minimum reaction time. Using a coordinate transformation we converted an independent-variable-minimization problem to a dependent-variable-minimization problem, and then successfully solved this two-point-boundary-value-problem to obtain the optimal temperature profile.

Although the reduction of the reaction time when we follow the optimal temperature profile has turned out to be smaller than expected due to the approximating assumptions of neglecting the solubility equation of TPA in EG, we have proved that the method adopted in this study successfully finds the optimal temperature profile in the batch reactor of TPA and EG. With an enhanced reaction model including the solubility equation, much better results are expected and we will report them in the

respectively, are imposed for this optimization problem. Interesting findings are obtained. First, in Fig. 5, as the imposed final conversion (τ_f) gets smaller, the reaction time (t_f) becomes shorter and the production of BHET ($y_{BHET,f}$), i.e., the yield of the esterification reaction, becomes larger. The reason for this seemingly odd result of a smaller final conversion producing a larger yield, is that the smaller final concentrations of the products caused by the smaller conversions allow higher reactor temperatures possible, which results in shorter reaction time and larger yield. The reaction time per unit dimensionless mole of BHET, i.e., $t_f/y_{BHET,f}$, is even better than either of the two as the imposed final conversion (τ_f) gets smaller.

In real industrial situations, however, there is a lower limit to small τ_f (normally 0.95 is the limit), because too small conversion results in too much unreacted EG and TPA which would adversely affect the optimal operation of the downstream processes of PET production, i.e., polycondensation.

future.

APPENDIX

The standard solution method of the two-point-boundary-value problem is illustrated in the following (See Bryson and Ho [1975] for details.).

The state equation of the system:

$$\dot{y}(\tau) \equiv \frac{dy(\tau)}{d\tau} = g[y(\tau),\ u(\tau),\ \tau];\ y(\tau_0)\ \text{given},\ \tau_0 \le \tau \le \tau_f \quad \text{(A1)}$$

where y is the state variable, τ is time, and u is the control (manipulating) variable.

The objective function (performance index):

$$J = \phi[y(\tau_f),\ \tau_f] + \int_{\tau_0}^{\tau_f} L[y(\tau),\ u(\tau),\ \tau]\, d\tau \quad \text{(A2)}$$

where ϕ denotes the penalty function associated with the values at the terminal time and the second term on the right hand side denotes the penalty function associated with the values along the path.

When the constraints at the terminal time

$$\psi[y(\tau_f),\ \tau_f] = 0 \quad \text{(q equations)} \quad \text{(A3)}$$

are imposed, the objective function J becomes

$$J = \phi[y(\tau_f),\ \tau_f] + v^T \psi + \int_{\tau_0}^{\tau_f} L[y(\tau),\ u(\tau),\ \tau]\, d\tau \quad \text{(A4)}$$

where v denotes the q-vector multiplier which is to be determined.

The scalar function, Hamiltonian, is defined as follows.

$$H[y(\tau),\ u(\tau),\ \lambda(\tau),\ \tau] = L[y(\tau),\ u(\tau),\ \tau] + \lambda^T(\tau)\, g[y(\tau),\ u(\tau),\ \tau] \quad \text{(A5)}$$

where λ (transpose of $\lambda = \lambda^T$) denotes the adjoint (costate) variable.

Then the equation of the adjoint variable, λ, becomes

$$\dot{\lambda} \equiv \frac{d\lambda(\tau)}{d\tau} = -\frac{\partial H}{\partial y} \equiv -\frac{\partial L}{\partial y} - \frac{\partial g}{\partial y}\lambda \quad \text{(A6)}$$

where the values of λ at the terminal time are given by

$$\lambda(\tau_f) = \left[\frac{\partial \phi}{\partial y} + \frac{\partial \psi}{\partial y} v\right]_{\tau_f} \quad \text{(A7)}$$

And the control (manipulating) variable is determined by the equation which represents the stationary points of H with respect to u, i.e., the gradient of the Hamiltonian with respect to u being zero.

$$\frac{\partial H}{\partial u} \equiv \frac{\partial g}{\partial u}\lambda + \frac{\partial L}{\partial u} = 0 \quad \text{(A8)}$$

In summary, the two-point-boundary-value problem comprises Eq. (A1) with the initial condition, Eq. (A6) with the

boundary condition of Eq. (A7), the stationary condition of Eq. (A8) and the terminal constraints of Eq. (A3), all of which will be solved yielding the control variable $u(\tau)$ as the solution together with the multiplier v.

In this study we have chosen the following conditions.

(1) We set L equal to zero, i.e., no penalty associated with the path being considered, and the only final conditions, $\phi[y(\tau_f), \tau_f]$, to be minimized is the reaction time per unit mole of BHET, $y_1(\tau_f)/y_3(\tau_f)$.

(2) The only final constraint, $\psi[y(\tau_f), \tau_f]$, is the DEG content level in the product, $W_{DEG,f}$, so that the multiplier vector v becomes a scalar p.

(3) The reactor temperature, T, is selected as the control (manipulating) variable as a function of time is our sought-after solution.

With these conditions, we have the optimization problem as follows. The state equation, Eq. (A1), is obtained from Table 4 with the coordinate transformation of Eq. (3). The objective function becomes Eq. (8), and the temperature profile is improved using the information of the gradient of the Hamiltonian with respect to temperature as shown in the scheme of Eq. (9). Also the differential equations of the adjoint variables, λ, are given as follows.

$$\frac{d\lambda_1}{d\tau} = -\frac{\partial H}{\partial y_1} = 0$$

For i=2 to 8,

$$\frac{d\lambda_i}{d\tau} = -\frac{\partial H}{\partial y_i}$$

$$= -\lambda_1\left[\frac{-f_{1,yi}}{f_1^2}\right] - \lambda_2\left[\frac{f_{2,yi}f_1 - f_{1,yi}f_2}{f_1^2}\right] - \lambda_3\left[\frac{f_{3,yi}f_1 - f_{1,yi}f_3}{f_1^2}\right]$$

$$-\lambda_4\left[\frac{f_{4,yi}f_1 - f_{1,yi}f_4}{f_1^2}\right] - \lambda_5\left[\frac{f_{5,yi}f_1 - f_{1,yi}f_5}{f_1^2}\right]$$

$$-\lambda_6\left[\frac{f_{6,yi}f_1 - f_{1,yi}f_6}{f_1^2}\right] - \lambda_7\left[\frac{f_{7,yi}f_1 - f_{1,yi}f_7}{f_1^2}\right]$$

$$-\lambda_8\left[\frac{f_{8,yi}f_1 - f_{1,yi}f_8}{f_1^2}\right] \quad \text{(A9)}$$

where $f_{i,y_j} \equiv \dfrac{\partial f_i}{\partial y_j}$ (i=1-8, j=1-8) are shown below. (A10)

$$\frac{\partial f_1}{\partial y_1} = 0$$

$$\frac{\partial f_1}{\partial y_2} = k_1(1-\tau)N_{1,0}/m_f$$

$$\frac{\partial f_1}{\partial y_3} = [-k_2 y_5 + k_3(1-\tau)]N_{1,0}/m_f$$

$$\frac{\partial f_1}{\partial y_4} = -k_4 y_5 N_{1,0}/m_f$$

$$\frac{\partial f_1}{\partial y_5} = [(-k_2 y_3 - k_4 y_4 - k_2 y_7)m_f + (r_1 + r_2 + r_7)M_5]N_{1,0}/m_f$$

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$$\frac{\partial f_1}{\partial y_6} = 0$$

$$\frac{\partial f_1}{\partial y_7} = -k_2 y_5 N_{1,0}/m_L$$

$$\frac{\partial f_1}{\partial y_8} = k_1(1-\tau)N_{1,0}/m_L$$

$$\frac{\partial f_2}{\partial y_1} = 0$$

$$\frac{\partial f_2}{\partial y_2} = [-k_1(1-\tau)-k_6 y_4 - k_8 y_3 - 4k_9 y_2]N_{1,0}/m_L$$

$$\frac{\partial f_2}{\partial y_3} = (k_2 y_5 + 2k_5 y_3 - k_8 y_2)N_{1,0}/m_L$$

$$\frac{\partial f_2}{\partial y_4} = -k_6 y_2 N_{1,0}/m_L$$

$$\frac{\partial f_2}{\partial y_5} = [(k_2 y_3)m_L + (-r_1 + r_3 - r_5 - 2r_6)M_5]N_{1,0}/m_L$$

$$\frac{\partial f_2}{\partial y_6} = 0$$

$$\frac{\partial f_2}{\partial y_7} = 0$$

$$\frac{\partial f_2}{\partial y_8} = 0$$

$$\frac{\partial f_3}{\partial y_1} = 0$$

$$\frac{\partial f_3}{\partial y_2} = [k_1(1-\tau)+2k_6 y_4 - k_8 y_3]N_{1,0}/m_L$$

$$\frac{\partial f_3}{\partial y_3} = [-k_2 y_5 - k_3(1-\tau)-4k_5 y_3 - 4k_7 y_3 - k_8 y_2]N_{1,0}/m_L$$

$$\frac{\partial f_3}{\partial y_4} = (k_4 y_5 + 2k_6 y_2)N_{1,0}/m_L$$

$$\frac{\partial f_3}{\partial y_5} = [(-k_2 y_3 + k_4 y_4)m_L + (r_1 - r_2 - 2r_3 - 2r_4 - r_5)M_5]N_{1,0}/m_L$$

$$\frac{\partial f_3}{\partial y_6} = 0$$

$$\frac{\partial f_3}{\partial y_7} = 0$$

$$\frac{\partial f_3}{\partial y_8} = 0$$

$$\frac{\partial f_4}{\partial y_1} = 0$$

$$\frac{\partial f_4}{\partial y_2} = -k_6 y_4 N_{1,0}/m_L$$

$$\frac{\partial f_4}{\partial y_3} = [k_3(1-\tau)+2k_5 y_3]N_{1,0}/m_L$$

$$\frac{\partial f_4}{\partial y_4} = (-k_4 y_5 - k_6 y_2)N_{1,0}/m_L$$

$$\frac{\partial f_4}{\partial y_5} = [(-k_4 y_4)m_L + (r_2 + r_3)M_5]N_{1,0}/m_L$$

$$\frac{\partial f_4}{\partial y_6} = 0$$

$$\frac{\partial f_4}{\partial y_7} = 0$$

$$\frac{\partial f_4}{\partial y_8} = 0$$

$$\frac{\partial f_5}{\partial y_1} = 0$$

$$\frac{\partial f_5}{\partial y_2} = [k_1(1-\tau)+k_8 y_3 - 2k_9 y_2]N_{1,0}/m_L$$

$$\frac{\partial f_5}{\partial y_3} = [-k_2 y_5 + k_3(1-\tau)+2k_7 y_3 + k_8 y_2]N_{1,0}/m_L$$

$$\frac{\partial f_5}{\partial y_4} = -k_4 y_5 N_{1,0}/m_L$$

$$\frac{\partial f_5}{\partial y_5} = [(-k_2 y_3 - k_4 y_4 - k_2 y_7)m_L + (r_1 + r_2 + r_4 + r_5 + r_6 + r_7)M_5]N_{1,0}/m_L$$

$$\frac{\partial f_5}{\partial y_6} = 0$$

$$\frac{\partial f_5}{\partial y_7} = -k_2 y_5 N_{1,0}/m_L$$

$$\frac{\partial f_5}{\partial y_8} = k_1(1-\tau)N_{1,0}/m_L$$

$$\frac{\partial f_6}{\partial y_1} = 0$$

$$\frac{\partial f_6}{\partial y_2} = 0$$

$$\frac{\partial f_6}{\partial y_3} = 2k_7 y_3 N_{1,0}/m_L$$

$$\frac{\partial f_6}{\partial y_4} = 0$$

$$\frac{\partial f_6}{\partial y_5} = 0$$

$$\frac{\partial f_6}{\partial y_6} = 0$$

$$\frac{\partial f_6}{\partial y_7} = 0$$

$$\frac{\partial f_6}{\partial y_8} = 0$$

$$\frac{\partial f_7}{\partial y_1} = 0$$

$$\frac{\partial f_7}{\partial y_2} = k_8 y_3 N_{1,0}/m_L$$

$$\frac{\partial f_7}{\partial y_3} = k_8 y_2 N_{1,0}/m_L$$

$$\frac{\partial f_7}{\partial y_4} = 0$$

$$\frac{\partial f_7}{\partial y_5} = [(-k_2 y_7)m_L + (r_5 + r_7)M_5)]N_{1,0}/m_L$$

$$\frac{\partial f_7}{\partial y_6} = 0$$

$$\frac{\partial f_7}{\partial y_7} = -k_2 y_5 N_{1,0}/m_L$$

$$\frac{\partial f_7}{\partial y_8} = k_1(1-\tau)N_{1,0}/m_L$$

$$\frac{\partial f_8}{\partial y_1} = 0$$

$$\frac{\partial f_8}{\partial y_2} = 2k_9 y_2 N_{1,0}/m_L$$

$$\frac{\partial f_8}{\partial y_3} = 0$$

$$\frac{\partial f_8}{\partial y_4} = 0$$

$$\frac{\partial f_8}{\partial y_5} = [(k_2 y_7)m_L + (r_6 - r_7)M_5)]N_{1,0}/m_L$$

$$\frac{\partial f_8}{\partial y_6} = 0$$

$$\frac{\partial f_8}{\partial y_7} = k_2 y_5 N_{1,0}/m_L$$

$$\frac{\partial f_8}{\partial y_8} = -k_1(1-\tau)N_{1,0}/m_L$$

The boundary conditions at the final time $(\tau=\tau_f)$ for the above equations are given below.

$$\lambda_1(\tau_f) = \frac{1}{y_3(\tau_f)} \Bigg/ \left[\frac{y_1(\tau_f)}{y_3(\tau_f)}\right]_0$$

$$\lambda_2(\tau_f) = 0$$

$$\lambda_3(\tau_f) = -\frac{y_1(\tau_f)}{y_3^2(\tau_f)} \Bigg/ \left[\frac{y_1(\tau_f)}{y_3(\tau_f)}\right]_0 - p\frac{W_{DEG,f}/y_3(\tau_f)}{[W_{DEG,f}]_0}$$

$$\lambda_4(\tau_f) = 0$$

$$\lambda_5(\tau_f) = 0$$

$$\lambda_6(\tau_f) = p\frac{M_6/[y_3(\tau_f)M_3]}{[W_{DEG,f}]_0}$$

$$\lambda_7(\tau_f) = p\frac{M_7/[y_3(\tau_f)M_3]}{[W_{DEG,f}]_0}$$

$$\lambda_8(\tau_f) = p\frac{M_8/[y_3(\tau_f)M_3]}{[W_{DEG,f}]_0}$$

The stationary conditions producing the optimal temperature profile are as follows.

$$\frac{\partial H}{\partial u} = \frac{\partial H}{\partial T}$$

$$= \lambda_1\left[\frac{-f_{1,T}}{f_1^2}\right] + \lambda_2\left[\frac{f_{2,T}f_1 - f_{1,T}f_2}{f_1^2}\right] + \lambda_3\left[\frac{f_{3,T}f_1 - f_{1,T}f_3}{f_1^2}\right]$$

$$+ \lambda_4\left[\frac{f_{4,T}f_1 - f_{1,T}f_4}{f_1^2}\right] + \lambda_5\left[\frac{f_{5,T}f_1 - f_{1,T}f_5}{f_1^2}\right]$$

$$+ \lambda_6\left[\frac{f_{6,T}f_1 - f_{1,T}f_6}{f_1^2}\right] + \lambda_7\left[\frac{f_{7,T}f_1 - f_{1,T}f_7}{f_1^2}\right]$$

$$+ \lambda_8\left[\frac{f_{8,T}f_1 - f_{1,T}f_8}{f_1^2}\right] \tag{A11}$$

where $f_{i,T} \equiv \frac{\partial f_i}{\partial T}$ $(i=1\text{-}8)$, i.e., $\tag{A12}$

$$\frac{\partial f_1}{\partial T} = [k_{1,T}(1-\tau)y_2 - k_{2,T}y_3y_5 + k_{3,T}(1-\tau)y_3 - k_{4,T}y_4y_5 + k_{1,T}(1-\tau)y_8 - k_{2,T}y_5y_7]N_{1,0}/m_L$$

$$\frac{\partial f_2}{\partial T} = [-k_{1,T}(1-\tau)y_2 + k_{2,T}y_3y_5 + k_{5,T}y_3^2 - k_{6,T}y_2y_4 - k_{8,T}y_2y_3 - 2k_{9,T}y_2^2]N_{1,0}/m_L$$

$$\frac{\partial f_3}{\partial T} = [k_{1,T}(1-\tau)y_2 - k_{2,T}y_3y_5 - k_{3,T}(1-\tau)y_3 + k_{4,T}y_4y_5 - 2k_{5,T}y_3^2 + 2k_{6,T}y_2y_4 - 2k_{7,T}y_3^2 - k_{8,T}y_2y_3]N_{1,0}/m_L$$

$$\frac{\partial f_4}{\partial T} = [k_{3,T}(1-\tau)y_3 - k_{4,T}y_4y_5 + k_{5,T}y_3^2 - k_{6,T}y_2y_4]N_{1,0}/m_L$$

$$\frac{\partial f_5}{\partial T} = [k_{1,T}(1-\tau)y_2 - k_{2,T}y_3y_5 + k_{3,T}(1-\tau)y_3 - k_{4,T}y_4y_5 + k_{7,T}y_3^2 + k_{3,T}y_2y_3 + k_{9,T}y_2^2 + k_{1,T}(1-\tau)y_8 - k_{2,T}y_5y_7]N_{1,0}/m_L$$

$$\frac{\partial f_6}{\partial T} = [k_{7,T}y_3^2]N_{1,0}/m_L$$

$$\frac{\partial f_7}{\partial T} = [k_{8,T}y_2y_3 - k_{1,T}(1-\tau)y_8 - k_{2,T}y_5y_7]N_{1,0}/m_L$$

$$\frac{\partial f_8}{\partial T} = [k_{9,T}y_2^2 - k_{1,T}(1-\tau)y_8 + k_{2,T}y_5y_7]N_{1,0}/m_L$$

$$k_{i,T} \equiv \frac{dk_i}{dT} = \left(\frac{E_i}{RT^2}\right)A_i\exp\left(-\frac{E_i}{RT}\right)\ (i=1\text{-}9) \tag{A13}$$

NOMENCLATURE

A_i : frequency factor of i-th reaction described in Table 2 [kg/g-mol hr]

C_1 : concentration of carboxyl end groups per unit mass of the liquid phase [g-mol/kg]

C_2 : concentration of EG per unit mass of the liquid phase [g-mol/kg]

C_3 : concentration of hydroxyl end groups per unit mass of the liquid phase [g-mol/kg]

C_4 : concentration of diester groups per unit mass of the liquid phase [g-mol/kg]

C_5 : concentration of water per unit mass of the liquid phase [g-mol/kg]

C_6, C_7, and C_8 : concentrations of free and bound DEG's per unit mass of the liquid phase [g-mol/kg]

DEG : diethyl glycol

E_i : activation energy of i-th reaction described in Table 2 [cal/g-mol]

f_i : time derivative of state variable x_i described in Table 4

$f_{i,T}$: derivative of f_i with respect to reaction temperature described by (A12) in Appendix

$f_{i,j}$: derivative of f_i with respect to j-component described by (A10) in Appendix

g : vector consisting of g_i's described in Eq. (3)

g_i : time derivative of state variable y_i described in Eq. (4)

h : constraint at $\tau=\tau_f$

H : Hamiltonian

J : objective function (performance index)

k_i : reaction rate constant of i-th reaction described in Table 2 [kg/g-mol hr K]

$k_{i,T}$: derivative of k_i with respect to T described by (A13) in Appendix [kg/g-mol hr]

$m_{DEG,f}$: total mass of DEG in the product [kg]

m_L : mass of the liquid phase [kg]

M_i : molecular weight of i-component explained in C_i [kg/g-mol]

N_i : moles of i-component explained in C_i [g-mol]

$N_{i,0}$: value of N_i at $\tau=0$ [g-mol]

$N_{i,f}$: value of N_i at $\tau=\tau_f$ [g-mol]

p   : parameter denoting the relative weight of DEG level in the objective function

q   : number of constraints at the terminal time

$\dot{q}_W$: the dimensionless moles of the water which leaves the reactor by evaporation per unit time [1/hr]

Q_W : the moles of the water which leaves the reactor by evaporation per unit time [g-mol/kg hr]

r_i : reaction rate of i-th reaction described in Table 4 [kg/g-mol hr]

R   : gas constant [cal/g-mol K]

R_i : reaction rate of i-th reaction described in Table 3 [g-mol/kg hr]

t   : reaction time [hr]

t_f : final reaction time [hr]

T   : reaction temperature [K]

u   : control (manipulating) variable

$W_{DEG,f}$: total mass of DEG in the product per unit mass of BHET produced

x   : state vector consisting of x_i's

x_i : state variable denoting the dimensionless concentration of i-component explained in C_i

y   : state vector consisting of y_i's

y_1 : dimensional state variable denoting reaction time

y_2 : dimensionless state variable denoting EG concentration

y_3 : dimensionless state variable denoting BHET concentration

y_4 : dimensionless state variable denoting diester groups concentration

y_5 : dimensionless state variable denoting water concentration

y_6, y_7, and y_8 : dimensionless state variables denoting free and bound DEG's concentration

$y_{i,0}$: value of y_i at $\tau=0$

$y_{i,f}$: value of y_i at $\tau=\tau_f$

Greek Letters

$\varepsilon_{opt,j}$: optimum step size in the iteration of temperature profile

λ : adjoint (costate) vector consisting of λ_i's

λ_i : adjoint (costate) variable corresponding to y_i

ν : q-vector multiplier representing the terminal constraint in the objective function

τ : new time variable denoting the conversion of the esterification reaction

τ_f : final time denoting the final conversion

τ_0 : initial time denoting zero conversion

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