Mathematical Model for a Semicontinuous Esterification Process with Recycle Between Terephthalic Acid and Ethylene Glycol

T. YAMADA

Toyobo Co., Ltd., Toyobo Research Institute, 1-1 Katata 2-chome, Ohtsu, Shiga, 520-02, Japan

SYNOPSIS

A new mathematical model has been derived for a semicontinuous recycle esterification process that consists of two reactors, one has the recycle flow to or from another and the discharge flow of the main flow and another has only recycle flow without the discharge flow. This model can give useful information about the optimum design of a new plant through the predictions of oligomer characteristics such as concentrations of carboxyl and hydroxyl end groups, number-average molecular weight, number-average degree of polymerization, esterification and saponification degree, diethylene glycol content, melting point, concentrations of ethylene glycol and water in the vapor phase, and so on.

INTRODUCTION

It is important to study a manufacturing process for poly(ethylene terephthalate) (PET) with the superior characteristics, which has occupied the top seat among general-purpose polymers. From a economical point of view, it is practical and useful to study a continuous process for terephthalic acid (TPA) and ethylyne glycol (EG) as raw materials. Several attempts have been reported on the study for the continuous process.[1,2]

In an esterification process of TPA and EG, the amount of heat required in the first esterification ractor is especially large, when compared with other reactors. Therefore, the larger heat transfer area for heating reaction mixtures by heating medium to be provided becomes indispensable. Usual means to secure large heat transfer area is to increase the number of heating coils. On the other hand, the denser the heating coils are packed in the reactor the easier the stagnant part, where the flow of reaction mixtures is not enough and may be one reason of obt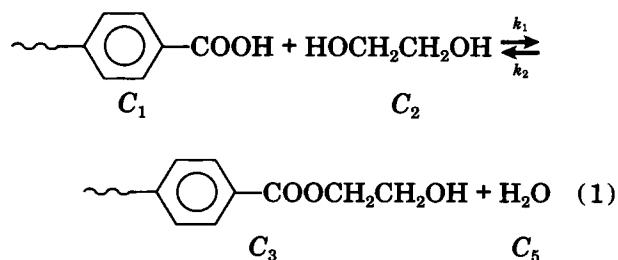aining PET of inferior quality. To reduce heat load and avoid this problem, the study of a semicontinuous recycle process is required.
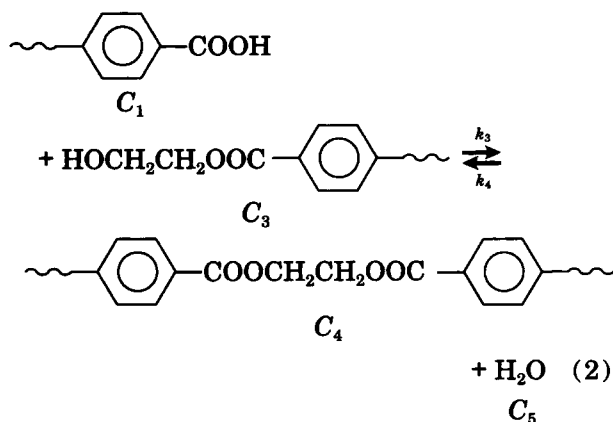
In this study a new mathematical model for the continuous recycle process in the steady state is proposed in order to know the effect of recycling the oligomer in the direct esterification reactions of TPA and EG.

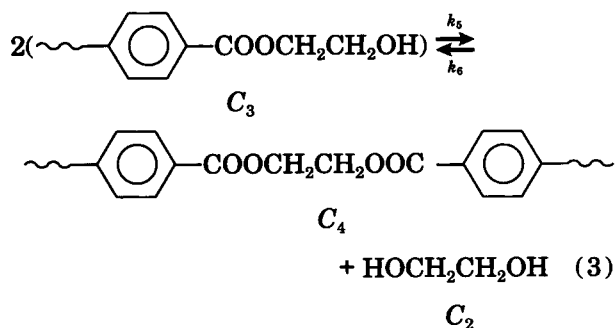## REACTION SCHEME FOR DIRECT ESTERIFICATION

It is assumed that the following reactions occur in an esterification reactor.[1]
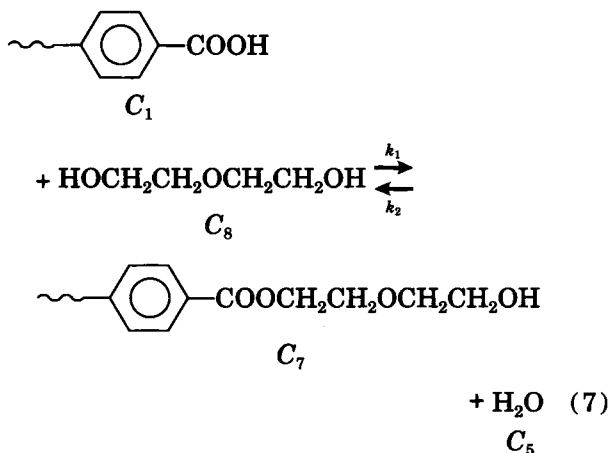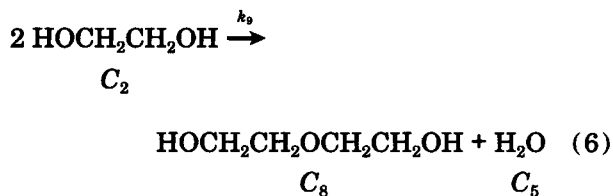
Esterification Reactions

~⟨◯⟩—COOH
C_1

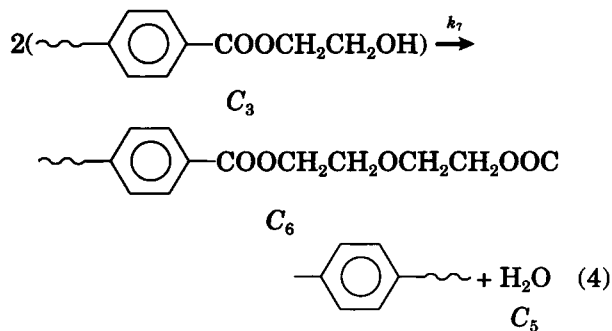+ HOCH$_2$CH$_2$OOC—⟨◯⟩~ $\underset{k_4}{\overset{k_3}{\rightleftharpoons}}$
C_3

~⟨◯⟩—COOCH$_2$CH$_2$OOC —⟨◯⟩~
C_4

+ H$_2$O (2)
C_5

Polycondensation Reactions

2(~⟨◯⟩—COOCH$_2$CH$_2$OH) $\underset{k_6}{\overset{k_5}{\rightleftharpoons}}$
C_3

~⟨◯⟩—COOCH$_2$CH$_2$OOC —⟨◯⟩~
C_4

+ HOCH$_2$CH$_2$OH (3)
C_2

Side Reactions Leading to the Formation of Diethylene Glycol (DEG) in the Oligomer

2(~⟨◯⟩—COOCH$_2$CH$_2$OH) $\overset{k_7}{\rightarrow}$
C_3

~⟨◯⟩—COOCH$_2$CH$_2$OCH$_2$CH$_2$OOC
C_6
—⟨◯⟩~ + H$_2$O (4)
C_5

~⟨◯⟩—COOCH$_2$CH$_2$OH
C_3

+ HOCH$_2$CH$_2$OH $\overset{k_8}{\rightarrow}$
C_2

~⟨◯⟩—COOCH$_2$CH$_2$OCH$_2$CH$_2$OH
C_7

+ H$_2$O (5)
C_5

2 HOCH$_2$CH$_2$OH $\overset{k_9}{\rightarrow}$
C_2

HOCH$_2$CH$_2$OCH$_2$CH$_2$OH + H$_2$O (6)
C_8 $\qquad$ C_5

~⟨◯⟩—COOH
C_1

+ HOCH$_2$CH$_2$OCH$_2$CH$_2$OH $\underset{k_2}{\overset{k_1}{\rightleftharpoons}}$
C_8

~⟨◯⟩—COOCH$_2$CH$_2$OCH$_2$CH$_2$OH
C_7

+ H$_2$O (7)
C_5
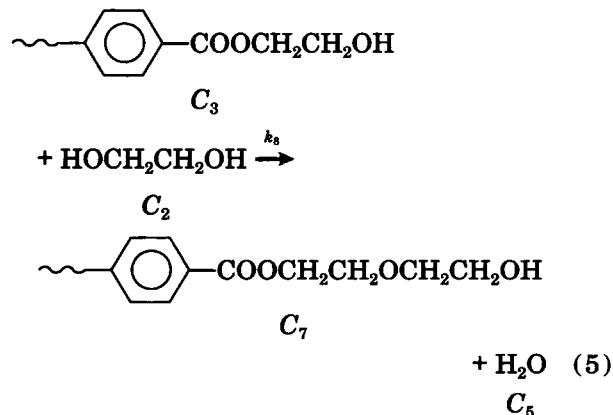
where C_i is the concentration of component i in the liquid phase and k_1 to k_9 are the reaction rate constants.

REACTION RATE EQUATIONS

The reaction rate equations of C_1 to C_8 are obtained from the reaction scheme mentioned earlier as follows.[1]

$$\frac{dC_1}{d\theta} = -k_1 C_1 C_2 + k_2 C_3 C_5 - k_3 C_1 C_3 + k_4 C_4 C_5$$
$$- k_1 C_1 C_8 + k_2 C_5 C_7 \quad (8)$$

$$\frac{dC_2}{d\theta} = -k_1 C_1 C_2 + k_2 C_3 C_5 + k_5 C_3^2 - k_6 C_2 C_4$$
$$- k_8 C_2 C_3 - 2k_9 C_2^2 \quad (9)$$

$$\frac{dC_3}{d\theta} = k_1 C_1 C_2 - k_2 C_3 C_5 - k_3 C_1 C_3 + k_4 C_4 C_5$$
$$- 2k_5 C_3^2 + 2k_6 C_2 C_4 - 2k_7 C_3^2 - k_8 C_2 C_3 \quad (10)$$

$$\frac{dC_4}{d\theta} = k_3 C_1 C_3 - k_4 C_4 C_5 + k_5 C_3^2 - k_6 C_2 C_4 \quad (11)$$

$$\frac{dC_5}{d\theta} = k_1 C_1 C_2 - k_2 C_3 C_5 + k_3 C_1 C_3 - k_4 C_4 C_5 + k_7 C_3^2$$

$$+ k_8 C_2 C_3 + k_9 C_2^2 + k_1 C_1 C_8 - k_2 C_5 C_7 \quad (12)$$

$$\frac{dC_6}{d\theta} = k_7 C_3^2 \quad (13)$$

$$\frac{dC_7}{d\theta} = k_8 C_2 C_3 + k_1 C_1 C_8 - k_2 C_5 C_7 \quad (14)$$

$$\frac{dC_8}{d\theta} = k_9 C_2^2 - k_1 C_1 C_8 + k_2 C_5 C_7 \quad (15)$$

where θ denotes the reaction time.

PREPARATION OF MATHEMATICAL MODEL FOR ESTERIFICATION REACTIONS

Assumptions for Modeling

Assumptions for modeling of direct esterification are as follows.[1]

1. Reactions occur only in the liquid phase. TPA is partly dissolved in the reaction mixtures, and this dissolved TPA participates in the reaction.
2. The rate of dissolution of TPA is very fast. The rate determination step, therefore, is not the dissolution of TPA, but the reaction of TPA.
3. Only undissolved TPA forms the solid component of the heterogeneous system.
4. All acidic functions entail carboxyl end groups.
5. The concentration of DEG is given by the sum of C_6, C_7, and C_8.
6. The pressure in the reactor is given only by the sum of partial pressures of EG and water existing in it. The partial pressure of DEG is lower than those of EG and water.
7. All the nonvolatile components in reaction mixtures are defined as oligomer.
8. Reactivity of functional group does not depend on the polymer chain length as it can be assumed that the degree of polymerization is not very high in the esterification step.
9. In the formation of DEG the reactivity of each hydroxyl end group will be assumed to be the same. That is, $k_8 = 2k_7$ and $k_9 = 4k_7$ (refer to Appendix A).

Determination of Weight Fraction of Liquid Phase (β) in Reaction Mixtures

From the assumptions mentioned earlier, the weight fraction of the liquid phase in the reaction mixtures, β, and carboxyl end group concentration in the liquid phase, C_1, can be obtained as follows.[1]

When undissolved TPA remains in the reaction mixtures (the solid phase exists in the reaction mixtures),

$$\beta = \frac{AV - \eta_{TPA}}{\alpha + AV(w_{EG} + w_{H_2O}) - \eta_{TPA}}$$

$$\text{and} \quad C_1 = \alpha \quad (16)$$

where AV = concentration of total carboxyl end groups in dried oligomer; α = the mean solubility of TPA in the liquid phase of reaction mixtures, which is estimated from $\alpha = 18124 \exp(-9692/RT)w_{EG} + 748 \exp(-7612/RT)w_{OLG}$ [see Eqs. (18)–(21)]; R = gas constant; T = absolute temperature; η_{TPA} = equivalents of carboxyl end groups per 1 kg of pure TPA (i.e., η_{TPA} = 12.039 —COOH equiv./kg TPA); w_{EG} = weight fraction of EG in the liquid phase of reaction mixtures; w_{H_2O} = weight fraction of water in the liquid phase of reaction mixtures.

When all TPA is dissolved in the reaction mixtures (the solid phase exists in the reaction mixtures),

$$\beta = 1 \quad \text{and} \quad C_1 = \zeta \quad (17)$$

where ζ = concentration of carboxyl end groups in the reaction mixtures without undissolved TPA, which is defined by $\zeta = AV \cdot w_{OLG}$; w_{OLG} = weight fraction of oligomer in the liquid phase of reaction mixtures.

Mean Solubility of TPA (α)

The temperature dependencies of the solubility of TPA in EG, α_{EG}, and that in BHET, α_{BHET}, are given as follows.[1]

$$\alpha_{EG} = 18,124 \exp(-9692/RT) \quad (18)$$

$$\alpha_{BHET} = 758 \exp(-7612/RT) \quad (19)$$

where α_{EG} = solubility of TPA in EG
α_{BHET} = solubility of TPA in BHET
R = gas constant, R = 1.987 cal/mol K
T = absolute temperature, T = t + 273.15

The mean solubility of TPA in reaction mixtures containing EG and water can be calculated by the following equation:

$$\alpha = \alpha_{H_2O} w_{H_2O} + \alpha_{EG} w_{EG} + \alpha_{OLG} w_{OLG} \quad (20)$$

where α_{H_2O} = solubility of TPA in water, α_{OLG} = solubility of TPA in oligomer.

If the amount of dissolved TPA in the water component of reaction mixtures is negligible because of the very little amount of water in them and the solubility of TPA in oligomer, α_{OLG}, is equivalent to that in BHET, α_{BHET}, α is given by

$$\alpha \doteq \alpha_{EG} w_{EG} + \alpha_{BHET} w_{OLG} \quad (21)$$

Relations among Oligomer Properties

The relations among oligomer properties (AV, OHV, ϕ, M_n, P_n, SV, E_s, e, and d) are given in the following equations.

$$\phi = \frac{OHV}{AV + OHV} \quad (22)$$

$$M_n = \frac{2000}{AV + OHV} \quad (23)$$

$$P_n = \frac{M_n(1 + e) + 26.03 + 70.09e - \phi(88.10 + 176.20e)}{192.17 + 236.23e}$$

$$\text{(see Appendix B)} \quad (24)$$

$$SV = \frac{2000 P_n}{M_n} \quad (25)$$

$$E_S = \frac{SV - AV}{SV} \quad (26)$$

$$d = 100 \left(\frac{P_n + 2\phi - 1}{P_n} \right) \left(\frac{e}{(1 + e)} \right) \quad (27)$$

where ϕ = ratio of hydroxyl end groups to total end groups, M_n = number-average molecular weight, P_n = number-average degree of polymerization, SV = saponification value, E_s = esterification degree, e = molar ratio of DEG to bound EG, d = percentage of DEG content based on TPA.

The value of e is measured by a gas chromatographic analysis after methanolysis of oligomer.

Prediction of Melting Points

The melting points of oligomer, T_m, can be obtained from the following equation, which is applicable not only to estimation of melting points of oligomer but also to prediction of polymer for PET.[3,4]

$$\frac{1}{T_m} = 0.111049 \times 10^{-3} \cdot OHV^2 - 0.200468$$

$$\times 10^{-4} \cdot OHV^3 - 0.298614 \times 10^{-3} \exp(-OHV)$$

$$- \frac{0.196193 \times 10^{-2} \cdot AV}{P_n + OHV} + \frac{0.605210 \times 10^{-3} \cdot AV^2}{(P_n + OHV)^2}$$

$$- \frac{0.971548 \times 10^{-2} \cdot AV}{(P_n + OHV)^2} + \frac{0.98087 \times 10^{-3} \cdot OHV}{(P_n + OHV)^2}$$

$$+ 0.142510 \times 10^{-3} \exp \frac{AV}{P_n + OHV} - 0.655692$$

$$\times 10^{-4} \ln(P_n) + 0.415790 \times 10^{-2} \quad (28)$$

Effect of Polycondensation Catalysts or Additive on Reaction Rate Constants

References 5, 6, and 7 report the effect of diantimony trioxide (Sb_2O_3) and potassium titanium oxyoxalate [$K_2TiO(C_2O_4)_2 \cdot 2H_2O$], which are polycondensation catalysts, and titanium dioxide (TiO_2), which is an additive on the esterification reaction between TPA and EG.

The reaction rate constants shown in Eqs. (1)–(7) were determined by fitting the experimental data obtained from the pilot plant of throughput about 50 kg/h. From the results obtained, it was made clear that the effects of diantimony trioxide (Sb_2O_3), potassium titanium oxyoxalate [$K_2TiO(C_2O_4)_2 \cdot 2H_2O$], and titanium dioxide (TiO_2) on the reaction rate constants are expressed as follows:

$$k_1 = (3.75 \times 10^{-4} \cdot Sb^{3+} + 0.015T_i + 1)$$
$$\times 1.5657 \times 10^9 \exp(-19,640/RT) \quad (29)$$

$$k_2 = (4.75 \times 10^{-4} \cdot Sb^{3+} + 9.1667 \times 10^{-3}T_i + 1)$$
$$\times 1.5515 \times 10^8 \exp(-18,140/RT) \quad (30)$$

$$k_3 = (6.25 \times 10^{-4} \cdot Sb^{3+}$$
$$+ 0.019167T_i + 0.1[TDO] + 1)$$
$$\times 3.5165 \times 10^9 \exp(-22,310/RT) \quad (31)$$

$$k_4 = (4.50 \times 10^{-4} \cdot Sb^{3+} + 1.6667 \times 10^{-3}T_i + 1)$$
$$\times 6.7640 \times 10^7 \exp(-18,380/RT) \quad (32)$$

$$k_5 = (3.50 \times 10^{-4} \cdot Sb^{3+}$$

$$+ \ 0.015833T_i + 0.08[\text{TDO}] + 1)$$

$$\times \ 7.7069 \ \exp(-2810/RT) \quad (33)$$

$$k_6 = (1.75 \times 10^{-4} \cdot Sb^{3+}$$

$$+ \ 3.3333 \times 10^{-3}T_i + 0.04[\text{TDO}] + 1)$$

$$\times \ 6.2595 \times 10^6 \ \exp(-14,960/RT) \quad (34)$$

$$k_7 = (3.75 \times 10^{-4} \cdot Sb^{3+} + 0.0125T_i$$

$$+ \ 0.085714[\text{TDO}] + 1)$$

$$\times \ 2.0583 \times 10^{15} \ \exp(-42,520/RT) \quad (35)$$

where Sb^{3+} = mole of antimony ion (Sb^{3+}) in diantimony trioxide supplied for 10^6 mol of TPA

T_i = mole number of potassium titanium oxyoxalate supplied for 10^6 mol of TPA

R = gas constant

T = absolute temperature

MODELLING FOR ESTERIFICATION REACTIONS IN A SEMICONTINUOUS RECYCLE PROCESS

Continuous Recycle Process

We consider a recycle process under the steady state shown in Figure 1, which is designated as a semicontinuous recycle process. In Figure 1 the slurry of TPA-EG mixtures is fed into RA-1 controlled at reaction pressure of P, at reaction temperature of t by the heating medium in coils with a heating area of A and at the content weight of W, and TPA reacts with EG in RA-1. The reaction mixtures discharged from RA-1 is fed partly to the next reactor at a flow rate of F_P and partly to RA-2 at a flow rate of f'_B. And then, the reactions proceed at the reaction pressure of P' and reaction temperature of t' in RA-2, whose content weight is controlled at W' and where the heating coils with a heating area of A' are installed, through adding EG of $\delta_{EG}F_S$ into it. The reaction mixtures are recycled from RA-2 to RA-1 at a flow rate of f_B.

In this study a new mathematical model for the above-mentioned process is derived by using the same reaction scheme, assumptions, and approaches as the continuous process reported by the authors.[1,2]
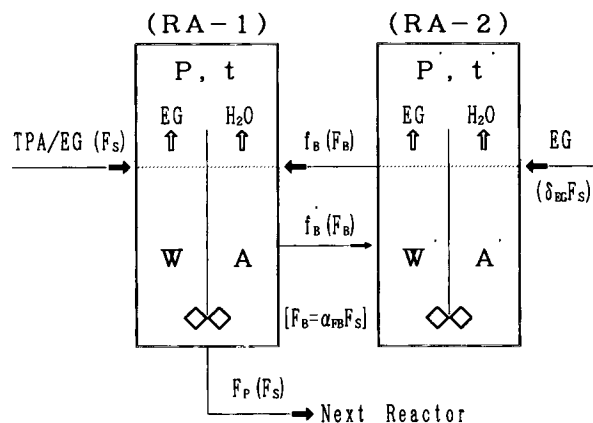

Figure 1 Semicontinuous Recycle Esterification Process in Steady State: P, P' = reaction pressures; t, t' = reaction temperature; W, W' = weights of reaction mixtures; A, A' = heat transfer areas; F_S = throughput based on PET polymer; F_B = recycle flow rate based on PET polymer, $F_B = \alpha_{FB}F_S$; α_{FB} = recycle ratio; F_P = actual discharge flow rate from reactor; f_B, f'_B = actual recycle flow rates into which F_B is converted; δ_{EG} = flow rate of EG added anew into RA-2 per 1 kg/h of throughput based on PET polymer; where prime denotes RA-2.

Relation between Actual Recycle Flow Rates (f_B, f'_B) and Recycle Flow Rate Based on PET Polymer (F_B)

As total number of TPA units (namely, PET units) in the reaction mixtures is given by the sum of moles of undissolved TPA and number of TPA units in the liquid phase, the actual recycle flow rates (f_B, f'_B) with EG and water are related to the recycle flow rate based on PET polymer (F_B) without EG and water by Eqs. (36) and (37). From the following relation,

Number of TPA molecules undissolved into f_B or

f'_B + number of TPA units in oligomer with

dissolved TPA into f_B or f'_B = total number of

TPA units into F_B based on PET polymer

for f_B, we can obtain

$$\frac{(1 - \beta')f_B}{M_{TPA}} + \frac{\beta'f_B w'_{OLG}P'_{nL}}{M'_{nL}} = \frac{F_B}{M_{PET}} \quad (36)$$

for f'_B, we can obtain

$$\frac{(1 - \beta)f'_B}{M_{TPA}} + \frac{\beta f'_B w_{OLG}P_{nL}}{M_{nL}} = \frac{F_B}{M_{PET}} \quad (37)$$

By rearrangement of Eqs. (36) and (37), the following expressions for f_B and f'_B are obtained:

$$f_B = \frac{F_B/M_{\text{PET}}}{(1 - \beta')/M_{\text{TPA}} + \beta' w'_{\text{OLG}} P'_{nL}/M'_{nL}} \quad (38)$$

$$f'_B = \frac{F_B/M_{\text{PET}}}{(1 - \beta)/M_{\text{TPA}} + \beta W_{\text{OLG}} P_{nL}/M_{nL})} \quad (39)$$

where, the prime represents RA-2 and no superscript represents RA-1; β is the weight fraction of liquid phase; M_{PET} and M_{TPA} are the molecular weight of PET polymer unit and TPA, respectively, that is, $M_{\text{PET}} = 192.17$ and $M_{\text{TPA}} = 166.13$; P_{nL} and M_{nL} are the number-average degree of polymerization and number-average molecular weight of oligomers in the liquid phase free from undissolved TPA, respectively, here M_{nL} can be estimated by the relation of $M_{nL} = 2000\beta w_{\text{OLG}}/[\beta C_1 + \text{OHV}\{1 - \beta(w_{\text{EG}} + w_{\text{H}_2\text{O}})\}]$ (see Appendix D), and P_{nL} can be obtained from Eq. (24); w_{OLG} is the weight fraction of oligomer in the liquid phase free from undissolved TPA.

Amount of EG Bound in PET Chain (q_{EG}, q'_{EG})

By neglecting the errors for the amount of EG bound in the PET chain by the reaction due to a few percent of DEG content in the oligomer, the amount of bound EG can be given by Eqs. (40) and (41) for RA-1 and RA-2, respectively (refer to Appendix E).

RA-1

$$q_{\text{EG}} = \frac{M_{\text{EG}}}{M_{\text{PET}}} F_B \left(\frac{P_n + 2\phi - 1}{P_n} \right.$$
$$\left. - \frac{P'_n + 2\phi' - 1}{P'_n} \right) + \frac{M_{\text{EG}}}{M_{\text{PET}}} F_S \frac{P_n + 2\phi - 1}{P_n} \quad (40)$$

RA-2

$$q'_{\text{EG}} = \frac{M_{\text{EG}}}{M_{\text{PET}}} F_B \left(\frac{P'_n + 2\phi' - 1}{P'_n} - \frac{P_n + 2\phi - 1}{P_n} \right) \quad (41)$$

where M_{EG} is the molecular weight of EG ($M_{\text{EG}} = 62.07$); P_n is the number-average of polymerization of dried oligomer, $P_n = (M_n - 88.1\phi + 26)$ when ether linkage concentration (DEG content) is neglected; M_n is the number-average molecular weight of dried oligomer, $M_n = 2000/(\text{AV} + \text{OHV})$; ϕ is the ratio of hydroxyl end groups to total end groups of dried oligomer, $\phi = \text{OHV}/(\text{AV} + \text{OHV})$; AV is

the concentration of carboxyl end groups; OHV is the concentration of hydroxyl end groups; F_S is the throughput based on PET polymer.

Amount of Water Generated by the Reactions ($q_{\text{H}_2\text{O}}$, $q'_{\text{H}_2\text{O}}$)

By neglecting the influence of DEG content on the amount of water generated by the reactions, the amount of water generated can be given by Eqs. (42) and (43) for RA-1 and RA-2, respectively (refer to Appendix E).

RA-1

$$q_{\text{H}_2\text{O}} = \frac{2M_{\text{H}_2\text{O}}}{M_{\text{PET}}} F_B \left(\frac{P_n + \phi - 1}{P_n} - \frac{P'_n + \phi' - 1}{P'_n} \right)$$
$$+ \frac{2M_{\text{H}_2\text{O}}}{M_{\text{PET}}} F_S \frac{P_n + \phi - 1}{P_n} \quad (42)$$

By using esterification degree (E_s), Eq. (42) can be expressed by Eq. (43):

$$q_{\text{H}_2\text{O}} = \left(\frac{2M_{\text{H}_2\text{O}}}{M_{\text{PET}}} \right) F_B(E_s - E'_s)$$
$$+ \left(\frac{2M_{\text{H}_2\text{O}}}{M_{\text{PET}}} \right) F_S E_s \quad (43)$$

where $M_{\text{H}_2\text{O}}$ is the molecular weight of water, that is, $M_{\text{H}_2\text{O}} = 18.02$ and E_s is the esterification degree defined as $(\text{SV} - \text{AV})/\text{SV}$. Here, SV is the saponification value.

RA-2

Similar to the procedure for RA-1, following formulas are obtained:

$$q'_{\text{H}_2\text{O}} = \frac{2M_{\text{H}_2\text{O}}}{M_{\text{PET}}} F_B$$
$$\times \left(\frac{P'_n + \phi' - 1)}{P'_n} - \frac{P_n + \phi - 1}{P_n} \right) \quad (44)$$

By using esterification degree, Eq. (44) can be expressed by Eq. (45):

$$q'_{\text{H}_2\text{O}} = \frac{2M_{\text{H}_2\text{O}}}{M_{\text{PET}}} F_B(E'_s - E_s) \quad (45)$$

Input Rate of EG to Reactor (F_{EG}^i, F_{EG}^{ii})

The input rates of EG (F_{EG}^i, F_{EG}^{ii}) into RA-1 and RA-2 can be expresses by Eqs. (46) and (47) from the material balances of EG, respectively.

RA-1

$$F_{EG}^i = \frac{M_{EG}}{M_{PET}} F_S a + \beta' f_B w_{EG}' \qquad (46)$$

where a = molar ratio of EG against TPA charged into RA-1, $a = E/T$, and w_{EG} = weight fraction of EG in the liquid phase free from undissolved TPA.

RA-2

$$F_{EG}^{ii} = \beta f_B' w_{EG} + \delta_{EG} F_S \qquad (47)$$

where δ_{EG} is the flow rate of EG added anew into RA-2 per 1 kg/h of F_S.

Input Rate of Water to Reactor ($F_{H_2O}^i$, $F_{H_2O}^{ii}$)

The input rates of EG ($F_{H_2O}^i$, $F_{H_2O}^{ii}$) into RA-1 and RA-2 can be expressed by Eqs. (48) and (49) from the material balances of water, respectively.

RA-1

$$F_{H_2O}^i = \beta' f_B w_{H_2O}' \qquad (48)$$

where w_{H_2O}' = weight fraction of water in the liquid phase free from undissolved TPA in RA-2.

RA-2

$$F_{H_2O}^{ii} = \beta f_B' w_{H_2O} \qquad (49)$$

Total Input Rate to Reactor (F_T^i, F_T^{ii})

The total input rates (F_T^i, F_T^{ii}) into RA-1 and RA-2 can be expresses by Eqs. (50) and (51) from the material balances of water, respectively.

RA-1

$$F_T^i = \frac{F_S(M_{TPA} + M_{EG}a)}{M_{PET}} + f_B \qquad (50)$$

RA-2

$$F_T^{ii} = f_B' + \delta_{EG} F_S \qquad (51)$$

Material Balance around RA-1

The material balances of EG, water, and total in RA-1 are given as follows:

EG

$$F_{EG}^i = Q_{EG} + q_{EG} + (F_P + f_B')\beta w_{EG} \qquad (52)$$

Water

$$F_{H_2O}^i + q_{H_2O} = Q_{H_2O} + (F_P + f_B')\beta w_{H_2O} \qquad (53)$$

Total Balance

$$F_T^i = Q_{EG} + Q_{H_2O} + F_P + f_B' \qquad (54)$$

Material Balance around RA-2

The material balances of EG, water, and total in RA-2 are given as follows:

EG

$$F_{EG}^{ii} = Q_{EG}' + q_{EG}' + f_B \beta' w_{EG}' \qquad (55)$$

Water

$$F_{H_2O}^{ii} + q_{H_2O}' = Q_{H_2O}' + f_B \beta' w_{H_2O}' \qquad (56)$$

Total Balance

$$F_T^{ii} = Q_{EG}' + Q_{H_2O}' + f_B \qquad (57)$$

Determination of Mole Fractions of EG and Water in Vapor or Liquid Phases

By combining Eqs. (52) through (54), the vapor (distillate) flow rates of EG and water (Q_{EG}, Q_{H_2O}) from RA-1 can be expressed by Eqs. (58) and (59):

$$Q_{EG} = \frac{(F_{EG}^i - q_{EG})(1 - \beta w_{EG}) - \beta w_{EG}(F_T^i - F_{H_2O}^i - q_{H_2O})}{1 - \beta(w_{EG} + w_{H_2O})} \qquad (58)$$

$$Q_{H_2O} = \frac{F_{H_2O}^i + q_{H_2O} - \beta w_{H_2O}(F_T^i - Q_{EG})}{1 - \beta w_{H_2O}} \qquad (59)$$

By combining Eqs. (55) through (57), the vapor (distillate) flow rates of EG and water (Q_{EG}', Q_{H_2O}') from RA-2 can be expressed by Eqs. (60) and (61):

$$Q'_{EG} = F^{i'}_{EG} - q'_{EG} - \beta' f_B w'_{EG} \qquad (60)$$

$$Q'_{H_2O} = F^{i'}_{H_2O} + q'_{H_2O} - \beta' f_B w'_{EG} \qquad (61)$$

On the assumption that the total pressure in the reactor is obtained by the sum of the partial pressure of EG and water, the vapor phase mole fractions of EG and water are given by the following equations:

$$y_{EG} = \frac{Q_{EG}/M_{EG}}{Q_{EG}/M_{EG} + Q_{H_2O}/M_{H_2O}} \qquad (62)$$

$$y'_{EG} = \frac{Q'_{EG}/M_{EG}}{Q'_{EG}/M_{EG} + Q'_{H_2O}/M_{H_2O}} \qquad (63)$$

Because the vapor–liquid equilibrium in the esterification stage follows Rault's law with little problem of practical use,[2] the following relations hold in RA-1 and RA-2:

$$y_{EG} + y_{H_2O} = 1 \qquad y'_{EG} + y'_{H_2O} = 1 \qquad (64)$$

$$x_{EG} + x_{H_2O} + x_{OLG} = 1$$

$$x'_{EG} + x'_{H_2O} + x'_{OLG} = 1 \qquad (65)$$

$$x_{EG}P_{EG} = y_{EG}P \qquad x'_{EG}P'_{EG} = y'_{EG}P' \qquad (66)$$

$$x_{H_2O}P_{H_2O} = y_{H_2O}P \qquad x'_{H_2O}P'_{H_2O} = y'_{H_2O}P' \qquad (67)$$

where x_{EG}, X_{H_2O}, X_{OLG} = liquid phase mole fractions of EG, water, and oligomer

y_{EG}, y_{H_2O} = vapor phase mole fractions of EG and water

P_{EG}, P_{H_2O} = vapor pressures of EG and water at a reaction pressure

$$\log P_{EG} = 7.8808 - \frac{1957}{(t + 193.8)} \qquad (68)$$

$$\log P_{H_2O} = 7.9668 - \frac{1668.2}{t + 228} \qquad (69)$$

P = total pressure (reaction pressure) and prime = RA-2.

From Eqs. (58) through (69) we can determine the liquid phase or vapor phase mole fractions; thus the weight fractions of each component can be obtained from the following relations:

$$w_i = \frac{x_i M_i}{\sum\limits_{j=1}^{N} x_j M_j} \qquad w'_i = \frac{x'_i M_i}{\sum\limits^{N} x'_j M_j} \qquad (70)$$

where x_i, x_j = liquid phase mole fractions of component i and j

w_i = liquid phase weight fraction of component i

N = number of components

M_i, M_j = molecular weights of component i and j

and the subscripts of i and j represent water, EG and oligomer.

As the concentrations and flow rates of each component in RA-1 and RA-2 are needed for determining Q_{EG}, Q'_{EG}, Q_{H_2O}, and Q'_{H_2O}, respectively, the way of determining vapor (distillate) flow rates for this process are far more complicated than that for a continuous cascade process; because while the concentrations and flow rates at inlet are given as input data for the continuous cascade process as reported by the Refs. 1 and 2, they are not given in advance for the recycle process, but they are used as parameters to be determined.

Material Balance of Each Component

The material balance of each component in RA-1 and RA-2 is as follows.

1. Material balance of carboxyl end groups
   a. in RA-1

$$F^i C_{10} - F_P AV_a + f_B AV'_a$$
$$- f'_B AV_a + \beta W \left(\frac{dC_1}{d\theta} \right) = 0 \qquad (71)$$

   b. in RA-2

$$f'_B AV_a - f_B AV'_a + \beta' W' \left(\frac{dC'_1}{d\theta} \right) = 0 \qquad (72)$$

2. Material balance of hydroxyl end groups
   a. in RA-1

$$\beta' f_B C'_3 - \beta f_B C_3 - \beta F_P C_3$$
$$+ \beta W \left(\frac{dC_3}{d\theta} \right) = 0 \qquad (73)$$

   b. in RA-2

$$\beta f_B C_3 - \beta' f_B C'_3 + \beta' W' \left(\frac{dC'_3}{d\theta} \right) = 0 \qquad (74)$$

3. Material balance of diester groups (ester linkages)
a. in RA-1

$$\beta' f_B C_4' - \beta f_B' C_4 - \beta F_P C_4$$
$$+ \beta W \left(\frac{dC_4}{d\theta} \right) = 0 \quad (75)$$

b. in RA-2

$$\beta f_B' C_4 - \beta' f_B C_4' + \beta' W' \left(\frac{dC_4'}{d\theta} \right) = 0 \quad (76)$$

4. Material balance of DEG (ether linkages)
a. in RA-1

$$\beta' f_B (C_6' + C_7' + C_8') - \beta f_B' (C_6 + C_7 + C_8)$$
$$- \beta F_P (C_6 + C_7 + C_8)$$
$$+ \beta W \left(\frac{dC_6}{d\theta} + \frac{dC_7}{d\theta} + \frac{dC_8}{d\theta} \right) = 0 \quad (77)$$

b. in RA-2

$$\beta f_B' (C_6 + C_7 + C_8) - \beta' f_B (C_6' + C_7' + C_8')$$
$$+ \beta' W' \left(\frac{dC_6'}{d\theta} + \frac{dC_7'}{d\theta} + \frac{dC_8'}{d\theta} \right) = 0 \quad (78)$$

5. Material balance of water
a. in RA-1

$$\beta' f_B C_5' - \beta f_B' C_5 - \beta F_P C_5 - Q_{H_2O} \eta_{H_2O}$$
$$+ \beta W \left(\frac{dC_5}{d\theta} \right) = 0 \quad (79)$$

b. in RA-2

$$\beta f_B' C_5 - \beta' f_B C_5' - Q_{H_2O} \eta_{H_2O}$$
$$+ \beta' W' \left(\frac{dC_5'}{d\theta} \right) = 0 \quad (80)$$

6. Material balance of EG
a. in RA-1

$$F^i C_{20} - \beta F_P C_2 + \beta' f_B C_2' - \beta f_B' C_2$$
$$+ Q_{EG} \eta_{EG} + \beta W \left(\frac{dC_2}{d\theta} \right) = 0 \quad (81)$$

b. in RA-2

$$\beta f_B' C_2 - \beta' f_B C_2' - Q_{EG}' \eta_{EG} + \delta_{EG} F_S \eta_{EG}$$
$$+ \beta' W' \left(\frac{dC_2'}{d\theta} \right) = 0 \quad (82)$$

where prime expresses RA-2; F^i = total input flow rate of TPA–EG slurry; C_{10}, C_{20} = concentration of TPA or EG in TPA–EG slurry, i.e., $C_{10} = 1/(aM_{EG} + M_{TPA})$, $C_{20} = a/(aM_{EG} + M_{TPA})$; AV_a = concentration of total carboxyl end groups (dissolved, undissolved TPA, and carboxyl end groups bound to oligomer) in the reaction mixtures; $(dC_k/d\theta)$ = reaction rate of component k; θ = reaction time; η_{H_2O} = equivalent concentration of water, η_{H_2O} = 55.494 mol/kg(H_2O); η_{EG} = equivalent concentration of EG, η_{EG} = 16.111 mol/kg (EG).

Simulation Procedures

1. Determine the reaction rate constants by a nonlinear optimization technique such as a simplex method with the experimental data in a continuous esterification process of cascade type reported in the previous works,[1,2] applying the reaction scheme in Eqs. (1)–(7).
2. Input the conditions preferred to be simulated or sets of parameters for formation of first simplex in order to seek the optimum values for six parameters (AV, OHV, DEG, AV', OHV', DEG') by using a simplex method (suppose the initial values of AV, OHV, DEG, AV', OHV', and DEG').
3. Calculate the vapor (distillate) flow rates from Eqs. (36) to (61); and from these values, calculate the weight fraction in the liquid phase or the concentration of each component.
4. Calculate the values (ϵ_k) of the left hand of material balances in Eqs. (71)–(82) by the substitution of the calculated weight fractions and concentrations and obtain the sum ($\Sigma \epsilon_k^2$) of their square values.
5. Adopt the values of AV, OHV, DEG, AV', OHV', and DEG', which make the sum minimum (theoretically, zero), as the values under the steady state. And then stop searching by the simplex method.
6. Print out final results and stop the simulation.

CONCLUSION

A new mathematical model for a material balance and a heat balance of esterification reaction in the semicontinuous recycle process was derived. This model will give such useful information on the design of a new effective process as the optimum values of oligomer characteristics, a recycle ratio, etc.
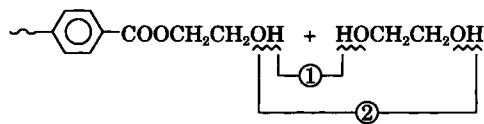
APPENDIX A: DERIVATION OF $k_8 = 2k_7$ AND $k_9 = 4k_7$

Considering that the reaction rate constants of k_7, k_8, and k_9 correspond to the encounter probability of each hyroxyl end group, the probability where one end group reacts with the others is proportional to the number of combinations for each end group given below.
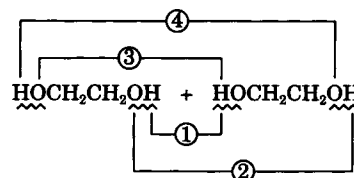
For k_7 in Eq. (4), its combination number is one from the following expression:
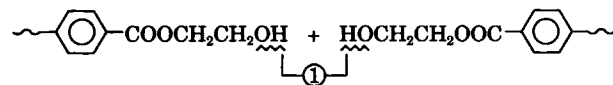
For k_8 in Eq. (5), its combination number is two from the following expression:
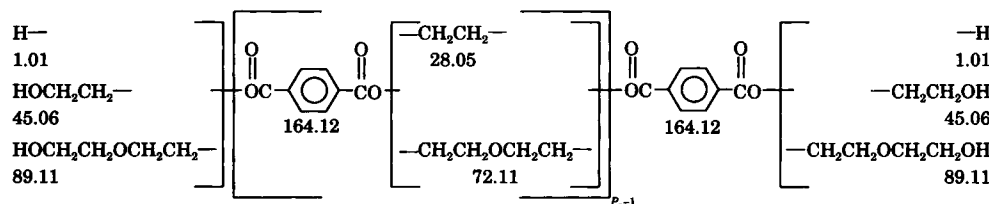

For k_9 in Eq. (6), its combination number is four from the following expression:

If the hydroxyl end groups have the same reactivity, it can be derived from the above combinations that $k_8 = 2k_7$ and $k_9 = 4k_7$.

APPENDIX B: DERIVATION OF P_n

The chemical structure of oligomer with P_n of polymerization degree can be expressed as follows:

where atomic weights of carbon, hydrogen, and oxygen are 12.011, 1.008, and 15.999, respectively.

The relation between M_n and P_n can be given by Eq. (24).

$$M_n = \frac{(P_n - 1)(164.12 + 28.05)}{1 + e}$$
$$+ \frac{(P_n - 1)(164.12 + 72.11)e}{1 + e}$$
$$+ 164.12 + 2(1 - \phi) \times 1.008$$
$$+ 2\phi \left(\frac{45.06}{1 + e} + \frac{89.11e}{1 + e} \right) \quad \text{(B.1)}$$

By rearrangement of Eq. (B.1), P_n can be expressed by Eq. (24).

$$P_n = \frac{M_n(1 + e) + 26.03 + 70.09e - \phi(88.10 + 176.20e)}{192.17 + 236.23e} \quad (24)$$

APPENDIX C: DERIVATION OF d

As the sum of EG linkages and ether linkages (DEG) can be expressed as $P_n - 1 + 2\phi$, if the number of ether linkages is represented by x, x is found by the following relation:

$(1 + e):e = (P_n - 1 + 2\phi):x$, that is,

$$x = \frac{(P_n - 1 + 2\phi)e}{1 + e} \quad \text{(C.1)}$$

As number of TPA units is equal to P_n, d is found by $100x/P_n$.

$$d = 100 \left(\frac{P_n + 2\phi - 1}{P_n} \right) \left(\frac{e}{1 + e} \right) \quad (27)$$

APPENDIX D: DERIVATION OF M_{nL}

Now, we consider the reaction mixtures of W kilogram, which consist of the liquid phase (βW kilogram; oligomer without undissolved TPA and with dissolved TPA, EG, and water) and the solid phase [$(1 - \beta)W$ kilogram; undissolved TPA].

As the weight of oligomer in the liquid phase is $\beta W w_{OLG}$ kilogram, the number of molecules of oligomer with the number-average molecular weight of M_{OLG} in the liquid phase is expressed by $\beta W w_{OLG}/(M_{nL}/1000)$. On the other hand, the number of the oligomer molecules can be also given by $[\beta W C_1 + \text{OHV} \{1 - \beta(w_{EG} + w_{H_2O})\}]/2$. From these results, we can obtain the following relation:

$$\frac{\beta W w_{OLG}}{M_{nL}/1000}$$

$$= \frac{\beta W C_1 + \text{OHV}[1 - \beta(w_{EG} + w_{H_2O}]}{2} \quad (D.1)$$

Rearrangement of Eq. (D.1) gives the following equation:

$$M_{nL} = \frac{2000\beta w_{OLG}}{\beta C_1 + \text{OHV}[1 - \beta(w_{EG} + w_{H_2O})]} \quad (D.2)$$

APPENDIX E: DERIVATION OF q_{EG} AND q_{H_2O}

Derivation of q_{EG}

We consider a molecule of oligomer of poly(ethylene terephthalate) (PET) with the polymerization degree of P_n.

The amount of ethylene glycol (EG) bound into the polymer chain is given by $(P_n - 1)/(1 + e)$ and that of the end group by $2\phi/(1 + e)$. Then the amount of EG due to ether (DEG) linkage bound into the polymer chain is given by $2(P_n - 1)e/(1 + e)$ and that of the end group by $4\phi e/(1 + e)$.

The ratio of bound EG to a polymer chain linkage is given by $\{(P_n - 1)/(1 + e) + 2\phi/(1 + e) + 2(P_n - 1)e/(1 + e) + 4\phi e/(1 + e)\}/P_n$.

From the above, the changed amount of bound EG (q_{EG}) from the polymerization degree of P_{ni} to P_{nf}, is expressed by the following equation:

$$q_{EG} = F_{TPA} \left(\frac{M_{EG}}{M_{TPA}} \right) \left(\frac{(P_{nf} - 1)/(1 + e) + 2\phi_f/(1 + e) + 2(P_{nf} - 1)e/(1 + e) + 4\phi_f e/(1 + e)}{P_{nf}} \right.$$

$$\left. - \frac{(P_{ni} - 1)/(1 + e) + 2\phi_i/(1 + e) + 2(P_{ni} - 1)e/(1 - e) + 4\phi_i e/(1 + e)}{P_{ni}} \right) \quad (E.1)$$

where M_{EG} = molecular weight of EG, M_{EG} = 62.07
M_{TPA} = molecular weight of TPA, M_{TPA} = 166.13

Judging from the DEG content in oligomer of a few percents, the influence of DEG on q_{EG} is negligible. If so ($e = 0$), the above equation reduces to the following equation:

$$q_{EG} = \frac{M_{EG}}{M_{TPA}} F_{TPA} \left(\frac{P_{nf} + 2\phi_f - 1}{P_{nf}} \right.$$

$$\left. - \frac{P_{ni} + 2\phi_i - 1}{P_{ni}} \right) \quad (E.2)$$

By use of the above, q_{EG} shown in Eq. (40) for RA-1 is derived by the sum of the changed amount of bound EG due to the recycle flow (F_B) from $P_{ni} = P'_n$ and $\phi_i = \phi'$ to $P_{nf} = P_n$ and $\phi_f = \phi$ and that

due to the main flow (F_s) from $P_{ni} = 1$ and $\phi_i = 0$ to $P_{nf} = P_n$ and $\phi_f = \phi$.

Similarly, q'_{EG} shown in Eq. (41) also can be derived.

Derivation of q_{H_2O}

After the manner of the derivation of q_{EG}, we consider a molecule of PET oligomer with the polymerization degree of P_n. When a polymer chain linkage is formed by the reactions shown in Eqs. (1) and (2), two molecules of water are generated. Therefore, for the formation of the oligomer with the polymer chain linkages of $P_n - 1$, the water molecules of $2(P_n - 1)$ are generated. Then, as the formation of a hydroxyl end group brings about the generation of a molecule of water, the water mole-

cules of 2ϕ are generated for the formation of the oligomer with the hydroxyl end group ratio of ϕ.

On the other hand, for the formation of an ether (DEG) linkage bound into the polymer chain, three molecules of water are generated from Eq. (4); for the formation of the DEG end group, two molecules are generated from Eqs. (5)–(7). An oligomer with the polymerization degree of P_n comprises of the polymer chains with the EG linkages of $(P_n - 1)/$

$(1 + e)$ and DEG linkages of $(P_n - 1)e/(1 + e)$, and the bifunctional end groups with the carboxyl end groups of $2(1 - \phi)$ and hydroxyl end groups of 2ϕ; the hydroxyl end groups comprise of EG molecules of $2\phi/(1 + e)$ and the DEG molecules of $2\phi e/(1 + e)$.

From the above results, the amount of water (q_{H_2O}) generated by the reactions is expressed by the following equation after the manner of the derivation of q_{EG}.

$$q_{H_2O} = F_{TPA} \left(\frac{M_{EG}}{M_{TPA}}\right) \left[\frac{2(P_{nf} - 1)/(1 + e) + 2\phi_f/(1 + e) + 3(P_{nf} - 1)e/(1 + e) + 4\phi_f e/(1 + e)}{P_{nf}} \right.$$
$$\left. - \frac{2(P_{ni} - 1)/(1 + e) + 2\phi_i/(1 + e) + 3(P_{ni} - 1)e/(1 + e) + 4\phi_i e/(1 + e)}{P_{ni}} \right] \quad (E.3)$$

Judging from the DEG content in oligomer of a few percents, the influence of DEG on q_{H_2O} is negligible. If so ($e = 0$), the above equation reduces to the following equation.

$$q_{H_2O} = \frac{2 M_{EG}}{M_{TPA}} F_{TPA} \left\{ \frac{P_{nf} + \phi_f - 1}{P_{nf}} - \frac{P_{ni} + \phi_i - 1}{P_{ni}} \right\} \quad (E.4)$$

By use of the above, q_{H_2O} shown in Eq. (42) for RA-1 is derived by the sum of the amount of water generated by the reactions due to the recycle flow (F_B) from $P_{ni} = P'_n$ and $\phi_i = \phi'$ to $P_{nf} = P_n$ and $\phi_f = \phi$ and that due to the main flow (F_S) from $P_{ni} = 1$ and $\phi_i = 0$ to $P_{nf} = P_n$ and $\phi_f = \phi$.

Similarly, q'_{H_2O} shown in Eq. (43) also can be derived.

NOMENCLATURE

a = molar ratio of EG against TPA charged into RA-1; $a = E/T$

AV, AV' = concentrations of total carboxyl end groups in dried oligomer, eq/kg; AV $= C_T/[T_S + W_e\{1 - (w_{EG} + w_{H_2O})\}]$

AV_a = concentration of total carboxyl end groups in the reaction mixtures, eq/kg; $AV_a = C_T/(T_S + W_e)$

C_1 = concentration of carboxyl end groups in the liquid phase of reaction mixtures, eq/kg

C_2 = concentration of EG in the liquid phase of reaction mixtures, mol/kg

C_3 = concentration of hydroxyl end groups in the liquid phase of reaction mixtures, eq/kg

C_4 = concentration of diester groups in the liquid phase of reaction mixtures, mol/kg

C_5 = concentration of water in the liquid phase of reaction mixtures, mol/kg

C_6, C_7, C_8 = concentration of free and bound DEG in the liquid phase of reaction mixtures, mol/kg

C_{k0} = input concentration of component k, eq/kg or mol/kg

C_T = total amount of carboxyl end groups, equiv.

$dC_i/d\theta$ = reaction rate of component i, eq/kg h or mol/kg h

d = percentage of DEG content in dried oligomer based on bound TPA, 10^{-2} mol/mol(TPA)

e = molar ratio of DEG content to bound EG in dried oligomer, mol/mol(bound EG)

E_s, E'_s = esterification degrees of dried oligomer

E/T = molar ratio of EG to TPA of the slurry, which fed to the first reactor; $E/T = a$

f_B, f'_B = actual recycle flow rates into which F_B is converted, kg/h

F^i = total input rate, kg/h

F_B = recycle flow rate based on PET polymer, kg/h; $F_B = \alpha_{FB}F_S$

F^i_{EG}, F^{ii}_{EG} = input rates of EG, kg/h

$F^i_{H_2O}$ = input rate of water, kg/h

F_P, F'_P = actual output rates of reaction mixtures discharged from the reactor; kg/h

F_S = throughput based on PET, kg/h

F_{TPA} = throughput based on TPA, kg/h

k_1 to k_9 = reaction rate constants as defined in Eqs. (1) to (7)

M_{EG} = molecular weight of EG, g/mol; M_{EG} = 62.07

M_{H_2O} = molecular weight of water, g/mol; M_{H_2O} = 18.02

M_{PET} = molecular weight of a PET unit, g/mol; M_{EG} = 192.17

M_{TPA} = molecular weight of TPA, g/mol; M_{EG} = 166.13

M_i, M_j = molecular weight of component i, j, g/mol

M_n = number-average molecular weight, g/mol

M_{nL} = number-average molecular weight of oligomer in the liquid phase free from undissolved TPA, g/mol

N = number of components

OHV, = concentrations of hydroxyl end groups

OHV' = in 1 kg dried oligomer, eq/kg

P, P' = total presures (= reaction pressures), mmHg or torr

P_{EG} = vapor pressure of EG at a reaction temperature, mmHg

P_{H_2O} = vapor pressure of water at a reaction temperature, mmHg

P_n, P'_n = number-average degree of polymerization of oligomer

P_{nL}, P'_{nL} = number-average degree of polymerization of oligomer in the liquid phase free from undissolved TPA

q_{EG}, q'_{EG} = amounts of EG bound in PET chain, kg/h

q_{H_2O}, q'_{H_2O} = amounts of water generated by the reaction, kg/h

Q_{EG} = vapor flow rate of EG, kg/h

Q_{H_2O} = vapor flow rate of water, kg/h

R = gas constant, R = 1.987 cal/mol K

Sb^{3+} = mole number of antimony ion (Sb^{3+}) in diantimony trioxide supplied for 10^6 mole of TPA, μmol/TPAmol

SV = saponification value, eq/kg

t, t' = reaction temperatures, °C

T = absolute temperature, $T = t + 273.15$, K

T_i = mole number of potassium titanium oxyoxalate supplied for 10^6 mol of TPA, μmol/TPAmol

T_m = melting point of dried oligomer, °C

T_S = weight of TPA undissolved, kg

[TDO] = weight percent of charged titanium dioxide against PET, wt %

w_{EG} = weight fraction of EG in the liquid phase of reaction mixtures free from undissolved TPA

w_{H_2O} = weight fraction of water in the liquid phase of reaction mixtures free from undissolved TPA

w_{OLG} = weight fraction of oligomer in the liquid phase of reaction mixtures free from undissolved TPA

W, W' = total weights of reaction mixtures in the reactor, kg

W_e = weight of liquid phase in the reaction mixtures, kg

x_{EG} = mole fraction of EG in the liquid phase of reaction mixtures free from undissolved TPA

x_{H_2O} = mole fraction of water in the liquid phase of reaction mixtures free from undissolved TPA

x_{OLG} = mole fraction of oligomer in the liquid phase of reaction mixtures free from undissolved TPA

y_{EG} = mole fraction of EG in the vapor phase

y_{H_2O} = mole fraction of water in the vapor phase

Greek Letters

α = mean solubility of TPA in the reaction mixtures expressed as equivalent moles of carboxyl end groups, eq/kg(reaction mixtures); $\alpha = (C_T - \eta_{TPA}T_S)/W_e$

α_{BHET} = solubility of TPA in BHET expressed as equivalent moles of carboxyl end groups, eq/kg(BHET)

α_{EG} = solubility of TPA in EG expressed as equivalent moles of carboxyl end groups, eq/kg(EG)

α_{FB} = recycle ratio defined as $\alpha_{FB} = F_B/F_S$

α_{H_2O} = solubility of TPA in water expressed as equivalent moles of carboxyl end groups, eq/kg(water)

α_{OLG} = solubility of TPA in oligomer expressed as equivalent moles of carboxyl end groups, eq/kg(oligomer)

β = weight fraction of liquid phase in the reaction mixtures; $\beta = W_e/(W_e/T_s)$

δ_{EG} = flow rate of EG added anew into the reactor per 1 kg/h of throughput based on PET polymer, (kg/h)/(kg/h)(PET)

ϵ_k = calculated value of the left hand (residue) in Eqs. (73) to (84)

ζ = concentration of carboxyl end groups in the

reaction mixtures without undissolved TPA ($\beta = 1$), eq/kg

η_{EG} = equivalent concentration of EG, η_{EG} = 16.111 mol/kg(EG)

η_{H_2O} = equivalent concentration of water, η_{H_2O} = 55.494 mol/kg(H_2O)

η_{TPA} = equivalent concentration of TPA expressed as equivalent moles of carboxyl end groups, η_{TPA} = 12.039 eq/kg(TPA)

θ = reaction time, h

ϕ = ratio of hydroxyl end groups to total end groups of dried oligomer; ϕ = OHV/(AV + OHV)

Subscripts

BHET = bis-β-hydroxylethyl terephthalate
  EG = ethylene glycol
  H_2O = water
  OLG = oligomer
  P = at constant pressure or reaction mixtures
  TPA = terephthalic acid

Superscripts

d = distillate (vapor phase)
  EG = ethylene glycol
  TPA = terephthalic acid
' (prime) = RA-2

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