A Mathematical Model for a Continuous Esterification Process with Recycle between Terephthalic Acid and Ethylene Glycol

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SYNOPSIS

A new mathematical model for a continuous recycle esterification process has been derived by basically the same procedure as the continuous process of a cascade type, reported earlier, which includes material and heat balances. Such a model can give extensive information about the optimum design of a new plant through the predictions of oligomer characteristics (concentrations of carboxyl and hydroxyl end groups, number average molecular weight, number average degree of polymerization, esterification and saponification degree, DEG content, melting point of oligomer, etc.), distillate properties (concentrations of EG and water in the vapor phase), heat transfer area, mass flow rate of heating medium, amount of heat supplied by heating medium, enthalpy moving with recycle, and amount of heat removed from each reactor. © 1992 John Wiley & Sons, Inc.
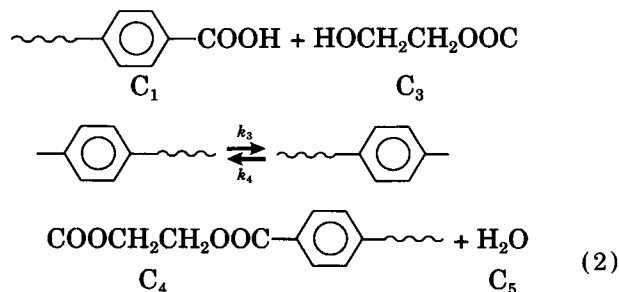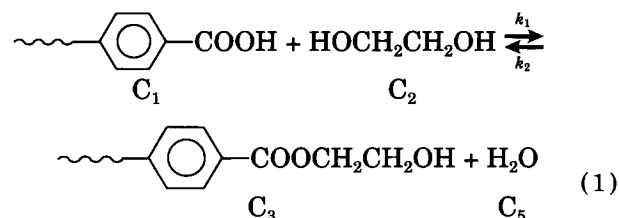
INTRODUCTION

In a continuous esterification process, the amount of heat required in the first esterification reactor is large, when compared with successive reactors. Therefore, a large heat transfer area for heating the reaction mixtures by heating medium must be provided. The usual means to secure a large heat transfer area is to increase the number of heating coils. However, the more densely the heating coils are packed in the reactor, the more likely is stagnation to result, and the flow of the reaction mixture would be inadequate and may result in PET of inferior quality. To reduce heat load, and to avoid the above problem, a study of a continuous recycle process is required.

In this article, a new mathematical model for the continuous recycle process in the steady state is proposed in order to determine the effect of the recycling oligomer in the direct esterification reaction of terephthalic acid (TPA) and ethylene glycol (EG); heat balances for the continuous process are derived for the purpose of determining an optimum heating area.
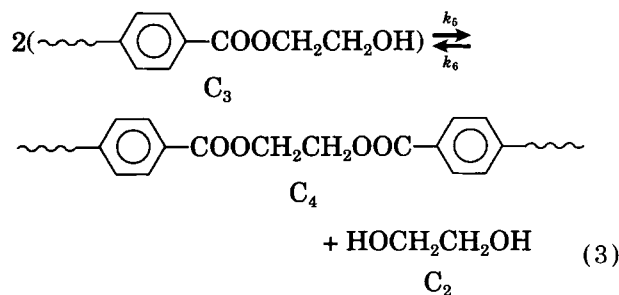
REACTION SCHEME FOR DIRECT ESTERIFICATION

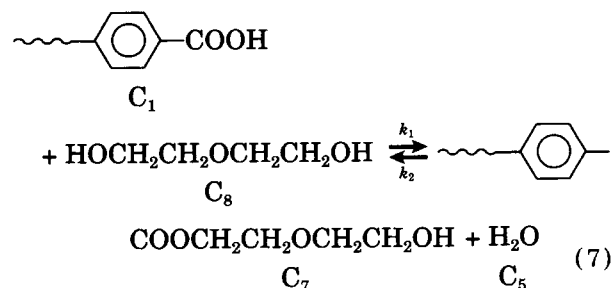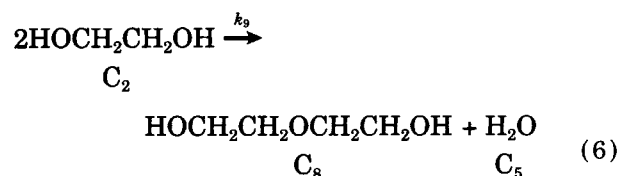Various reactions occurring in an reactor are given as follows.[1]

Esterification Reactions

$$
\begin{aligned}
&\sim\!\!\!\langle\bigcirc\rangle\!\!-\text{COOH} + \text{HOCH}_2\text{CH}_2\text{OH} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \\
&\qquad C_1 \qquad\qquad\qquad C_2 \\
&\sim\!\!\!\langle\bigcirc\rangle\!\!-\text{COOCH}_2\text{CH}_2\text{OH} + \text{H}_2\text{O} \\
&\qquad\qquad C_3 \qquad\qquad\qquad C_5
\end{aligned} \tag{1}
$$

$$
\begin{aligned}
&\sim\!\!\!\langle\bigcirc\rangle\!\!-\text{COOH} + \text{HOCH}_2\text{CH}_2\text{OOC} \\
&\qquad C_1 \qquad\qquad\qquad C_3 \\
&\langle\bigcirc\rangle\!\!\sim \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \sim\!\!\langle\bigcirc\rangle \\
&\text{COOCH}_2\text{CH}_2\text{OOC}\!\!-\!\langle\bigcirc\rangle\!\!\sim + \text{H}_2\text{O} \\
&\qquad\qquad C_4 \qquad\qquad\qquad C_5
\end{aligned} \tag{2}
$$

Polycondensation Reactions

$$2(\sim\!\!\!-\!\!\langle\bigcirc\rangle\!-\!COOCH_2CH_2OH) \underset{k_6}{\overset{k_5}{\rightleftharpoons}}$$

$$C_3$$

$$\sim\!\!\!-\!\!\langle\bigcirc\rangle\!-\!COOCH_2CH_2OOC\!-\!\langle\bigcirc\rangle\!-\!\sim$$

$$C_4$$

$$+ HOCH_2CH_2OH \qquad (3)$$

$$C_2$$

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

$$2(\sim\!\!\!-\!\!\langle\bigcirc\rangle\!-\!COOCH_2CH_2OH) \overset{k_7}{\rightarrow} \sim\!\!\!-\!\!\langle\bigcirc\rangle\!-$$

$$C_3$$

$$COOCH_2CH_2OCH_2CH_2OOC\!-\!\langle\bigcirc\rangle\!-\!\sim + H_2O \qquad (4)$$

$$C_6 \qquad\qquad\qquad\qquad\qquad\qquad C_5$$

$$\sim\!\!\!-\!\!\langle\bigcirc\rangle\!-\!COOCH_2CH_2OH$$

$$C_3$$

$$+ HOCH_2CH_2OH \overset{k_8}{\rightarrow} \sim\!\!\!-\!\!\langle\bigcirc\rangle\!-$$

$$C_2$$

$$COOCH_2CH_2OCH_2CH_2OH + H_2O \qquad (5)$$

$$C_7 \qquad\qquad\qquad\qquad\qquad C_5$$

$$2HOCH_2CH_2OH \overset{k_9}{\rightarrow}$$

$$C_2$$

$$HOCH_2CH_2OCH_2CH_2OH + H_2O \qquad (6)$$

$$C_8 \qquad\qquad\qquad\qquad\qquad C_5$$

$$\sim\!\!\!-\!\!\langle\bigcirc\rangle\!-\!COOH$$

$$C_1$$

$$+ HOCH_2CH_2OCH_2CH_2OH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \sim\!\!\!-\!\!\langle\bigcirc\rangle\!-$$

$$C_8$$

$$COOCH_2CH_2OCH_2CH_2OH + H_2O \qquad (7)$$

$$C_7 \qquad\qquad\qquad\qquad\qquad C_5$$
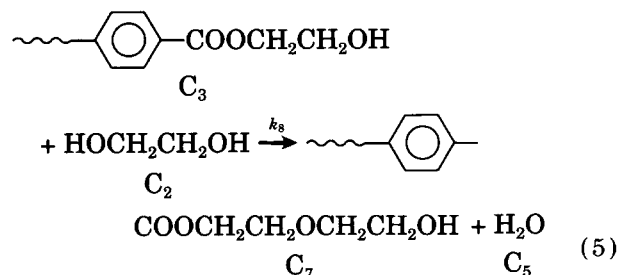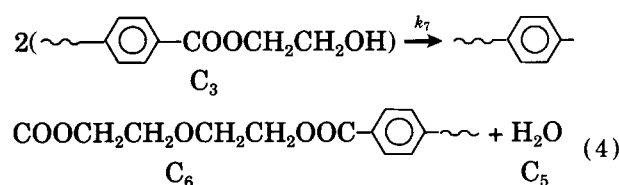
where C_i is the concentration of component i in the liquid phase and k_1 to k_9 are the reaction rate constants, and there are the relations $k_8 = 2k_7$ and $k_9 = 4k_7$ (see Appendix A).

REACTION RATE EQUATIONS

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

$$(dC_1/d\theta) = -k_1C_1C_2 + k_2C_3C_5 - k_3C_1C_3$$
$$+ k_4C_4C_5 - k_1C_1C_8 + k_2C_5C_7 \quad (8)$$

$$(dC_2/d\theta) = -k_1C_1C_2 + k_2C_3C_5 + k_5C_1C_3^2$$
$$- k_6C_2C_4 - k_8C_2C_3 - 2k_9C_2^2 \quad (9)$$

$$(dC_3/d\theta) = k_1C_1C_2 - k_2C_3C_5 - k_3C_1C_3 + k_4C_4C_5$$
$$- 2k_5C_3^2 + 2k_6C_2C_4 - 2k_7C_3^2 - k_8C_2C_3 \quad (10)$$

$$(dC_4/d\theta) = k_3C_1C_3 - k_4C_4C_5 + k_5C_3^2 - k_6C_2C_4 \quad (11)$$

$$(dC_5/d\theta) = k_1C_1C_2 - k_2C_3C_5 + k_3C_1C_3 - k_4C_4C_5$$
$$+ k_7C_3^2 + k_8C_2C_3 + k_9C_2^2 + k_1C_1C_8 - k_2C_5C_7 \quad (12)$$

$$(dC_6/d\theta) = k_7C_3^2 \quad (13)$$

$$(dC_7/d\theta) = k_8C_2C_3 + k_1C_1C_8 - k_2C_5C_7 \quad (14)$$

$$(dC_8/d\theta) = k_9C_2^2 - k_1C_1C_8 + k_2C_5C_7 \quad (15)$$

where $k_8 = 2k_7$ and $k_9 = 4k_7$, and θ denotes the reaction time.

PREPARATION OF MATHEMATICAL MODEL FOR ESTERIFICATION REACTIONS

Assumptions for Modeling

Assumptions for modeling of direction esterification are given 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 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 significantly lower than those of EG and water.

7. All the nonvolatile components in reaction mixtures are defined as oligomer.
8. Reactivity of a functional group does not depend on the polymer chain length, since it can be assumed that the degree of polymerization is not high in the esterification step.
9. In the formation of DEG, the reactivity of each hydroxyl end group is assumed to be the same. That is, $k_8 = 2k_7$ and $k_9 = 4k_7$.

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

By the above-mentioned assumptions, the weight fraction of the liquid phase in the reaction mixtures, β, and carboxyl end group concentration in the liquid phase, C_1, have been derived by Yamada et al.[1] as follows.

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

$$\beta = \frac{AV - \eta_{TPA}}{\alpha + AV \cdot (w_{EG} + w_{H_2O}) - \eta_{TPA}} \quad \text{and} \quad C_1 = \alpha \quad (16)$$

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 $\alpha = 18,124 \cdot \exp(-9692/RT) \cdot w_{EG} + 748 \cdot \exp(-7612/RT) \cdot w_{OLG}$ (see eqs. (18) to (21); R = gas constant; T = absolute temperature; η_{TPA} = equivalents of carboxyl end groups per 1 kg of pure TPA (that is, $\eta_{TPA} = 12.039\text{-COOH}$ 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 (no 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 dependences of the solubilities of TPA in EG, α_{EG}, and that in BHET, α_{BHET}, are given as follows.[1]

$$\alpha_{EG} = 18,124 \cdot \exp(-9696/RT) \quad (18)$$

$$\alpha_{BHET} = 748 \cdot \exp(-7612/RT) \quad (19)$$

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.

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

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 the reaction mixture is negligible because of the very small amount of water in it, the solubility of TPA in oligomer, α_{OLG}, is equivalent to that in BHET, α_{BHET}, and α is given by

$$\alpha \fallingdotseq \alpha_{EG} \times w_{EG} + \alpha_{BHET} \times w_{OLG} \quad (21)$$
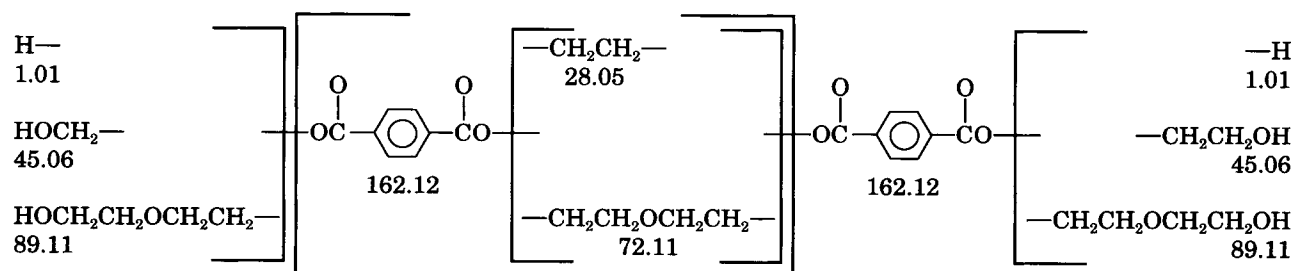
Relations among Oligomer Properties

The relationships among oligomer properties are given in the following equations.

$$\phi = OHV/(AV + OHV) \quad (22)$$

$$M_n = 2000/(AV + OHV) \quad (23)$$

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

H—
1.01

HOCH$_2$—
45.06

HOCH$_2$CH$_2$OCH$_2$CH$_2$—
89.11

O   O
‖   ‖
—OC—⟨◯⟩—CO—
162.12

—CH$_2$CH$_2$—
28.05

—CH$_2$CH$_2$OCH$_2$CH$_2$—
72.11

O   O
‖   ‖
—OC—⟨◯⟩—CO—
162.12

—H
1.01

—CH$_2$CH$_2$OH
45.06

—CH$_2$CH$_2$OCH$_2$CH$_2$OH
89.11

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).

$$M_n = (P_n - 1)(164.12 + 28.05)/(1 + e)$$
$$+ (P_n - 1)(164.12 + 72.11)e/(1 + e)$$
$$+ 164.12 + 2(1 - \phi) \times 1.008$$
$$+ 2\phi\{45.06/(1 + e) + 89.11e/(1 + e)\} \quad (24)$$

By rearrangement of eq. (24), P_n can be expressed by eq. (25).

$$P_n = \{M_n(1 + e) + 26.03 + 70.09e - \phi(88.10$$
$$+ 176.20e)\}/(192.17 + 236.23e) \quad (25)$$

And then, SV and E_S are given by the following relationships.

$$SV = 2000 \times P_n/M_n \quad (26)$$

$$E_S = (SV - AV)/SV \quad (27)$$

Since 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:

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

$$x = (P_n - 1 + 2\phi)e/(1 + e) \quad (28)$$

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

$$d = 100\{(P_n + 2\phi - 1)/P_n\} \times \{e/(1 + e)\} \quad (29)$$

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 gas chromatographic analysis after methanolysis of oligomer.

PREDICTION OF MELTING POINTS

The melting points of oligomer, T_m, can be predicted from the following equation.[3,4]

$$1/T_m = 0.111049 \times 10^{-3} \cdot OHV^2$$
$$- 0.200468 \times 10^{-4} \cdot OHV^3$$
$$- 0.298614 \times 10^{-3} \cdot \exp(-OHV)$$
$$- 0.196193 \times 10^{-2} \cdot AV/(P_n + OHV)$$
$$+ 0.605210 \times 10^{-3} \cdot AV^2/(P_n + OHV)^2$$
$$- 0.971548 \times 10^{-2} \cdot AV/(P_n + OHV)^2$$
$$+ 0.980871 \times 10^{-3} \cdot OHV/(P_n + OHV)^2$$
$$+ 0.142510 \times 10^{-3} \cdot \exp\{AV/(P_n + OHV)\}$$
$$- 0.655692 \times 10^{-4} \cdot \ln(P_n)$$
$$+ 0.415790 \times 10^{-2} \quad (30)$$

Effect of Polycondensation Catalysts or Additive on Reaction Rate Constants

Yamada and Imamura[5,6,7] have reported earlier on the effect of diantimony trioxide (Sb_2O_3) and potassium titanium oxyoxalate ($K_2TiO(C_2O_4)_2 \times 2H_2O$), 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) through (7) were determined by fitting the experimental data obtained from a pilot plant with throughput about 50 kg/h. From the results obtained, it was clear that the effects of diantimony trioxide (Sb_2O_3), potassium titanium oxyoxalate ($K_2TiO(C_2O_4)_2 \times 2H_2O$), titanium dioxide ($TiO_2$) on the reaction rate constants are expressed as follows.

$$k_1 = (3.75 \times 10^{-4} \cdot Sb^{3+} + 0.015 \cdot T_i + 1)$$
$$\times 1.5657 \times 10^9 \cdot \exp(-19640/RT) \quad (31)$$
$$k_2 = (4.75 \times 10^{-4} \cdot Sb^{3+} + 9.1667 \times 10^{-3} \cdot T_i + 1)$$
$$\times 1.5515 \times 10^8 \cdot \exp(-18140/RT) \quad (32)$$
$$k_3 = (6.25 \times 10^{-4} \cdot Sb^{3+}$$
$$+ 0.019167 \cdot T_i + 0.1[TDO] + 1)$$
$$\times 3.5165 \times 10^9 \cdot \exp(-22310/RT) \quad (33)$$
$$k_4 = (4.50 \times 10^{-4} \cdot Sb^{3+} + 1.6667 \times 10^{-3} \cdot T_i + 1)$$
$$\times 6.7640 \times 10^7 \cdot \exp(-18380/RT) \quad (34)$$

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

$$+ \; 0.015833 \cdot \mathrm{T}_i + 0.08\,[\mathrm{TDO}] + 1)$$

$$\times \; 7.7069 \cdot \exp(-2810/RT) \quad (35)$$

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

$$+ \; 3.3333 \times 10^{-3} \cdot \mathrm{T}_i + 0.04\,[\mathrm{TDO}] + 1)$$

$$\times \; 6.2595 \times 10^6 \cdot \exp(-14960/RT) \quad (36)$$

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

$$+ \; 0.0125 \cdot \mathrm{T}_i + 0.085714\,[\mathrm{TDO}] + 1)$$

$$\times \; 2.0583 \times 10^{15} \cdot \exp(-42520/RT) \quad (37)$$

where Sb^{3+} = mol of antimony ion (Sb^{3+}) in diantimony trioxide supplied for 10^6 moles of TPA; T_i = mol number of potassium titanium oxyoxalate supplied for 10^6 mol of TPA; R = gas constant; T = absolute temperature.

MODELING FOR ESTERIFICATION REACTIONS IN A CONTINUOUS RECYCLE PROCESS

Continuous Recycle Process

We consider a continuous recycle process in steady state, shown in Figure 1. In Figure 1, the slurry of TPA–EG mixtures is fed into RA-1, controlled at reaction pressure P, at a reaction temperature t, by the heating medium in coils with the heating area of A, and at the content weight of W. TPA reacts with EG in RA-1. Then, the reaction mixture discharged from RA-1 is fed at a flow rate of (F_P + f'_B) into RA-2, controlled at reaction pressure P', at reaction temperature t', by the heating medium in coils with the heating area of A', and the content weight of W'. The reaction continues in RA-2 through the addition of EG of $\delta_{EG}F_S$ into it. The reaction mixtures are recycled at a flow rate of f_B from RA-2 to RA-1 and the reaction mixtures discharged from RA-2 are fed at a flow rate of F'_P into the next reactor.

In this section, 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 Yamada et al.[1]
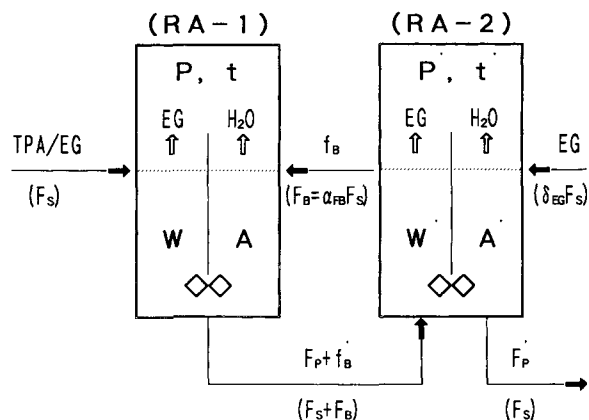

Figure 1 Continuous recycle esterification process in steady state. P, P' = Reaction pressures; t, t' = Reaction temperature; W, W' = Weights of reaction mixtures; A, A' = Heat transfer areas; F_s = Throughput based on PET polymer; F_B = Recycle flow rate based on PET polymer, $F_B = \alpha_{FB}F_S$; α_{FB} = Recycle ratio; F_P, F'_P = Actual discharge flow rates from reactor; f_B, f'_B = Actual recycle flow rates into which F_B and 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 superscript with 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 the total number of TPA units (namely, PET units) in the reaction mixture is given by the sum of mol 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. (38) and (39).

A material balance of TPA units is expressed as follows; TPA units based on undissolved TPA in actual recycle flow + TPA units based on oligomer (with dissolved TPA) of the liquid phase in actual recycle flow = total TPA units in recycle flow converted to PET polymer flow rate (F_B), which is constant for f_B and f'_B. From this we can obtain eqs. (38) and (39).

$$(1 - \beta')f_B/M_{\mathrm{TPA}} + \beta'f_B w'_{\mathrm{OLG}}P'_{\mathrm{nL}}/M'_{\mathrm{nL}}$$

$$= F_B/M_{\mathrm{PET}} \quad (38)$$

$$(1 - \beta)f'_B/M_{\mathrm{TPA}} + \beta f'_B w_{\mathrm{OLG}}P_{\mathrm{nL}}/M_{\mathrm{nL}}$$

$$= F_B/M_{\mathrm{PET}} \quad (39)$$

By rearrangement of eqs. (38) and (39), the following expressions for f_B and f'_B are obtained:

$$f_B = (F_B/M_{PET})/$$
$$((1 - \beta')/M_{TPA} + \beta'w'_{OLG}P'_{nL}/M'_{nL}) \quad (40)$$

$$f'_B = (F_B/M_{PET})/$$
$$((1 - \beta)/M_{TPA} + \beta w_{OLG}P_{nL}/M_{nL}) \quad (41)$$

where the superscript prime ($'$) represents RA-2, and no superscript represents RA-1; β is the weight fraction of liquid phase defined earlier; M_{PET} and M_{TPA} are the molecular weight of PET polymer unit and TPA, respectively, that is, $M_{PET} = 192.17$ and $M_{TPA} = 166.13$; 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 $M_{nL} = 2000\beta w_{OLG}/[\beta C_1 + OHV\{1 - \beta(w_{EG} + w_{H_2O})\}]$ (see Appendix C), and P_{nL} can be obtained from eq. (25); 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 PET chain by reaction due to a few percent of DEG content in oligomer, the amount of bound EG can be given by eqs. (42) and (43) for RA-1 and RA-2, respectively (refer to Appendix B).

(1) $\langle$RA-1$\rangle$

$$q_{EG} = (M_{EG}/M_{PET})F_B$$
$$\times \{(P_n + 2\phi - 1)/P_n - (P'_n + 2\phi' - 1)/P'_n\}$$
$$+ (M_{EG}/M_{PET})F_S(P_n + 2\phi - 1)/P_n \quad (42)$$

(2) $\langle$RA-2$\rangle$

$$q'_{EG} = (M_{EG}/M_{PET})(F_s + F_B)\{(P'_n + 2\phi' - 1)/$$
$$P'_n - (P_n + 2\phi - 1)/P_n\} \quad (43)$$

Where M_{EG} is the molecular weight of EG ($M_{EG} = 62.07$); P_n is the number average degree 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, $M_n = 2000/(AV + OHV)$; ϕ is the ratio of hydroxyl end groups to total end groups of dried oligomer $\phi = OHV/(AV + OHV)$; 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_{H_2O}, q'_{H_2O})

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. (44) and (45) for RA-1 and RA-2, respectively (refer to Appendix B).

(1) $\langle$RA-1$\rangle$

$$q_{H_2O} = (2M_{H_2O}/M_{PET})F_B$$
$$\times \{(P_n + \phi - 1)/P_n - (P'_n + \phi' - 1)/P'_n\}$$
$$+ (2M_{H_2O}/M_{PET})F_S(P_n + \phi - 1)/P_n \quad (44)$$

By using esterification degree (E_S), eq. (44) can be expressed by eq. (45).

$$q_{H_2O} = (2M_{H_2O}/M_{PET})F_B(E_S - E'_S)$$
$$+ (2M_{H_2O}/M_{PET})F_S E_S \quad (45)$$

Where, M_{H_2O} is the molecular weight of water, that is, $M_{H_2O} = 18.02$ and E_S is the esterification degree defined as $(SV - AV)/SV$. Here, SV is the saponification value.

(2) $\langle$RA-2$\rangle$

In a similar manner as for RA-1, the following formulae are obtained.

$$q_{H_2O} = (2M_{H_2O}/M_{PET})(F_S + F_B)$$
$$\times \{(P'_n + \phi' - 1)/P'_n - (P_n + \phi - 1)/P_n\} \quad (46)$$

By using esterification degree, eq. (46) can be expressed by eq. (47).

$$q_{H_2O} = (2M_{H_2O}/M_{PET})(F_S + F_B)(E'_S - E_S) \quad (47)$$

Input Rate of EG to Reactor (F^i_{EG}, $F^{i'}_{EG}$)

The input rates of EG (F^i_{EG}, $F^{i'}_{EG}$) into RA-1 and RA-2 can be expressed by eqs. (48) and (49) from the EG material balances, namely:

(1) $\langle$RA-1$\rangle$

$$F^i_{EG} = (M_{EG}/M_{PET})F_S \cdot a + \beta' f_B w'_{EG} \quad (48)$$

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.

(2) $\langle$RA-2$\rangle$

$$F_{EG}^{i'} = \beta(F_P + f_B')w_{EG} + \delta_{EG}F_S \qquad (49)$$

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 ($F_{H_2O}^i$, $F_{H_2O}^{i'}$)

The input rates of water ($F_{H_2O}^i$, $F_{H_2O}^{i'}$) into RA-1 and RA-2 can be expressed by eqs. (50) and (51) from the material balances of water, namely.

(1) $\langle$RA-1$\rangle$

$$F_{H_2O}^i = \beta' f_B w_{H_2O}' \qquad (50)$$

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

(2) $\langle$RA-2$\rangle$

$$F_{H_2O}^{i'} = \beta(F_P + f_B')w_{H_2O} \qquad (51)$$

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

The total input rates (F_T^i, $F_T^{i'}$) into RA-1 and RA-2 can be expressed by eqs. (52) and (53).

(1) $\langle$RA-1$\rangle$

$$F_T^i = F_S(M_{TPA} + M_{EG} \cdot a)/M_{PET} + f_B \qquad (52)$$

(2) $\langle$RA-2$\rangle$

$$F_T^{i'} = F_P + f_B' + \delta_{EG}F_S \qquad (53)$$

Material Balance around RA-1

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

(1) $\langle$EG$\rangle$

$$F_{EG}^i = Q_{EG} + q_{EG} + (F_P + f_B')\beta w_{EG} \qquad (54)$$

(2) $\langle$Water$\rangle$

$$F_{H_2O}^i + q_{H_2O} = Q_{H_2O} + (F_P + f_B')\beta w_{H_2O} \qquad (55)$$

(3) $\langle$Total Balance$\rangle$

$$F_T^i = Q_{EG} + Q_{H_2O} + F_P + f_B' \qquad (56)$$

Material Balance around RA-2

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

(1) $\langle$EG$\rangle$

$$F_{EG}^{i'} = Q_{EG}' + q_{EG}' + (F_P' + f_B)\beta'w_{EG}' \qquad (57)$$

(2) $\langle$Water$\rangle$

$$F_{H_2O}^{i'} + q_{H_2O}' = Q_{H_2O}' + (F_P + f_B)\beta'w_{H_2O}' \qquad (58)$$

(3) $\langle$Total Balance$\rangle$

$$F_T^{i'} = Q_{EG}' + Q_{H_2O}' + F_P' + f_B \qquad (59)$$

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

By combining eqs. (54) through (56), the vapor (distillate) flow rates of EG and water (Q_{EG}, Q_{H_2O}) from RA-1 can be expressed by eqs. (60) and (61).

$$Q_{EG} = \{(F_{EG}^i - q_{EG})(1 - \beta w_{EG})$$
$$- \beta w_{EG}(F_T^i - F_{H_2O}^i - q_{H_2O})\}/$$
$$\{1 - \beta(w_{EG} + w_{H_2O})\} \qquad (60)$$

$$Q_{H_2O} = \{(F_{H_2O}^i + q_{H_2O} - \beta w_{H_2O}(F_T^i - Q_{EG})\}/$$
$$(1 - \beta w_{H_2O}) \qquad (61)$$

By combining eqs. (57) through (59), the vapor (distillate) flow rates of EG and water (Q_{EG}', Q_{H_2O}') from RA-2 can be expressed by eqs. (62) and (63).

$$Q_{EG}' = \{(F_{EG}^{i'} - q_{EG}')(1 - \beta'w_{EG}')$$
$$- \beta'w_{EG}'(F_T^{i'} - F_{H_2O}^{i'} - q_{H_2O}')\}/$$
$$\{1 - \beta'(w_{EG}' + w_{H_2O}')\} \qquad (62)$$

$$Q_{H_2O}' = \{(F_{H_2O}^{i'} + q_{H_2O}' - \beta'w_{H_2O}'(F_T^{i'} - Q_{EG}')\}/$$
$$(1 - \beta'w_{H_2O}') \qquad (63)$$

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 mol fractions of EG and water are given by the following equations.

y_{EG}
$$= (Q_{EG}/M_{EG})/(Q_{EG}/M_{EG} + Q_{H_2O}/M_{H_2O}) \qquad (64)$$

y_{EG}'
$$= (Q_{EG}'/M_{EG})/(Q_{EG}'/M_{EG} + Q_{H_2O}'/M_{H_2O}) \qquad (65)$$

Because the vapor–liquid equilibrium in the esterification stage effectively follows Raoult's law, as described in the article of Yamada et al.,[2] the following relations hold true in RA-1 and RA-2.

$$y_{EG} + y_{H_2O} = 1; \quad y'_{EG} + y'_{H_2O} = 1 \quad (66)$$

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

$$x'_{EG} + x'_{H_2O} + x'_{OLG} = 1 \quad (67)$$

$$x_{EG}P_{EG} = y_{EG}P; \quad x'_{EG}P'_{EG} = y'_{EG}P' \quad (68)$$

$$x_{H_2O} = y_{H_2O}P; \quad x'_{H_2O}P'_{H_2O} = y'_{H_2O}P' \quad (69)$$

where x_{EG}, x_{H_2O}, x_{OLG} = liquid phase mol fractions of EG, water, and oligomer; y_{EG}, y_{H_2O} = vapor phase mol fractions of EG and water; P_{EG}, P_{H_2O} = vapor pressures of EG or water at a reaction temperature (mmHg).

$$\log P_{EG} = 7.8808 - 1957/(t + 193.8) \quad (70)$$

$$\log P_{H_2O} = 7.9668 - 1668.2/(t + 228) \quad (71)$$

A, B = constants of Van Laar equation; t = reaction temperature (°C); P = total pressure (reaction pressure); Superscript prime (') = RA-2.

From eqs. (60) through (71), we can determine the liquid phase or vapor phase mol fractions, so that the weight fractions of each component can be obtained from the following relations.

$$w_i = x_i M_i \Big/ \sum_{j=1}^{N} x_j M_j; \quad w'_i = x'_i M_i \Big/ \sum^{N} x'_j M_j \quad (72)$$

where subscripts i and j represent water, EG and oligomer; x_i, x_j = liquid phase mol fractions of component i and j; w_i = liquid phase weight fraction of component i; N = number of components; M_i, M_j = mol wt of component i and j.

Since the concentrations of 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 method for determining vapor (distillate) flow rates is far more complicated for this process than for a continuous cascade process; this is because, although the concentrations and flow rates at the inlet are given in advance as input data for the continuous cascade process, as reported by Yamada et al.,[1,2] they are given not as input data but as parameters to be determined for the recycle process.

Material Balance of Each Component

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

Material Balance of Carboxyl End Groups

in RA-1:

$$F^i C_{10} - F_P A V_a + f_B A V'_a - f'_B A V_a$$
$$+ \beta W (dC_1/d\theta) = 0 \quad (73)$$

in RA-2

$$F^{i'} C'_{10} - F'_P A V'_a + f'_B A V_a - f_B A V'_a$$
$$+ \beta' W' (dC'_1/d\theta) = 0 \quad (74)$$

Material Balance of Hydroxyl End Groups

in RA-1

$$F^i C_{30} - \beta F_P C_3 + \beta' f_B C'_3 - \beta f'_B C_3$$
$$+ \beta W (dC_3/d\theta) = 0 \quad (75)$$

in RA-2

$$F^{i'} C'_{30} - \beta' F'_P C'_3 + \beta f'_B C_3 - \beta' f_B C'_3$$
$$+ \beta' W' (dC'_3/d\theta) = 0 \quad (76)$$

Material Balance of Diester Groups (Ester Linkages)

in RA-1

$$F^i C_{40} - \beta F_P C_4 + \beta' f_B C'_4 - \beta f'_B C_4$$
$$+ \beta W (dC_4/d\theta) = 0 \quad (77)$$

in RA-2

$$F^{i'} C'_{40} - \beta' F'_P C'_4 + \beta f'_B C_4 - \beta' f_B C'_4$$
$$+ \beta' W' (dC'_4/d\theta) = 0 \quad (78)$$

Material Balance of DEG (Ether Linkages)

in RA-1

$$F^i (C_{60} + C_{70} + C_{80}) - \beta F_P (C_6 + C_7 + C_8)$$
$$+ \beta' f_B (C'_6 + C'_7 + C'_8) - \beta f'_B (C_6 + C_7 + C_8)$$
$$+ \beta W (dC_6/d\theta + dC_7/d\theta + dC_8/d\theta) = 0 \quad (79)$$

in RA-2

$$F^{i'} (C'_{60} + C'_{70} + C'_{80}) - \beta' F'_P (C'_6 + C'_7 + C'_8)$$
$$+ \beta f'_B (C_6 + C_7 + C_8) - \beta' f_B (C'_6 + C'_7 + C'_8)$$
$$+ \beta' W' (dC'_6/d\theta + dC'_7/d\theta + dC'_8/d\theta) = 0 \quad (80)$$

Material Balance of Water

in RA-1

$$F^i C_{50} - \beta F_P C_5 + \beta' f_B C_5' - \beta f_B' C_5 - Q_{H_2O} \eta_{H_2O}$$
$$+ \beta W (dC_5/d\theta) = 0 \quad (81)$$

in RA-2

$$F^{i'} C_{50}' - \beta' F'_P C_5' + \beta f_B' C_5 - \beta' f_B C_5' - Q'_{H_2O} \eta_{H_2O}$$
$$+ \beta' W' (dC_5'/d\theta) = 0 \quad (82)$$

Material Balance of EG

in RA-1

$$F^i C_{20} - \beta F_P C_2 + \beta' f_B C_2' - \beta f_B' C_2 - Q_{EG}\eta_{EG}$$
$$+ \beta W (dC_2/d\theta) = 0 \quad (83)$$

in RA-2

$$F^{i'} C_{20}' - \beta' F'_P C_2' + \beta f_B' C_2 - \beta' f_B C_2' - Q'_{EG}\eta_{EG}$$
$$+ \delta_{EG} F_S \eta_{EG} + \beta' W' (dC_2'/d\theta) = 0 \quad (84)$$

where the superscript prime (') expresses RA-2; F^i = total input flow rate of TPA–EG slurry; C_{i0} = input concentration of component k in TPA–EG slurry, that is, $C_{30} = C_{40} = C_{50} = C_{60} = C_{70} = C_{80} = 0$; 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; δ_{EG} = flow rate of EG added anew to the reactor per 1 kg/h of throughput, based on PET polymer; 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).

Simulation Procedures of Reactions

1. Determine the reaction rate constants by a nonlinear optimization technique, such as a Simplex method, with the experimental data on the continuous cascade esterification process, reported by Yamada et al.,[1,2] applying them to the reaction scheme shown in eqs. (1) to (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. (38) to (63); from these values, calculate the weight fraction in the liquid phase or the concentration of each component.
4. Calculate the values of (ϵ_k) of the left hand of material balances in eqs. (73) through (84) by the substitution of the calculated weight fractions and concentrations and obtain the sum ($\sum \epsilon_k^2$) 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. Then, stop searching by the Simplex method.
6. Print out final results and stop the simulation.

HEAT BALANCE OF RECYCLE PROCESS (NEGLIGIBLE WATER AND EG IN REACTION MIXTURES)

In the previous section, the basic theory for the continuous recycle reaction model of direct esterification between TPA and EG was derived. In this section, the heat balance for the recycle model is derived when EG and water, dissolved in the reaction mixtures, is negligible.

Basic Theory for Heat Balance of Continuous Recycle Process

Enthalpy Balances of Reactors

When the standard level of temperature is set at 0°C, for the recycle process shown in Figure 1, the amounts of heat (h_d, h_d') removed from RA-1 and RA-2 as latent heat of evaporation can be obtained from eqs. (85) and (86), respectively.

$$h_d = \lambda_{EG} Q_{EG} + \lambda_{H_2O} Q_{H_2O} \quad (85)$$

$$h_d' = \lambda_{EG}' Q_{EG}' + \lambda_{H_2O}' Q_{H_2O}' \quad (86)$$

The enthalpy moving with recycle (h_B) from RA-2 to RA-1 can be obtained by the following equation:

$$h_B = \bar{C}'_P F_B t' = \bar{C}'_P \alpha_{FB} F_S t' \quad (87)$$

By using eqs. (85) through (87), the enthalpy balances in RA-1 and RA-2 are given by eqs. (88) and (89), respectively.

$$C_P^{EG} F_{EG}^i t_i + C_P^{TPA} F_{TPA}^i t_i + h_a + h_B$$
$$= h_d + \bar{C}_P (F_B + F_S) t \quad (88)$$

$$C_P^{EG'} \delta_{EG} F_S t_i' + h_a' + \bar{C}_P (F_B + F_S) t$$
$$= h_d' + h_B + \bar{C}_P' F_S t' \quad (89)$$

where the superscript prime ($'$) means RA-2 and no superscript means RA-1;

λ_{EG}, λ_{H_2O} = Latent heats of vaporization of EG and water,

Q_{EG}, Q_{H_2O} = Vapor (distillate) flow rates of EG and water,

F_S, F_B = Throughput and recycle flow rate based on PET polymer,

$\bar{C}_P$ = Average specific heat of oligomer at constant pressure,

C_P^{EG}, C_P^{TPA} = Specific heat of EG, water, and TPA at constant pressure,

t = Reaction temperature,

t_i = Temperature of slurry fed to RA-1,

t_i' = Temperature of EG added anew into RA-2,

F_{EG}^i, $F_{H_2O}^i$ = Input (charged) rates of EG and water,

h_a = Amount of heat supplied by the heating medium, and

δ_{EG} = Flow rate of EG added anew into RA-2 per 1 kg/h of throughput, based on PET polymer.

Required Heat Transfer Areas (A, A') (When Recycle Ratio (α_{FB}) is Given)

When the recycle ratio (α_{FB}) is given, the required heat transfer area (A, A') to keep a fixed reaction temperature can be determined by the following procedures for each reactor.

RA-1

From eq. (88), the amount of heat (h_a) to be supplied by the heating medium is given in the following equation.

$$h_a = h_d + \bar{C}_P (F_B + F_S) t - C_P^{EG} F_{EG}^i t_i$$
$$- C_P^{TPA} F_{TPA}^i t_i - h_B \quad (90)$$

When the temperature of the heating medium at the inlet is expressed as t_{Si}, the temperature of the heating medium at the outlet as t_{So}, and the mass flow rate of the heating medium as W_S, the following relation exists:

$$h_a = \bar{C}_P^S W_S (t_{Si} - t_{So}) \quad (91)$$

where, $\bar{C}_P^S$ is the average specific heat of the heating medium defined in the following equation;

$$\bar{C}_P^S = \int_{t_{So}}^{t_{Si}} C_P^S \, dt / (t_{Si} - t_{So}) \quad (92)$$

Suppose the overall heat transfer coefficient is U, heat transfer area is A, and logarithmic mean temperature difference is $(\Delta t)_{\ell m}$, then h_a is given in the following equation (refer to Fig. 2):

$$h_a = UA (\Delta t)_{\ell m} \quad (93)$$

where

$$(\Delta t)_{\ell m} = \frac{(\Delta t)_i - (\Delta t)_o}{\ln [(\Delta t)_i / (\Delta t)_o]}$$

$$= \frac{t_{Si} - t_{So}}{\ln [(t_{Si} - t) / (t_{So} - t)]} \quad (94)$$
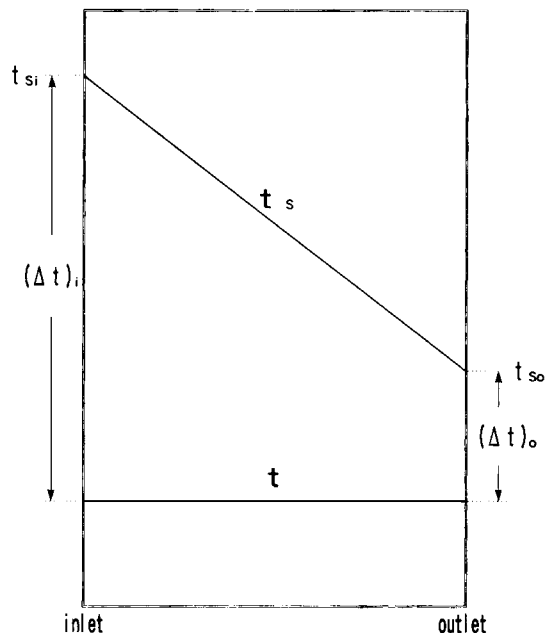

Figure 2 Temperature distribution of heating medium in heating coils. t = Reaction temperature; t_S = Heating medium temperature.

By introducing a dimensionless temperature difference ratio (η), defined in eq. (95), the outlet temperature (t_{So}) can be given by eq. (96), where $0 < \eta < 1$.

$$\eta = (t_{So} - t)/(t_{Si} - t) \qquad (95)$$
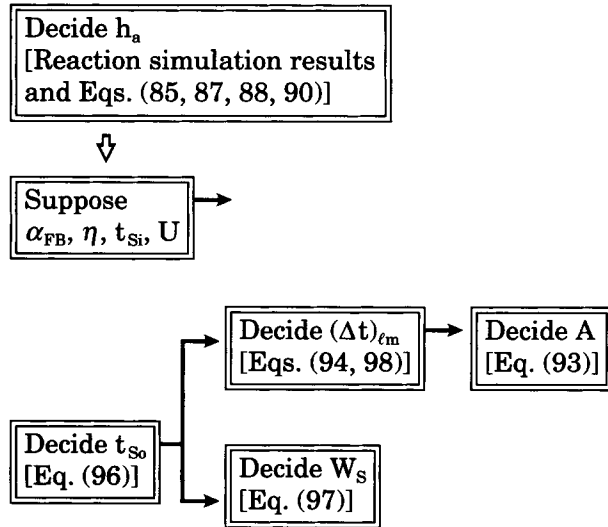
$$t_{So} = t + \eta(t_{Si} - t) \qquad (96)$$

Substituting eq. (96) into eq. (91) yields the mass flow rate of the heating medium (W_S) as follows:

$$W_S = h_a/\{\bar{C}_P^S(1 - \eta)(t_{Si} - t)\} \qquad (97)$$

On the other hand, when $\eta = 1$ (i.e., $W_S = \infty$), from l'Hospitas's law, ($\Delta t)_{\ell m}$ is given as:

$$\lim_{\eta=1} (\Delta t)_{\ell m} = t_{Si} - t \qquad (98)$$

When the recycle ratio (α_{FB}), η value, inlet heating medium temperature (t_{Si}), and overall heat transfer coefficient (U) are given, from the reaction simulation results by eqs. (38) through (84), and the heat balances of eqs. (95) through (98), the heat transfer area (A) and mass flow rate of heating medium (W_S) can be obtained in the following procedure.

```
┌─────────────────────────────────┐
│ Decide h_a                      │
│ [Reaction simulation results    │
│ and Eqs. (85, 87, 88, 90)]      │
└─────────────────────────────────┘
               ⇓
┌─────────────────┐
│ Suppose         │ ──▶
│ α_FB, η, t_Si, U│
└─────────────────┘
                    ┌──────────────────┐    ┌──────────────┐
                  ┌▶│ Decide (Δt)_ℓm   │──▶ │ Decide A     │
                  │ │ [Eqs. (94, 98)]  │    │ [Eq. (93)]   │
                  │ └──────────────────┘    └──────────────┘
┌──────────────┐  │
│ Decide t_So  │──┤
│ [Eq. (96)]   │  │ ┌──────────────┐
└──────────────┘  └▶│ Decide W_S   │
                    │ [Eq. (97)]   │
                    └──────────────┘
```

RA-2 (Refer to RA-1)

The required heat transfer of RA-2 (A') can be obtained in the same way as that of RA-1 for the recycle model shown in Figure 1 (refer to the previous section). From eq. (89), the amount of heat (h_a) to be

supplied by the heating medium is given as the following equation.

$$h'_a = h'_d + h_B + \bar{C}'_P F_S t' - C_P^{EG'} \delta_{EG} F_S t'_i$$
$$\qquad\qquad - C_P(F_B + F_S)t \qquad (99)$$

When the temperature of the heating medium at the inlet is expressed as t'_{Si}, the temperature of the heating medium at the outlet as t'_{So}, and the mass flow rate of the heating medium as W'_S, the amount of heat supplied by the heating medium (h'_a) is given in the following equation.

$$h'_a = \bar{C}_P^{S'} W'_S(t'_{Si} - t'_{So}) \qquad (100)$$

where $\bar{C}_P^{S'}$ is the average specific heat of the heating medium defined in the following equation:

$$\bar{C}_P^{S'} = \int_{t'_{So}}^{t'_{Si}} C_P^{S'}\, dt/(t'_{Si} - t'_{So}) \qquad (101)$$

Suppose the overall heat transfer coefficient is U, heat transfer area is (A'), and logarithmic mean temperature difference is $\{(\Delta t)'_{\ell m}\}$; h'_a is given in the following equation (refer to Fig. 2).

$$h'_a = U'A'(\Delta t)'_{\ell m} \qquad (102)$$

where

$$(\Delta t)'_{\ell m} = \frac{(\Delta t)'_i - (\Delta t)'_o}{\ln[(\Delta t)'_i/(\Delta t)'_o]}$$
$$= \frac{t'_{Si} - t'_{So}}{\ln[(t'_{Si} - t')/(t'_{So} - t')]} \qquad (103)$$

By introducing a dimensionless temperature difference ratio (η'), defined by $\eta' = (t'_{So} - t')/(t'_{Si} - t')$, the outlet temperature (t'_{So}) can be given by eq. (105), where $0 < \eta' < 1$.

$$t'_{So} = t' + \eta'(t'_{Si} - t') \qquad (104)$$

Substituting eq. (104) into eq. (100) yields the mass flow rate of the heating medium (W'_S) as follows.

$$W'_S = h'_a/\{\bar{C}_P^{S'}(1 - \eta')(t'_{Si} - t')\} \qquad (105)$$

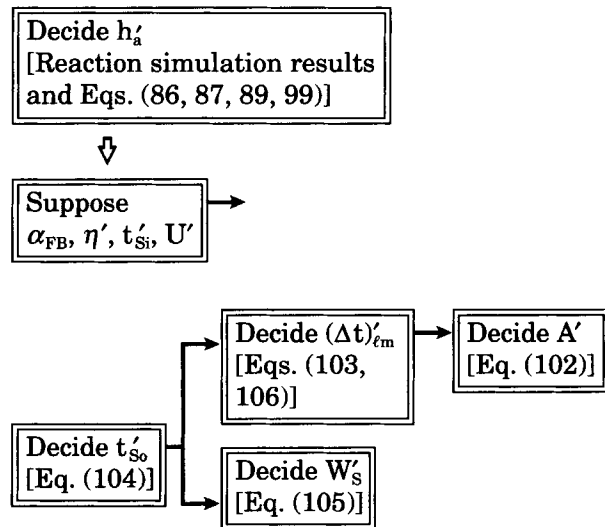On the other hand, when $\eta' = 1$ (i.e., $W'_S = \infty$), from l'Hospitas's law, ($\Delta t)'_{\ell m}$ is given as

$$\lim_{\eta=1} (\Delta t)'_{\ell m} = t'_{Si} - t' \qquad (106)$$

Table I   Simulation Results for a Continuous Recycle

	t (°C)	P $\left(\dfrac{\text{Kg}}{\text{cm}^2\text{G}}\right)$	τ (h)	E/T	δ_{EG}	AV (eq/kg)	OHV (eq/kg)	ϕ	E_s	M_n	P_n	$100e$ (%)	d (%)	w_{EG}
RA-1	255	0.1	4.0	2.0	—	2.930	1.324	0.311	0.717	470	2.436	1.237	1.032	0.0086
RA-2	255	0.1	4.0	—	0.05	0.841	0.542	0.392	0.919	1446	7.467	1.208	1.159	0.0009
RA-1	255	0.1	4.0	2.0	—	1.999	1.367	0.406	0.804	594	3.037	1.136	1.054	0.0078
RA-2	255	0.1	4.0	—	0.05	0.467	0.659	0.585	0.954	1776	9.095	1.167	1.176	0.0011
RA-1	255	0.1	4.0	2.0	—	1.574	1.376	0.466	0.845	678	3.445	1.126	1.092	0.0075
RA-2	255	0.1	4.0	—	0.05	0.405	0.780	0.658	0.960	689	8.605	1.189	1.218	0.0014
RA-1	255	0.1	4.0	2.0	—	1.328	1.374	0.509	0.869	740	3.747	1.142	1.135	0.0073
RA-2	255	0.1	4.0	—	0.05	0.375	0.858	0.696	0.963	1622	8.241	1.217	1.260	0.0016
RA-1	255	0.1	4.0	2.0	—	1.170	1.368	0.539	0.884	788	3.982	1.151	1.160	0.0071
RA-2	255	0.1	4.0	—	0.05	0.360	0.911	0.717	0.965	1574	7.979	1.227	1.278	0.0018
RA-1	255	0.1	4.0	2.0	—	1.048	1.366	0.566	0.896	829	4.180	1.168	1.191	0.0070
RA-2	255	0.1	4.0	—	0.05	0.344	0.958	0.736	0.966	1536	7.774	1.243	1.302	0.0019

F_s = 100 kg/h, no addition of catalysts and fillers.

When α'_{FB}, η', t'_{Si}, and U' are given, the heat transfer area (A') and mass flow rate of the heating medium (W'_S) can be obtained by a similar procedure to that for RA-1.

Decide h'_a
[Reaction simulation results and Eqs. (86, 87, 89, 99)]

⇩

Suppose
α_{FB}, η', t'_{Si}, U'

→

Decide t'_{So}
[Eq. (104)]

Decide $(\Delta t)'_{\ell m}$
[Eqs. (103, 106)]

→

Decide A'
[Eq. (102)]

Decide W'_S
[Eq. (105)]

Calculation Procedure of Recycle Ratio (α_{FB}) (When Heat Transfer Area of Either RA-1 or RA-2 (A or A') is Given)

When the heat transfer area of either RA-1 or RA-2 (A, A') is given, the recycle ratio (ratio of recycle flow rate to throughput based on PET) (α_{FB}) can be determined by the following procedures.

When the Heat Transfer Area (A) of RA-1 is Given

Substituting eq. (87) into eq. (88) yields the following equation.

$$C_P^{\text{EG}} F_{\text{EG}}^i t_i + C_P^{\text{TPA}} F_{\text{TPA}}^i t_i + h_a + \bar{C}'_P F_B t'$$
$$= h_d + \bar{C}_P(F_B + F_S)t \quad (107)$$

Therefore,

$$F_B = \frac{C_P^{\text{EG}} F_{\text{EG}}^i t_i + C_P^{\text{TPA}} F_{\text{TPA}}^i t_i + h_a - h_d - \bar{C}_P F_s t)}{\bar{C}_P t - \bar{C}'_P t')} \quad (108)$$

From $F_B = \alpha_{FB} F_S$, we can obtain the recycle ratio (α_{FB}) as follows.

$$\alpha_{FB} = F_B / F_S \quad (109)$$

Also, the required heat transfer area of RA-2 (A') can be obtained by substituting eq. (108) into eq. (99).

When the Heat Transfer Area (A') of RA-2 is Given

Substituting eq. (87) into eq. (89) yields the following equation.

$$C_P^{\text{EG}'} \delta_{\text{EG}} F_s t'_i + h'_a + \bar{C}_P(F_B + F_S)t$$
$$= h'_d + \bar{C}'_P(F_B + F_S)t' \quad (110)$$

Esterification Process of TPA with EG

$w_{H_2O}^d$	Q (kg/h)	F_P (kg/h)	F_P^O (kg/h)	β	T_m (°C)	α_{FB}	U $\left(\dfrac{kcal}{m^2 \cdot h \cdot °C}\right)$	A (m^2)	T_s (°C)	W_s (kg/h)	T_i °C	η	T_{SO} (°C)
0.269	50.0	101.0	100.3	0.793	227	0.0	250	3.1	290.0	11759	60.0	0.900	286.5
0.710	5.3	100.7	100.6	0.971	242	0.0	250	0.3	290.0	1224	30.0	0.900	286.5
0.283	48.3	102.4	101.7	0.873	224	0.5	250	3.1	290.0	11673	60.0	0.900	286.5
0.680	6.2	101.6	101.4	1.000	244	0.5	250	0.4	290.0	1331	30.0	0.900	286.5
0.290	47.2	103.0	102.3	0.909	224	1.0	250	3.1	290.0	11608	60.0	0.900	286.5
0.635	6.8	102.1	101.9	1.000	242	1.0	250	0.4	290.0	1373	30.0	0.900	286.5
0.294	46.4	103.3	102.6	0.930	225	1.5	250	3.1	290.0	11559	60.0	0.900	286.5
0.607	7.3	102.4	102.2	1.000	240	1.5	250	0.4	290.0	1407	30.0	0.900	286.5
0.296	45.7	103.5	102.8	0.944	225	2.0	250	3.1	290.0	11518	60.0	0.900	286.5
0.588	7.7	102.6	102.4	1.000	240	2.0	250	0.4	290.0	1435	30.0	0.900	286.5
0.299	45.2	103.7	102.9	0.955	226	2.5	250	3.1	290.0	11488	60.0	0.900	286.5
0.572	8.0	102.8	102.6	1.000	239	2.5	250	0.4	290.0	1456	30.0	0.900	286.5

Therefore,

$$F_B = \frac{C_P^{EG'} \delta_{EG} F_s t_i' + h_a' + \bar{C}_P F_s t - h_d' - \bar{C}_P' F_s t')}{(\bar{C}_P' t' - \bar{C}_P t)}$$

(111)

From eq. (109), we can obtain the recycle ratio (α_{FB}).

Also, the required heat transfer area of RA-1 (A) can be obtained by substituting eq. (111) into eq. (90).

Estimation Equations of Specific Heat and Latent Heat of Evaporization

Specific Heat (C_P)

1. β-Hydroxyethyl terephthalate (BHET): From Internal Technical Report of Toyobo Co.

$$C_P^{BHET} = 0.39 + 1 \times 10^{-3} t [\text{kcal/kg} °C];$$
$$t = 100 \sim 200°C \quad (112)$$

2. Ethylene glycol (EG): From Internal Technical Report of Toyobo Co.

$$C_P^{EG} = 0.535 + 0.115 \times 10^{-2} t [\text{kcal/kg} °C];$$
$$t [°C] \quad (113)$$

3. Water (vapor): From Reid, Prausnitz and Sherwood, "The Properties of Gases and Liquid," 1977, McGraw-Hill.

$$C_P^{H_2O}(\text{vapor}) = 7.701 + 4.595 \times 10^{-4} T$$
$$+ 2.521 \times 10^{-6} T^2 - 0.859 \times 10^{-9} T^3 \quad (114)$$
$$C_P^{H_2O}(\text{vapor}) [\text{cal/g-mol} °K]; \quad T [°K]$$

In order to convert a unit of $C_P^{H_2O}(\text{vapor})$ in eq. (114) to [kcal/kg°K], the value obtained from eq. (114) has to be divided by 18.02.

4. PET polymer (average): From Internal Technical Report of Toyobo Co.

$$\bar{C}_P = 0.245 + 9.5 \times 10^{-4} t [\text{kcal/kg} °C];$$
$$t = 270 \sim 290°C \quad (115)$$

5. Terephthalic acid (TPA; solid): From Internal Technical Report of Toyobo Co.

$$C_P^{TPA} = 0.23 + 1.25 \times 10^{-4} t [\text{kcal/kg} °C];$$
$$t [°C] \quad (116)$$

6. KSK330 oil (heating medium): From Catalogue of Soken Chemical Engineering.

$$C_P^S = 0.4 + 8 \times 10^{-4} t [\text{kcal/kg} °C];$$
$$t = 200 \sim 300°C \quad (117)$$

When linearly approximated from catalogue values between 200 and 300°C,

$$\bar{C}_P^S = \int_{t_o}^{t_i} C_P^S \, dt / (t_i - t_o)$$

$$= 0.4 + 4 \times 10^{-4}(t_i + t_o) \quad (118)$$

Latent Heat of Vaporization

1. Ethylene Glycol (EG): From Internal Technical Report of Toyobo Co.

$$\lambda_{EG} = 358 - 0.725t \ [\text{kcal/kg}];$$
$$t \ [°C] \quad (119)$$

2. Water

$$\lambda_{H_2O} = 538.9 - C_P^{H_2O}(\text{vapor})$$
$$\times (t - 100) \ [\text{kcal/kg}]; \quad t \ [°C] \quad (120)$$

$C_P^{H_2O}(\text{vapor})$ is given by eq. (114).

SIMULATION EXAMPLES

Table I shows several examples of simulation results for the continuous recycle process under the conditions of $t = 255°C$, $P = 0.1 \text{ kg/cm}^2\text{G}$, $\tau = 4$ h, $E/T = 2.0$, $F_S = 100$ kg/h, $\delta_{EG} = 0.05$, and $\alpha_{FB} = 0$, 0.5, 1.0, 1.5, 2.0, and 2.5.

These results suggest that the higher recycle ratio (α_{FB}) proceeds to the reactions.

CONCLUSIONS

A new mathematical model for a material balance and a heat balance of the esterification reaction in the continuous recycle process was derived. This model will give useful information on the design of a new process, such as the optimum values of oligomer characteristics, heating area, recycle ratio, and flow rate of heating medium.

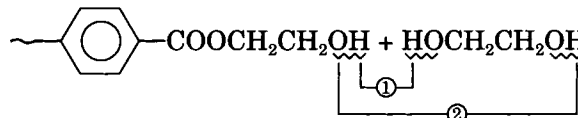## APPENDIX A: DERIVATION OF $k_8 = 2k_7$ AND $k_9 = 4k_7$

Considering that the reaction rate constants of k_7, k_8, and k_9 correspond to the encounter probability of each hydroxyl end group, the probability that one end group reacts with the others is proportional to

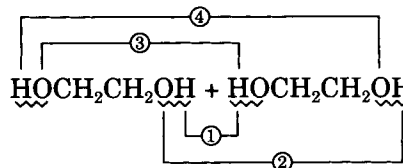the number of combinations for each end group given below.

For k_7 in eq. (4), the combination number is one from the following expression:
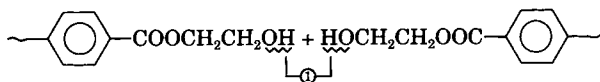
For k_8 in eq. (5), the combination number is two from the following expression:

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

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

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

Derivation of q_{EG}

We considered 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 is given 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 is given 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}, which is equal to that consumed by the reactions shown in eqs. (1) to (7), is expressed by the following equation:

$$q_{EG} = F_{TPA}(M_{EG}/M_{TPA})[\{(P_{nf} - 1)/(1 + e)$$
$$+ 2\phi_f/(1 + e) + 2(P_{nf} - 1)e/(1 + e)$$
$$+ 4\phi_f e/(1 + e)\}/P_{nf} - \{(P_{ni} - 1)/(1 + e)$$
$$+ 2\phi_i/(1 + e) + 2(P_{ni} - 1)e/(1 + e)$$
$$+ 4\phi_i e/(1 + e)\}/P_{ni} \quad (B.1)$$

where M_{EG} = mol wt of EG, M_{EG} = 62.07, and M_{TPA} = mol wt of TPA, M_{TPA} = 166.13.

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

$$q_{EG} = \frac{M_{EQ}}{M_{TPA}} \cdot F_{TPA} \cdot \{(P_{nf} + 2\phi_f - 1)/P_{nf}$$
$$- (P_{ni} + 2\phi_i - 1)/P_{ni}\} \quad (B.2)$$

By use of the above and the relation that $F_{TPA}/M_{TPA} = F_{PET}/M_{PET}$, q_{EG} shown in eq. (42) 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} 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 molecules 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) to (7). An oligomer with the polymerization degree of P_n comprises the poly-

mer 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 endgroups 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}.

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

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

$$q_{H_2O} = \frac{2 \times M_{H_2O}}{M_{TPA}} \cdot F_{TPA} \cdot \{(P_{nf} + \phi_f - 1)/P_{nf}$$
$$- (P_{ni} + \phi_i - 1)/P_{ni}\} \quad (B.4)$$

By use of the above and the relation that $F_{TPA}/M_{TPA} = F_{PET}/M_{PET}$, q_{H_2O} shown in eq. (44) 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} can be derived.

APPENDIX C: DERIVATION OF M_{nL}

The reaction mixtures of W kg, which consist of the liquid phase (βW kg; oligomer without undissolved TPA and with dissolved TPA, EG, and water) and the solid phase (($1 - \beta$)W kg; undissolved TPA) are considered.

As the weight of oligomer in the liquid phase is $\beta W w_{OLG}$ kg, 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 $[\beta W C_1 + OHV\{1 - \beta(w_{EG} + w_{H_2O})\}]/2$. From the above results, we can obtain, the following relation:

$$\beta W w_{\text{OLG}} / (M_{nL}/1000) = [\beta W C_1$$

$$+ OHV\{1 - \beta(w_{\text{EG}} + w_{\text{H}_2\text{O}})\}]/2 \quad (\text{C.1})$$

Rearrangement of the above equation gives the following equation:

$$M_{nL} = \frac{2000\beta w_{\text{OLG}}}{\beta C_1 + OHV[1 - \beta(w_{\text{EG}} + w_{\text{H}_2\text{O}})]} \quad (\text{C.2})$$

NOMENCLATURE

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

A, A' = Heat transfer areas.

A, B = Constants of Van Laar equation.

A_i = Frequency factor of the Arrhenius equation.

AV, AV' = Concentrations of total carboxyl end groups in dried oligomer, eq/kg; $AV = C_T/[T_S + W_e\{1 - (w_{\text{EG}} + w_{\text{H}_2\text{O}})\}]$.

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.

$\bar{C}_P, \bar{C}'_P$ = Average specific heats of oligomer at constant pressure, kcal/kg°C.

$C_P^{\text{EG}}, C_P^{\text{EG}'}$ = Specific heats of EG at constant pressure, kcal/kg°C.

C_P^{TPA} = Specific heat of TPA at constant pressure, kcal/kg°C.

C_P^S = Specific heat of heating medium at constant pressure, kcal/kg°C.

$\bar{C}_P^S, \bar{C}_P^{S'}$ = Average specific heats of heating medium at constant pressure, kcal/kg°C.

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_i = Apparent activation energy of the Arrhenius equation, cal/mol.

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; $F_B = \alpha_{FB}F_S$.

$F_{\text{EG}}^i, F_{\text{EG}}^{i'}$ = Input rates of EG, kg/h.

$F_{\text{H}_2\text{O}}^i$ = 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.

h_a, h'_a = Amounts of heat supplied by heating medium, kcal/h.

h_B = Enthalpy moving with recycle (based on 0°C), kcal/h.

h_d, h'_d = Amounts of heat removed from each reactor as latent heat of evaporation, kcal/h.

k_1 to k_9 = Reaction rate constants as defined in eqs. (1) to (7).

M_{EG} = Mol wt of EG, g/mol; $M_{\text{EG}} = 62.07$.

$M_{\text{H}_2\text{O}}$ = Mol wt of water, g/mol; $M_{\text{H}_2\text{O}} = 18.02$.

M_{PET} = Mol wt of a PET unit, g/mol; $M_{\text{EG}} = 192.17$.

M_{TPA} = Mol wt of TPA, g/mol; $M_{\text{EG}} = 166.13$.

M_i, M_j = Mol wt of component, i, j, g/mol.

M_n = Number average mol wt, 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, OHV' = Concentrations of hydroxyl end groups in 1 kg dried oligomer, eq/kg.

P, P' = Total pressures (= 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+} = Mol number of antimony ion (Sb^{3+}) in diantimony trioxide supplied for 10^6 mol of TPA, μ mol/TPA mol.

SV = Saponification value, eq/kg.

t, t' = Reaction temperatures, °C.

t_i = Temperature of TPA–EG slurry fed to RA-1, °C.

t'_i = Temperature of EG added anew into RA-2, °C.

t_{Si}, t'_{Si} = Temperatures of heating medium at inlet, °C.

t_{So}, t'_{So} = Temperatures of heating medium at outlet, °C.

T = Absolute temperature, T = t + 273.15, °K.

T_i = Mol number of potassium titanium oxyoxalate supplied for 10^6 mol of TPA, μmol/TP mol.

T_m = Melting point of dried oligomer, °C.

T_S = Weight of TPA undissolved, kg.

$(\Delta T)_{\ell m}$ = Logarithmic mean temperature difference, defined as in eq. (94), °C.

$(\Delta T)'_{\ell m}$ = Logarithmic mean temperature difference, defined as in eq. (103), °C.

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

U, U' = Overall heat transfer coefficients, kcal/m² h°C.

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.

W_S, W'_S = Mass flow rates of heating medium, kg/h.

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

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

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

y_{EG} = Mol fraction of EG in the vapor phase.

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

Greek Letters

α = Mean solubility of TPA in the reaction mixtures, expressed as equivalent mol 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 mol of carboxyl end groups, eq/kg (BHET).

α_{EG} = Solubility of TPA in EG, expressed as equivalent mol 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 mol of carboxyl end groups, eq/kg (water).

α_{OLG} = Solubility of TPA in oligomer, expressed as equivalent mol 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 each of eqs. (73) to (84).

ζ = Concentration of carboxyl end groups in the

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

η, η' = Values defined as $\eta = (t_{So} - t)/(t_{Si} - t)$ or $\eta' = (t'_{So} - t')/(t'_{Si} - t')$.

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 mol of carboxyl end groups, η_{TPA} = 12.039 eq/kg (TPA).

θ = Reaction time, h.

λ_{EG} = Latent heats of vaporization of EG, kcal/kg.

λ_{H_2O} = Latent heats of vaporization of water, kcal/kg.

ϕ = Ratio of hydroxyl end groups to total end groups of dried oligomer; $\phi = OHV/(AV + OHV)$.

Subscripts

BHET = Bis β-hydroxyethyl terephthalate.

EG = Ethylene glycol.

H_2O = Water.

OLG = Oligomer.

P = At constant pressure or reaction mixtures.

S = Heating medium.

TPA = Terephthalic acid.

Superscripts

d = Distillate (vapor phase).

EG = Ethylene glycol.

S = Heating medium.

TPA = Terephthalic acid.

$'$ (prime) = RA-2.

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