

## Optimal Reaction Conditions for Minimization of Energy and Byproducts in a Poly(ethylene terephthalate) Process

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### Abstract

The optimal reaction conditions are determined for a PET process, which consists of transesterification, prepolymerization and polycondensation reactors in series. Based on the simulation results of the reactor system, we scrutinize the cause and effect between the reaction conditions and the final properties of the polymer product. We then select the process variables with significant influence on the properties of polymer as control variables and calculate the optimal reaction conditions by iterative dynamic programming (IDP) algorithm with constraints. A new reaction scheme incorporating reactions for by-products as well as three main reactions is considered in the constrained IDP method.

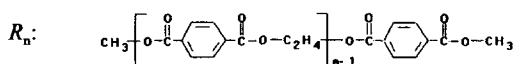
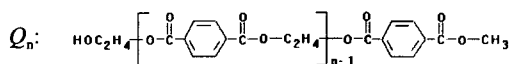
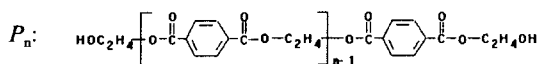
### 1. Introduction

Many researchers have devised and studied various algorithms for optimizing strategies for nonlinear processes in order to obtain the best policy. Among the algorithms, optimization and transformation methods are two main categories. Most of the approaches based on the transformation or Jacobian, partial or full linearization, have the advantage of well-developed theoretical analysis for stability and robustness. It is well known, however, that linear control theory based on transformation method cannot properly handle the characteristics of highly nonlinear systems such as polymerization reactor system. These approaches are often limited to certain classes of nonlinear systems and can generate physically unrealizable state variables, for example, mole fractions greater than unity [1].

Although computing speed of IDP is not so attractive, the possibility of finding the global optimum is much higher than almost all other algorithms. Moreover, constraints on control variables and states can be easily incorporated.

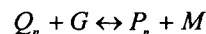
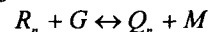
### 2. PET Polymerization Process

In the first stage of the PET polymerization process, transesterification, functional groups of dimethyl terephthalate (DMT) and ethylene glycol (EG) react to give bis(2-hydroxyethyl)terephthalate (BHET), various oligomers and the condensate methanol (MeOH) which should be removed. Three kinds of oligomers can be identified by their functional end groups [2].

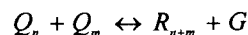


Although there are extra reactions forming by-products in the first reactor, it is advantageous to concentrate on some main reactions directly contributing to conversion and chain length since the fractions of by-products in this reactor are negligible. Therefore, only the following three main reactions are considered in the transesterification reactor:

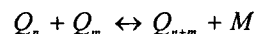
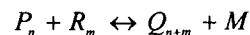
Ester Interchange Reaction:



Polycondensation Reaction:



Transesterification Reaction:

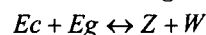
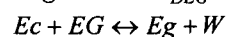
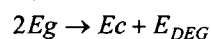
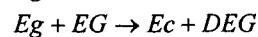
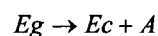


where  $M$  and  $G$  denote MeOH and EG, respectively.

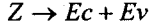
It is assumed that only MeOH which is more volatile than EG would be vaporized to the gas phase. The numbers of moles of each species and polymers are computed by the reaction rate equations and gas-liquid equilibrium. The zeroth, first, second and third moments of number of moles of polymer are used, and to prevent the order of moment from increasing, moment closing formula [3] is adopted.

In the following reactors, however, the amounts of by-products such as acetaldehyde, water, diethylene glycol (DEG) cannot be neglected because of the higher temperature and the lower pressure. So we adopt a new reaction scheme presented by Ravindranath and Marshelkar[4], where functional group model is used.

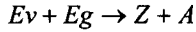
Besides the three main reactions mentioned above, following side reactions are considered:



Degradation of diester groups:



Polycondensation of vinyl groups:



where,  $Eg$ ,  $Ec$ ,  $Ev$ ,  $E_{DEG}$ ,  $EG$ ,  $DEG$ ,  $W$  and  $A$  denote hydroxyl end group, acid end group, vinyl end group, DEG end group, ethylene glycol, diethylene glycol, water and acetaldehyde, respectively.

The product of the first reactor goes to the second reactor called prepolymerization reactor where the reaction conditions are different from the first. In order to produce polymer with chain length of 20 to 30, temperature is kept higher while pressure is kept lower than in the first reactor. The condensates (methanol and acetaldehyde) are so volatile that they are assumed to be removed right after they form. The numbers of moles of EG and water evaporated to the gas phase should be calculated through a gas-liquid equilibrium correlation.

For the practical usage, however, the chain length of PET should be in the range of 80 to 100 or higher. The product from the second reactor needs to be reacted further. To do so removal of condensate EG is very important since the condensation reaction is reversible. In the polycondensation reactor the viscosity of polymer melt is so high that the transfer rate of EG may control the whole reaction rate and chain length. Thus some special forms of reactors are used [5] and under very low pressure EG is removed. In this study the reactor is assumed to be a rotating disk type reactor and is properly considered as a PFR [6]. In this reactor gas-liquid equilibrium compositions were computed via Flory-Huggins model.

### 3. Iterative Dynamic Programming (IDP) With Constraints

Through simulation study of the whole reactor system the reaction conditions mainly affecting the property of the final polymer product are chosen. Reaction temperatures  $T_1$  (in the first reactor),  $T_2$  (in the second reactor),  $T_3$  (in the third reactor) and the pressure  $P_3$  (in the third reactor) are selected as the conclusive process variables, also called control variables. The time interval is set to three since the whole system comprised three consecutive reactors. On the basis of these a grid for IDP algorithm with constraints is generated. Instead of a uniform grid, the procedure suggested by Luus [7] is adopted.

Firstly,  $N$  allowable values of the control profile in some region  $r$  are generated with respect to the control variable  $u$ . Then integration of the state equations gives  $N^2$  possible trajectories (grid by temperature and pressure). All states and control corresponding to each grid point must be saved. Now optimization starts from the third stage (the last stage) according to Bellman's theory. After the first turn of optimization the obtained best policy  $u^{best}$  is set as the initial control profile for the next turn and spectra of control regions are reduced by a factor  $\gamma$ .

Then the second turn begins. The procedure of this turn repeats similarly as in the first turn. After each turn we compare the present index with the previous minimum index and then choose the lower. This procedure can be schematically seen in the scalar case (one control variable) in Fig. 1. We also enumerate the steps of algorithm of this study as follows [8].

- (1) The system is composed of three consecutive reactors, thus each reactor corresponds to one time step.
- (2) The number of grid points is set to  $N$  per one control variable. And during backward pass, the control  $u$  can take on  $M$  allowable values inside the control region  $r$ , over which the allowable values of control can be selected.

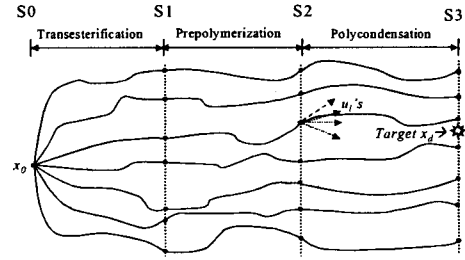


Fig. 1. Schematic diagram of the IDP procedure.

- (3) By guessing  $u^0$  for each stage and subsequently perturbing  $u^0$  uniformly inside the allowable region for control  $N^2$  initial values of control can be selected.
- (4) Using the  $N^2$  control trajectories from step (3), integrate the state equations to generate and store  $N^2$  values for the grid points at each stage.
- (5) Starting at the last stage, corresponding to from S2 to S3 (see Fig. 1) for each grid point, integrate the state equations of the third reactor once with each of the  $M^2$  allowable values for  $u$ . For each grid point, choose the value of  $u$  that gives minimum value of the index and store the value of the control for use in step (6).
- (6) Step back to the second stage, corresponding to from S1 to S2 and for each grid point, integrate the state equations of the second reactor once with each of the  $M$  allowable values of control (no control for pressure). To continue integration from S2 to S3, choose the control from step (5) that corresponds to the closest grid point. For each grid point, compare  $M$  values of indices and store the control that gives the minimum value.
- (7) Repeat the procedure for the first stage (in the first stage), corresponding to from S0 to S1. Store the control policy that minimizes index.
- (8) Reduce the region for the allowable control values by an amount  $\gamma$  such that  $r_{next} = \gamma \times r_{present}$ . Use the optimal control policy obtained in step (7) as the nominal value for  $u^0$ .
- (9) Go to step (3). Continue the procedure for a number of iterations and compare the present optimal index with the previous one. Then choose the lower index.

### 4. Objective Function and Constraints

The objectives of this optimization are to control the final chain length of polymer product, to lower the reaction temperatures in the three consecutive reactors and to raise the pressure in the third reactor within the ranges of control variables. In order to satisfy those competitive goals we suggest the following form of a function.

$$F(T_1, T_2, T_3, P_3, Xn, DEG, Acetaldehyde)$$

$$= \vec{f}^T \cdot \vec{w} = \begin{bmatrix} f_1(T_1) \\ f_2(T_2) \\ f_3(T_3) \\ f_4(P_3) \\ f_5(Xn) \\ f_6(DEG) \\ f_7(Acetaldehyde) \end{bmatrix}^T \cdot \begin{bmatrix} w_1 \\ w_2 \\ w_3 \\ w_4 \\ w_5 \\ w_6 \\ w_7 \end{bmatrix}$$

where  $f_i$ 's are defined as follows:

$$f_i(T_i) = (T_i - T_{i,low}) / (T_{i,up} - T_{i,low}), \quad i = 1, 2, 3.$$

$$f_4(P_3) = (P_{up} - P_3)/(P_{up} - P_{low})$$

$$f_5(Xn) = |Xn_{desired} - Xn|$$

$$f_6(DEG) = \left| \frac{C_{DEG}}{C_{DEG,max}} \right|$$

$$f_7(\text{Acetaldehyde}) = \left| \frac{C_{\text{Acetaldehyde}}}{C_{\text{Acetaldehyde,max}}} \right|$$

and  $w_i$ 's are weighting factors. The value of the above objective function is called index.

The constraints on  $T_i$ 's and  $P_3$  are as follows:

$$170^\circ\text{C} \leq T_1 \leq 190^\circ\text{C}, \quad 270^\circ\text{C} \leq T_2 \leq 290^\circ\text{C},$$

$$270^\circ\text{C} \leq T_3 \leq 290^\circ\text{C}, \quad 0.1\text{Torr} \leq P_3 \leq 1\text{Torr}.$$

$$C_{DEG,max} = 1\text{ weight } \%,$$

$$C_{\text{Acetaldehyde},max} = 1\text{ weight } \% .$$

## 5. Simulation Result and Discussion

Figure 2 shows the result of IDP optimization based on the mechanism of three main reactions without by-product formation. Constituting four different strategies by setting weighting vectors differently, we examine the difference of optimal trajectories and the trend of optimality according to the strategies. As far as the value of the final chain length is concerned, it reaches 90 (the desired value) in every case without any difficulty. In the first and second reactors the control variable is only one – the reaction temperature. On the other hand in the third reactor the control variables are reaction temperature and pressure. In particular, the reason why we select  $P_3$  as well as  $T_i$ 's as control variables is that we come to realize that the transfer rate of the condensates plays the key role in controlling the chain length, which is known by analytical study of simulation result. The weighting vectors in Fig. 2 are composed of five components which are weighting factors of  $T_1$ ,  $T_2$ ,  $T_3$ ,  $P_3$  and  $Xn$ , respectively.  $f_6$  and  $f_7$  are not included in this case.

The specific values of the indices in Fig. 2 have no physical meaning but the lowest of each case indicates the optimal condition. In the first place the weighting factor  $w_4$  of Fig. 2 (a) ( $w_4=0$ ) is different from that of Fig. 2 (b) ( $w_4=100$ ). Other  $w_i$ 's are set equal to 10. From this optimization strategy we want to know the effect of the pressure term in the index. The optimized pressure  $P_3$  in the case of (a) is determined to be 0.10 Torr which is lower by 0.52 Torr. This is the result of the strategy applied in the case of (b), which mainly lowers the cost terms of the chain length and the reaction temperatures rather than the cost of  $P_3$ . On the other hand, the reaction temperatures of (b) are decided to be higher than those of (a) since the pressure term is more sensitive than the temperature terms. Thus the effort to lower  $T_i$ 's are countervailed.

In the cases of (c) and (d) the optimal  $P_3$  of (d) is determined to be as high as possible (milder condition than (c)), and the  $T_i$ 's of (d) are determined to be as high as possible (severer condition than (c)).

Finally, let us look into the weighting factors of the reaction temperatures. The difference between group A ((a) and (b)) and group B ((c) and (d)) lies in the existence of non-zero  $w_i$ 's ( $i=1,2,3$ ). In comparison of (b) with (d),  $T_1$  and  $T_2$  of (b) are lower than those of (d). On the other hand,  $T_3$  of (b) and that of (d) are the same values and  $P_3$ 's of (b) and (d) are only slightly different.

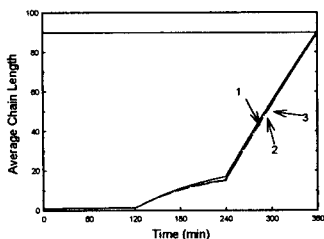
The results of (a) with (c), however, are not easily analyzed only with  $w_i$ 's. The reason is that the reaction conditions in the third reactor give major contribution to the physical property of polymer and to the index value. Since the optimizer focuses on the optimization of  $T_3$  in the case of (a), it cannot find lower values of  $T_1$  and  $T_2$  than those in the case of (c). The competitive goals are successfully attained by putting the analysis of the system together with customized optimization strategies having constrained allowable regions of control variables.

We now want to mention that minimization of energy cost as well as production of the polymer with the desired chain length is possible. Besides this work we have begun to study controlling the composition of by-products such as acetaldehyde and DEG. Simulation result from the new model incorporating the by-products is shown in Fig. 3. So far, however, we have not obtained the optimized reaction condition that minimizes the fractions of by-products in polymer melt since the suitable thermodynamic data and mass transfer coefficients of volatile species are hardly available for this system. Thus, by using the approximate data, the average chain length and the composition of DEG are shown under certain reaction conditions. We are trying to get more accurate values based on empirical relations as well as physical theories.

## 6. Conclusions

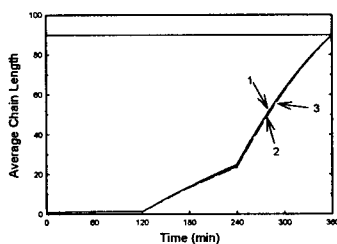
A new attempt to control the final chain length of PET and to lower the energy cost directly related to the reaction conditions is successfully implemented by applying the IDP algorithm within the allowable control regions. In addition, the fractions of byproducts deteriorating polymer quality such as diethylene glycol, acetaldehyde, etc can be minimized by using the well-designed objective function.

It should be pointed out that after some joint problems between the reactors are solved, the whole PET process combining transesterification, prepolymerization and polycondensation reactors is incorporated in our optimization work. Now, we adopt the new model describing the production of by-products and already formulated the whole process scheme. For lack of thermodynamic data and mass transfer data, however, the optimized result based on the new reaction scheme is not obtained yet. It is expected to complete the work soon by the constrained IDP method based on the new reaction mechanism



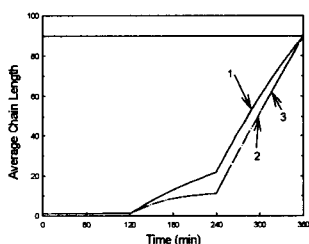
	Rxtor1	Rxtor2	Rxtor3	Index
Temp	167.9	273.8	276.7	7.96
Press	1 atm	20 Torr	0.10Torr	

(a) weighting [10, 10, 10, 0, 10, 0, 0]



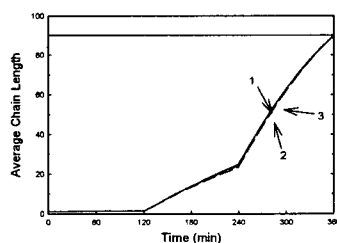
	Rxtor1	Rxtor2	Rxtor3	Index
Temp	178.4	281.8	283.3	60.59
Press	1 atm	20 Torr	0.62Torr	

(b) weighting [10, 10, 10, 100, 10, 0, 0]



	Rxtor1	Rxtor2	Rxtor3	Index
Temp	163.4	272.6	280.0	0.08
Press	1 atm	20 Torr	0.10Torr	

(c) weighting [0, 0, 0, 0, 10, 0, 0]

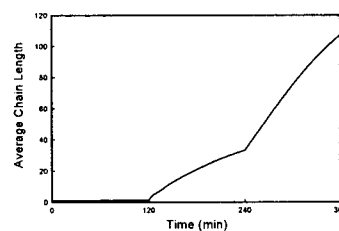


	Rxtor1	Rxtor2	Rxtor3	Index
Temp	180.0	282.1	283.3	40.91
Press	1 atm	20 Torr	0.63Torr	

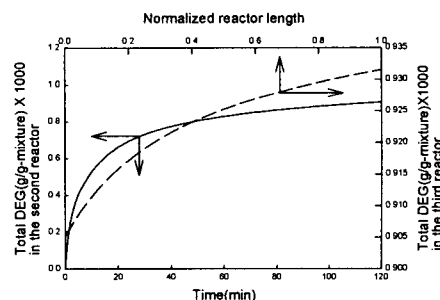
(d) weighting [0, 0, 0, 100, 10, 0, 0]

Fig. 2. Average chain length histories obtained by the IDP algorithm for four different weighting vectors based on the reaction scheme, where the production of by-products is not

considered.



(a) Average chain length



(b) DEG weight fractions in the reaction mixture

Fig. 3. Average chain length history and diethylene glycol weight fractions in the second and the third reactors based on the new reaction scheme, where the production of by-products is considered.

### Acknowledgement

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### References

- [1] Patwardhan, A. A., Rawlings, J. B. and Edgar, T. F., *Chem. Eng. Comm.*, **87**, 123 (1990).
- [2] Lei, G. D. and Choi, K. Y., *Ind. Eng. Chem. Res.*, **31**, 769 (1992).
- [3] Gupta, S. K., Mohan, D. and Kumar, A., *J. Appl. Polym. Sci.*, **30**, 445 (1985).
- [4] Ravindranath, K. and Mashelkar, R. A., *Polym. Eng. Sci.*, **22**, 619 (1982).
- [5] Ravindranath, K. and Mashelkar, R. A., *Chem. Eng. Sci.*, **41**, 2969 (1986).
- [6] Laubriet, C., LeCorre, B. and Choi, K. Y., *Ind. Eng. Chem. Res.*, **30**, 2 (1991).
- [7] Luus, R., *Hung. J. Ind. Chem.*, **17**, 523 (1989).
- [8] Dadebo, S. A., and Mcauley, K. B., *Computers Chem Engng*, **19**, 513 (1995).