Modeling of Poly(ethylene Terephthalate) Reactors. I. A Semibatch Ester Interchange Reactor*

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Synopsis

A comprehensive model for a semibatch ester interchange reactor has been developed with a view to investigate the effect of various process and operational variables on the DMT conversion rate as well as the by-product formation. The influence of important variables such as EG-to-DMT ratio, catalyst concentration, and operational variables such as temperature and pressure has been considered. Definite conclusions concerning the choice of the desirable range of process and operational variables to maximize productivity and minimize by-product formation have been reached.

INTRODUCTION

Poly(ethylene terephthalate) (PET) is the basic raw material for the production of synthetic fibers, films, filaments, and plastic objects. Production of PET proceeds via two stages: (1) transesterification stage or esterification stage; (2) polycondensation stage.

In the first stage, prepolymer (monomer for polycondensation stage) containing mainly bis(2-hydroxyethyl) terephthalate (and its linear oligomers) is prepared using any one of the following methods.

(1) Dimethyl terephthalate (DMT) is reacted with ethylene glycol (EG) in the presence of one or more metal acetate catalysts. Methanol formed is continually removed. Generally, zinc, manganese, cadmium, lead, calcium, and magnesium acetates are used as catalysts. This step is known as the transesterification stage.

(2) Terephthalic acid (TPA) is esterified with EG, and water is continuously removed. In this case, acid end groups of TPA catalyze the reaction. This step is known as the esterification stage. Pal and Pal[1] have compared the relative merits of technologies using DMT and TPA as raw materials for the manufacture of PET.

In the second stage, viz., the polycondensation stage, prepolymer produced in the first stage is polycondensed at high temperature (260–290 °C) using high vacuum (0.5–1 torr), and EG is removed continuously. Generally, antimony compounds (such as antimony trioxide) are used for catalyzing the polycondensation reaction. The equilibrium constant for polycondensation reaction is very low (≈ 0.5), and the rate of EG removal becomes the rate-controlling factor.

In view of the position of primacy that PET occupies in the synthetic fiber field in the world, it is essential to understand the behavior of the reactors used for

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the manufacture of PET. Since a series of complex reactions are accompanied by transport limitations in some stages, it is important to use reliable kinetic data along with sound concepts from reaction engineering and transport phenomena to model the process. We shall review in the following the previous efforts to model this process and demonstrate that there are still no comprehensive studies on PET reactor modeling. The present work, which is the first in the series of contributions, is meant to bridge this gap.

BACKGROUND

Due to lack of kinetic data and because of the complexity of the reaction model, very few attempts were made to model the transesterification and polycondensation stages. Ault and Mellichamp[2] were the first investigators who presented a mathematical model for the first stage of PET process. They showed that prepolymer containing unreacted DMT end groups (which ordinarily result in end capping) can lead to a high-molecular-weight product under certain conditions of relative reaction rates. Model results were presented for the EG-to-DMT ratio of 2 at a fixed temperature of 220°C. In industrial practice, transesterification is not done at a fixed temperature. Therefore, the simulations are not pragmatically relevant. Additionally, Ault and Mellichamp did not study the influence of process and operational variables such as EG-to-DMT ratio, temperature, etc.

Dijkman and Duvekot[3] have attempted the modeling of transesterification, but their investigation is not very comprehensive; and further, the semibatch transesterification process which is also widely used in commercial practice has not been modeled.

The aim of the present modeling work is to study the transesterification stage in depth with special reference to the investigation of the effect of various process and operational variables on the DMT conversion rate. The influence of process variables such as EG to DMT ratio and catalyst concentration and operational variables such as temperature and pressure will be considered explicitly in the present work. Some of the by-products formed have an important influence on the fiber properties. Thus, even though the amount of diethylene glycol (DEG) formed is very small (1–2 wt %), it has a strong influence on physical and chemical properties of PET. Indeed, the melting point of PET decreases by 5°C for each weight percent of DEG incorporated, and the presence of small amounts of DEG has a substantial influence on dyeing. It was therefore thought desirable to study the effect of process and operational variables on the rate of formation of DEG, acid end groups, and other side products.

TRANSESTERIFICATION PROCESS

The flow diagram of the first stage of PET manufacture process (transesterification stage) is shown in Figure 1. DMT melted in the melter (B) is fed to the ester interchange reactor (D). EG containing one or more metal acetate catalysts is added from the storage tank (C) to the ester interchange reactor (D). The temperature of the reactor is increased from 140°C to approximately 220°C. There is an alternate way of charging the reactants. Here, DMT is first dissolved in EG and the mixture is fed to the reactor. This procedure is not preferred since
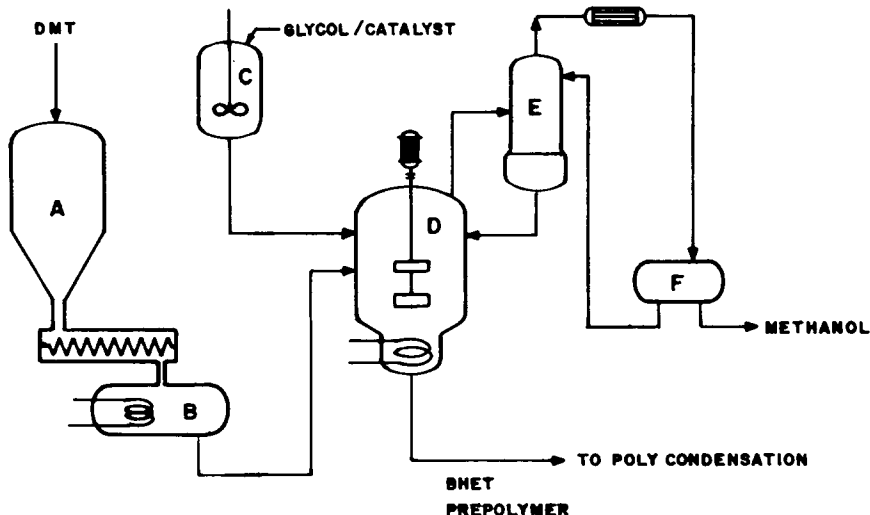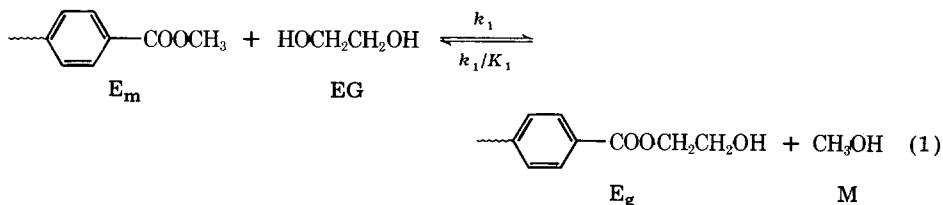
Fig. 1. Transesterification process. A, DMT storage tank; B, melter; C, glycol storage tank; D, ester interchange reactor; E, rectification column; F, methanol collecting tank.

it may lead to the formation of side products which affects the properties of PET. Part of the EG and methanol generated leaves the ester interchange reactor (D) in the form of vapor. The vapors are then passed through a rectification column (E), and EG is completely fed back to the ester interchange reactor (D). Methanol is collected separately (F), and part of it is used as reflux for the rectification column (E). After collecting a known amount of methanol, i.e., after a particular conversion of DMT (generally restricted to the 90 to 95% level) has taken place, the supply of heat is stopped and the prepolymer is passed on to the second stage for polycondensation. The prepolymer so prepared contains mainly bis(2-hydroxyethyl) terephthalate (BHET) and its linear oligomers. The distillate contains mainly methanol and to some extent EG, DEG, water, and ketones.

REACTION SCHEME

Various reactions occurring in the transesterification stage are given below. The main reactions[2,3] are:
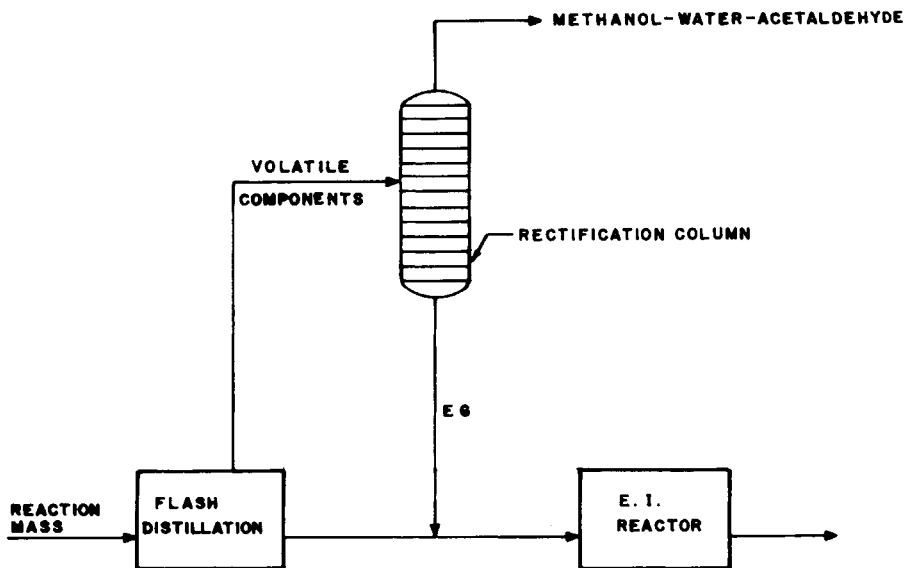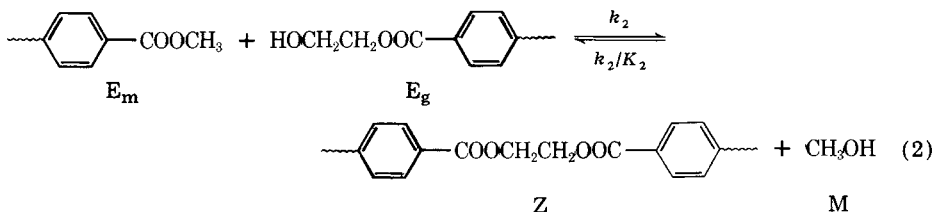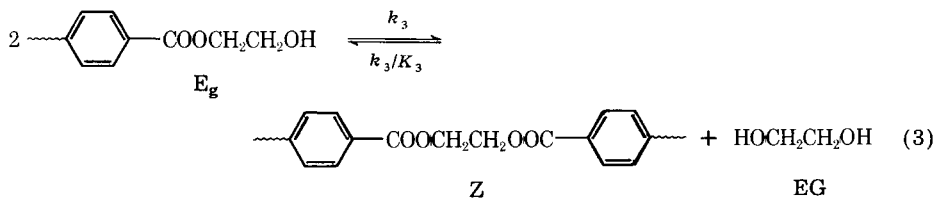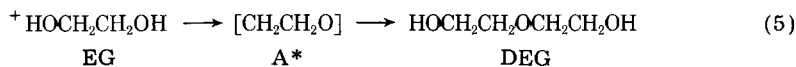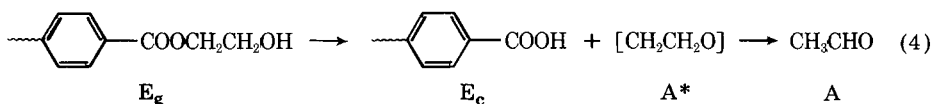
Ester interchange reaction:

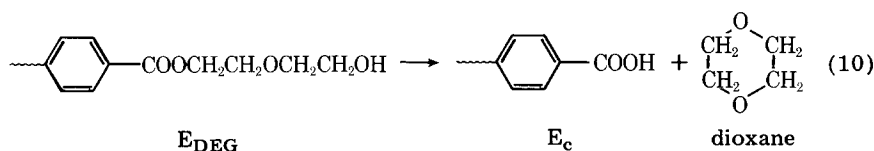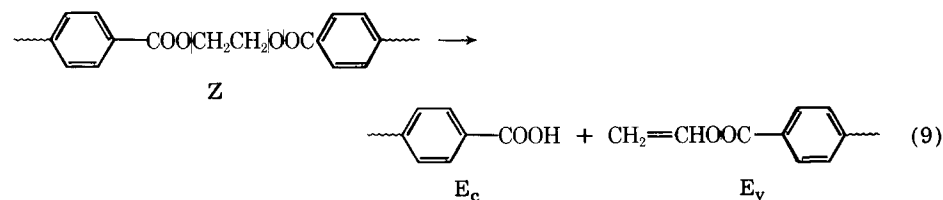Fig. 2. Model for transesterification process.

Transesterification reaction:

Polycondensation reaction:

There are also some important side reactions.[6] These are:

$$\sim\!\!\langle\!\!\bigcirc\!\!\rangle\!-COOCH_2CH_2OH + [CH_2CH_2O] \longrightarrow$$

$$E_g \qquad\qquad A*$$

$$\sim\!\!\langle\!\!\bigcirc\!\!\rangle\!-COOCH_2CH_2OCH_2CH_2OH \quad (6)$$

$$E_{DEG}$$

$$\sim\!\!\langle\!\!\bigcirc\!\!\rangle\!-COOH + HOCH_2CH_2OH \underset{k_7/K_4}{\overset{k_7}{\rightleftharpoons}}$$

$$E_c \qquad\qquad EG$$

$$\sim\!\!\langle\!\!\bigcirc\!\!\rangle\!-COOCH_2CH_2OH + H_2O \quad (7)$$

$$E_g \qquad\qquad W$$

$$\sim\!\!\langle\!\!\bigcirc\!\!\rangle\!-COOH + HOCH_2CH_2OOC\!\langle\!\!\bigcirc\!\!\rangle\!\sim \underset{k_8/K_5}{\overset{k_8}{\rightleftharpoons}}$$

$$E_c \qquad\qquad E_g$$

$$\sim\!\!\langle\!\!\bigcirc\!\!\rangle\!-COOCH_2CH_2OOC\!-\!\langle\!\!\bigcirc\!\!\rangle\!\sim + H_2O \quad (8)$$

$$Z \qquad\qquad W$$

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

$$Z$$

$$\sim\!\!\langle\!\!\bigcirc\!\!\rangle\!-COOH + CH_2\!\!=\!\!CHOOC\!-\!\langle\!\!\bigcirc\!\!\rangle\!\sim \quad (9)$$

$$E_c \qquad\qquad E_v$$

$$\sim\!\!\langle\!\!\bigcirc\!\!\rangle\!-COOCH_2CH_2OCH_2CH_2OH \longrightarrow \sim\!\!\langle\!\!\bigcirc\!\!\rangle\!-COOH + \begin{array}{c} O \\ CH_2 \;\; CH_2 \\ | \qquad | \\ CH_2 \;\; CH_2 \\ O \end{array} \quad (10)$$

$$E_{DEG} \qquad\qquad E_c \qquad\qquad dioxane$$
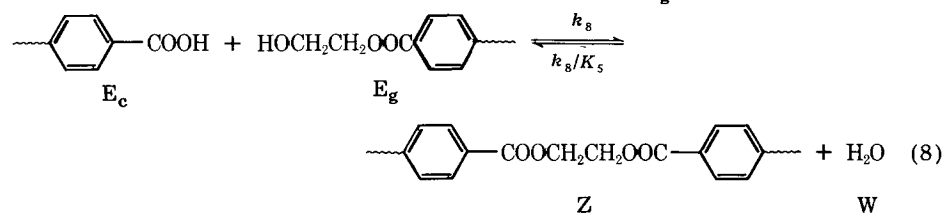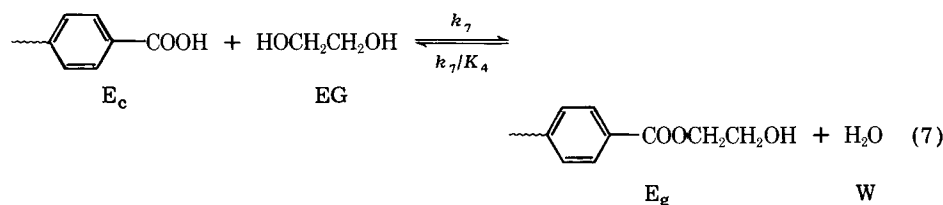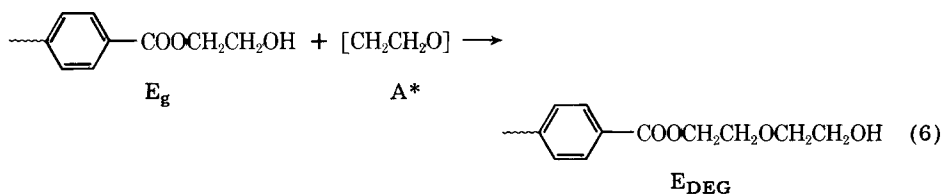
We shall discuss in detail some assumptions used while presenting the above reaction scheme. In writing eqs. (1) and (2), it is assumed[4] that the reactivities of methyl ester end groups on DMT and on half-esterified DMT are the same and that the reactivities of hydroxyl group on EG and on half-esterified EG are different.

Many investigators[4,5] in the past assumed that DEG was formed by dehydration of EG as follows:

$$2HOCH_2CH_2OH \rightarrow HOCH_2CH_2OCH_2CH_2OH + H_2O \qquad (11)$$

Later, Buxbaum[6] showed that the formation of DEG due to dehydration of EG is small even at 280°C and that DEG was formed via a different mechanism. This involved the formation of an active species (A*) by the degradation of 2-hydroxyethyl ester end group (E_g) as shown in eq. (4), with a seven-membered ring as the transition state. The active species can either leave the reaction mixture in the form of acetaldehyde or it can react with EG or with E_g as shown in eqs. (5) and (6). Reimschuessel[7] on the other hand suggested that E_g degra-

TABLE I
Kinetic Parameters Used in the Present Work

Reaction	Ester-interchange, eq. (1)	Trans esterification, eq. (2)	Poly-condensation, eq. (3)	Acetaldehyde formation, eq. (4)	Free DEG formation, eq. (14)	Incorporated DEG formation, eq. (17)	Esterification reaction, eq. (7)	Esterification reaction, eq. (8)
Activation energy (kcal/mol)	15.0	15.0	18.5	29.8	29.8	29.8	17.6	17.6
Frequency factor (L/mol min)	6.0×10^4 4.0×10^4 2.0×10^4	3.0×10^4 2.0×10^4 1.0×10^4	6.8×10^5	2.17×10^{9a}	2.17×10^9	2.17×10^9	1.0×10^6	1.0×10^6
Equilibrium constants	0.3	0.15	0.5	—	—	—	2.5	1.25

[a] Units are min^{-1}.

dation is likely to proceed via a five-membered orthoester-type intermediate and the formation of acetaldehyde via the intermediate formation of ethyleneoxide:

$$E_g \xrightarrow{k_4} E_c + CH_2\overset{O}{\overbrace{\quad}}CH_2 \longrightarrow CH_3CHO \qquad (12)$$
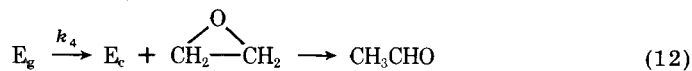
The formation of DEG is caused by an interaction of EG with E_g as shown below:

$$E_g + EG \overset{\nearrow\ E_{DEG} + H_2O}{\underset{\searrow_{k_5}\ E_c + DEG}{}} \qquad \begin{matrix}(13)\\ \\ (14)\end{matrix}$$
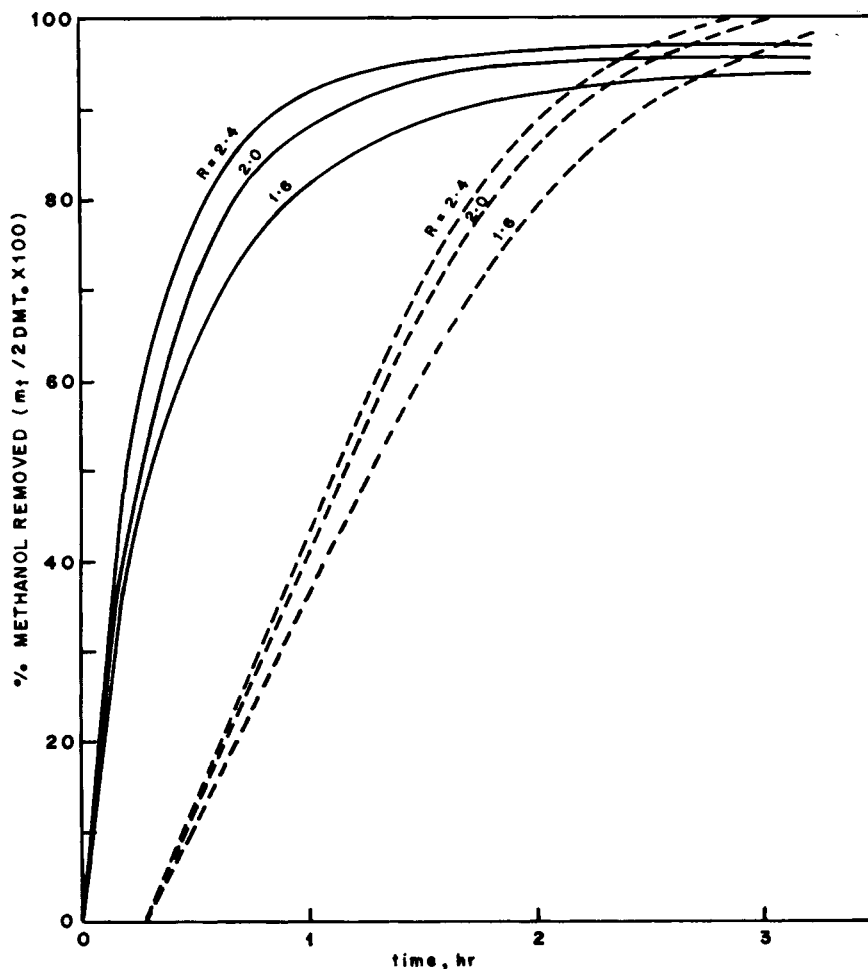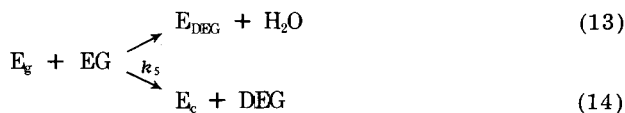

Fig. 3. Influence of EG/DMT ratio on the progress of reaction.   Cat. conc. = 5.6×10^{-4} mol/L; (- - -) 140°C + 30°C/h; (——) 200°C.
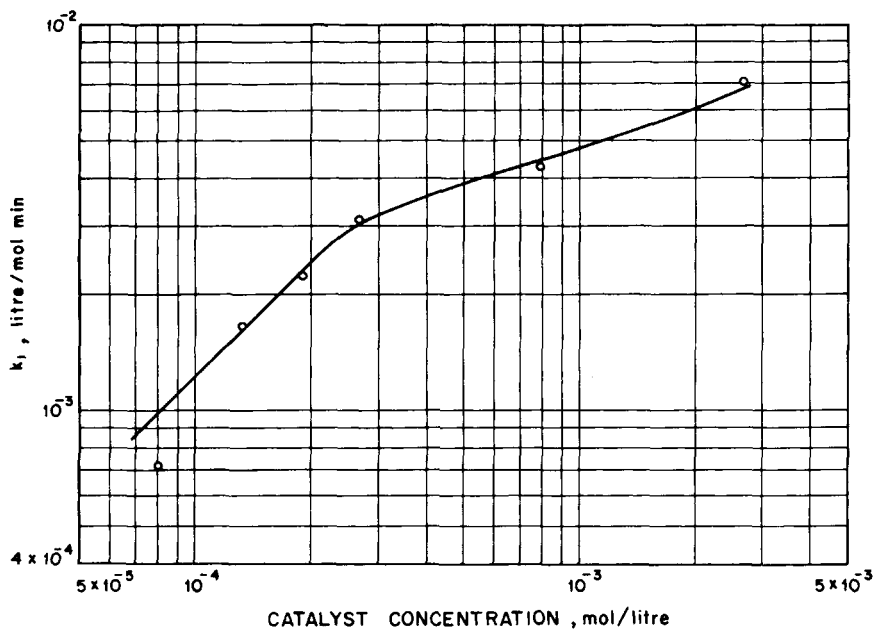
Fig. 4. Dependence of rate constant (k_1) on zinc acetate catalyst concentration at 197°C.

TABLE II
Vapor Pressure Data Constants in Eq. (43)

Component	Temperature range, °C	A_i	B_i, °C	C_i, °C
Methanol	140–220	8.50563	1979.38	290.0
Water	140–280	8.02406	1721.35	235.0

Reimschuessel[7] suggested that ethylene oxide can easily react with EG and E_g to form corresponding ether structure:

$$\overset{O}{\overset{\diagup\diagdown}{CH_2-CH_2}} + EG \longrightarrow DEG \qquad (15)$$

$$\overset{O}{\overset{\diagup\diagdown}{CH_2-CH_2}} + E_g \longrightarrow E_{DEG} \qquad (16)$$

TABLE III
Range of Processing and Operating Variables Studied in This Work

Variable	Parameter values		
R = Ethylene glycol/DMT_0	1.6	2.0	2.4
Zinc acetate cat. conc. mol/L	1.6×10^{-4}	5.6×10^{-4}	1.8×10^{-3}
Temperature °C (constant temperature case)	180	200	—
Temperature, °C (programmed)	140°C + 20°C/h	140°C + 30°C/h	150°C + 30°C/h
Pressure, mm Hg	200	760	

TABLE IV
Reaction Time for 90% Methanol Removal (Catalyst = Zinc Acetate)

	Time, h					
	Cat. Conc. 5.6×10^{-4} mol/L			$R = 2$		
				1.6×10^{-4}	5.6×10^{-4}	1.8×10^{-3}
Temperature	$R = 1.6$	$R = 2.0$	$R = 2.4$	mol/L[a]	mol/L[a]	mol/L[a]
200°C	1.66	1.16	0.88	2.20	1.16	0.76
140 + 30°C/h	2.46	2.20	2.06	2.68	2.20	1.98

[a] Catalyst concentration.

Equations (12), (15), and (16) are similar to eqs. (4), (5), and (6), except that the intermediate species is different. Equation (14) is nothing but the result of eqs. (12) and (15). It may be mentioned here that Dijkman and Duvekot[3] used eqs. (14) and (4) for the formation of DEG and acetaldehyde, respectively, for simulating the transesterification stage. Furthermore, Hovenkamp and Munting[8] found that DEG was formed by a mechanism presented in eqs. (13) and (17):

$$E_g + E_g \xrightarrow{k_6} E_c + E_{DEG} \tag{17}$$
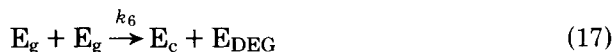
Even though there is a controversy about the reaction mechanism for the formation of DEG, eqs. (12), (14), and (17) probably represent the correct routes for the formation of DEG and acetaldehyde.

DEG and E_{DEG} can react with E_m, E_c, and E_g, but for simplicity these reactions are not shown in the above reaction scheme. Acid end groups formed in eqs. (4)–(6) will react with EG and E_g as shown in eqs. (7) and (8), resulting in the formation of water. The concentration of diester groups (Z) and E_{DEG} is very small, and hence the side reactions involving these species, eqs. (9) and (10), are not considered in the present model.

MATHEMATICAL MODEL FOR A SEMIBATCH REACTOR

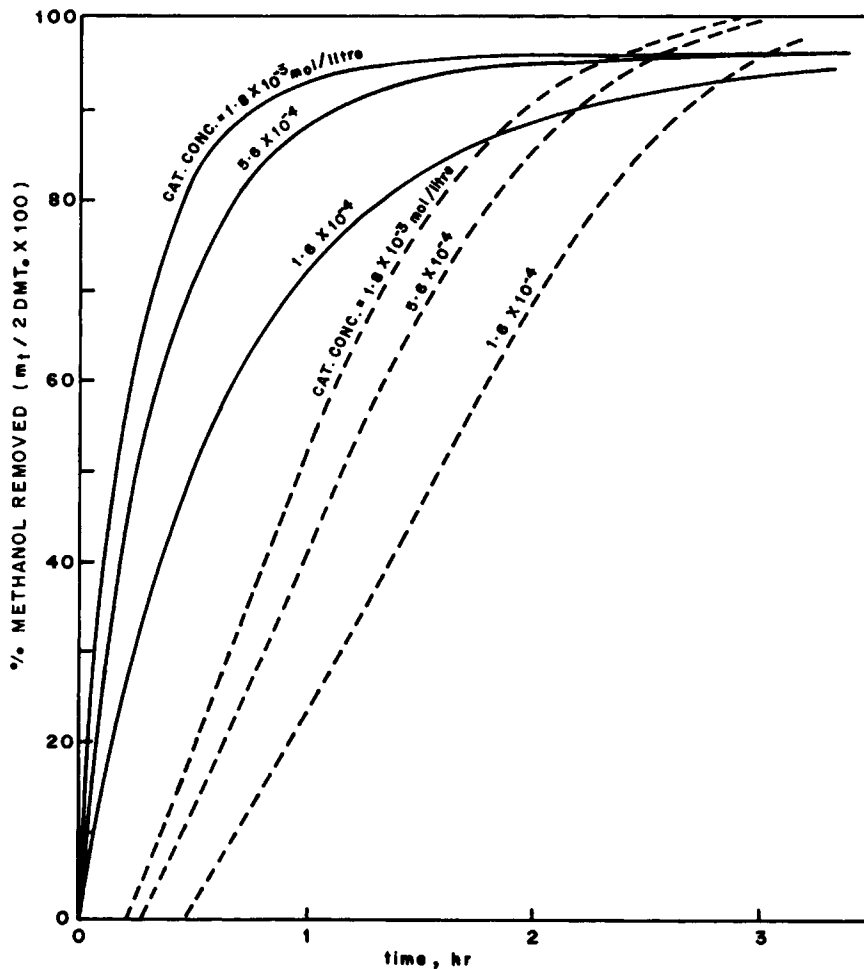The reaction mixture contains methanol, EG, DEG, water, and molecules of the following type:
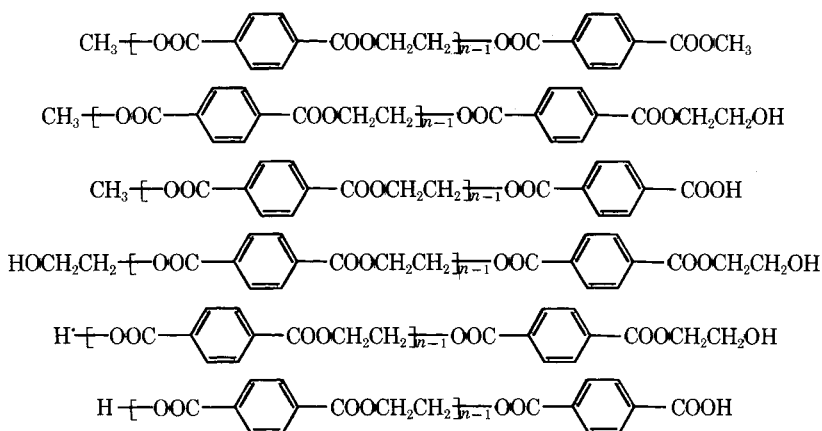
Fig. 5. Influence of catalyst concentration on progress of reaction. $R = 2$; (- - -) 140°C + 30°C/h; (——) 200°C.

where $n \geqslant 1$. In addition to the above type of molecules, the reaction mixture also contains molecules incorporating DEG. For simplicity, molecules containing DEG units are not shown separately, and they are included in the molecule containing EG units. In the first stage, the reaction mixture contains mainly a monomer ($n = 1$) and to some extent a dimer ($n = 2$), a trimer ($n = 3$), and a tetramer ($n = 4$). In the present work, only reactions (1)–(3), (7), (8), (12), (14), and (17) were considered. Assuming that the reactivity of functional groups does not depend on the polymer chain length, the material balance equations for an ideal semibatch reactor can be written as

$$\frac{1}{V}\frac{de_m}{dt} = -R_1 - R_2 \tag{18}$$

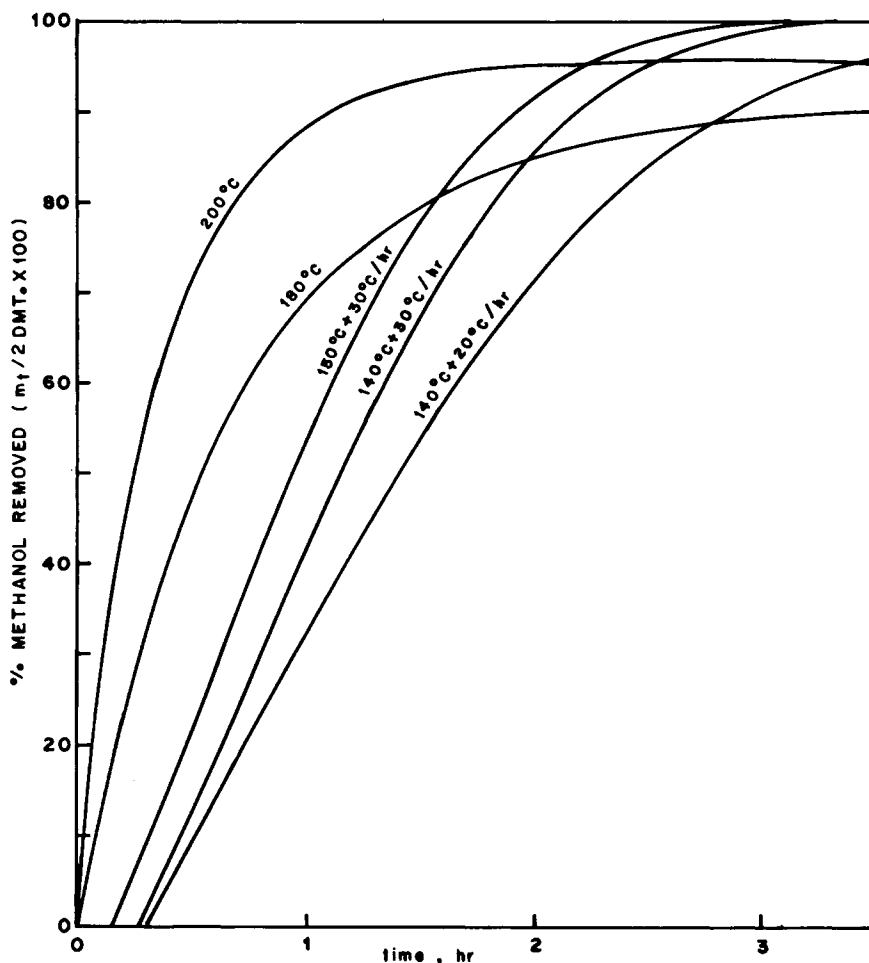$$\frac{1}{V}\frac{de_g}{dt} = R_1 - R_2 - 2R_3 - R_4 - R_5 - R_6 + R_7 - R_8 \tag{19}$$

Fig. 6. Influence of a prescribed temperature program on progress of reaction. $R = 2$; cat. conc. $= 5.6 \times 10^{-4}$ mol/L.

$$\frac{1}{V}\frac{dm}{dt} = R_1 + R_2 - Q_M(t) \tag{20}$$

$$\frac{1}{V}\frac{dg}{dt} = -R_1 + R_3 - R_7 - Q_G(t) \tag{21}$$

$$\frac{1}{V}\frac{dz}{dt} = R_2 + R_3 + R_8 \tag{22}$$

$$\frac{1}{V}\frac{de_c}{dt} = R_4 + R_5 + R_6 - R_7 - R_8 \tag{23}$$

$$\frac{1}{V}\frac{da}{dt} = R_4 \tag{24}$$
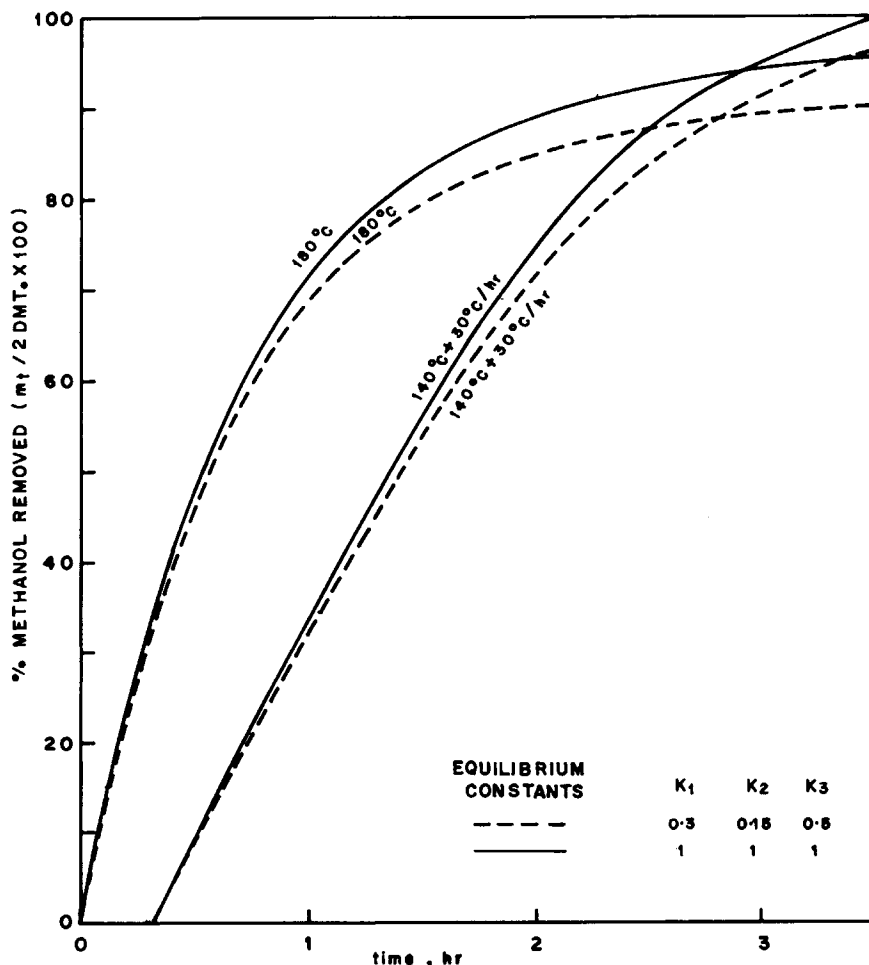
$$\frac{1}{V}\frac{dg^*}{dt} = R_5 + R_6 \tag{25}$$

Fig. 7. Effect of assumed values of equilibrium constants on predicted course of the progress of reaction. $R = 2$; cat. conc. $= 5.6 \times 10^{-4}$ mol/L.

$$\frac{1}{V}\frac{dw}{dt} = R_7 + R_8 - Q_W(t) \tag{26}$$

where g^* represents the total number of moles of free DEG and incorporated DEG in the polymer chain; and $e_m, e_g, m, g, z, e_c, a$, and w represent the number of moles or equivalents of the respective species (as shown in the reaction scheme with capital letters) present in the reaction mass. $Q_M(t)$, $Q_G(t)$, and $Q_W(t)$ represent methanol, EG, and water flow rates at any instant of the time t.

Assuming that the order and molecularity of the reactions are the same, the reaction rates R_1 to R_8 for reactions (1)–(3), (12), (14), (17), (7) and (8) can be written as

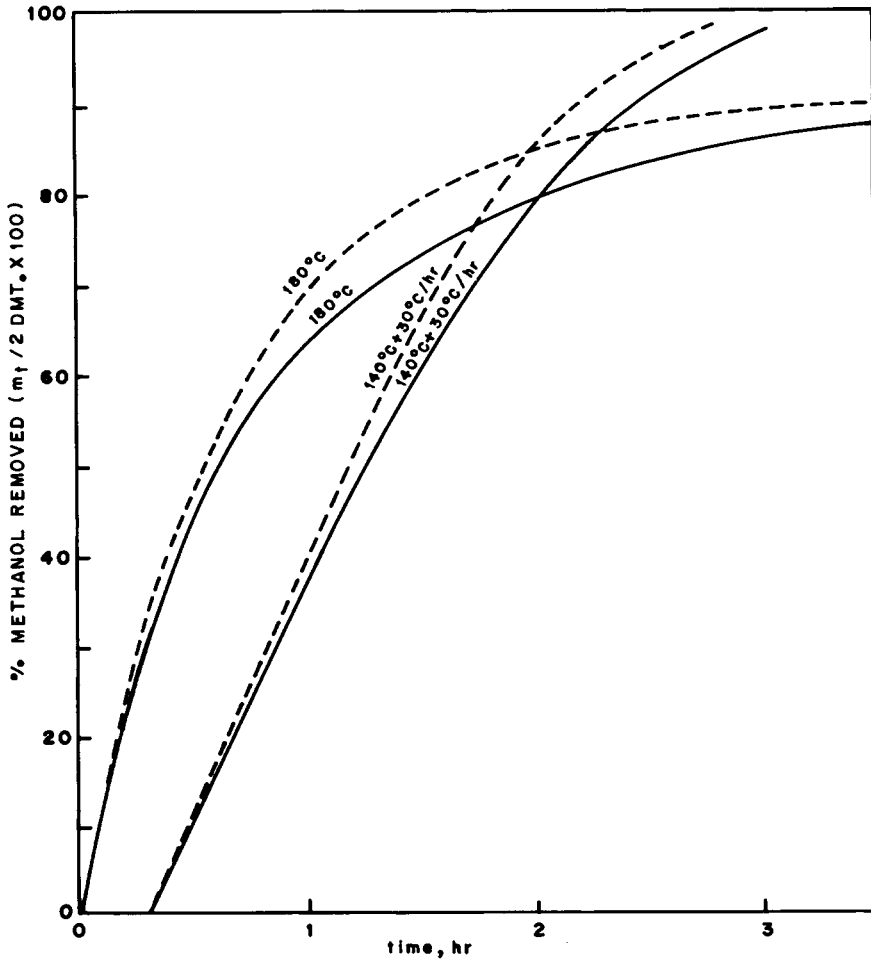$$R_1 = \frac{k_1\left(2e_m g - \frac{1}{K_1}e_g m\right)}{V^2} \tag{27}$$

Fig. 8. Effect of assumed value of $k_2 k_1$ on predicted course of the progress of reaction. $R = 2$; cat. conc. $= 5.6 \times 10^{-4}$ mol/L; $(---)$ $k_2/k_1 = 0.5$; $(—)$ $k_2/k_1 = 0.01$.

$$R_2 = \frac{k_2 \left(e_g e_m - \dfrac{2}{K_2} mz \right)}{V^2} \tag{28}$$

$$R_3 = \frac{k_3 \left(e_g^2 - \dfrac{4}{K_3} zg \right)}{V^2} \tag{29}$$

$$R_4 = \frac{k_4 e_g}{V} \tag{30}$$

$$R_5 = \frac{2k_5 g e_g}{V^2} \tag{31}$$
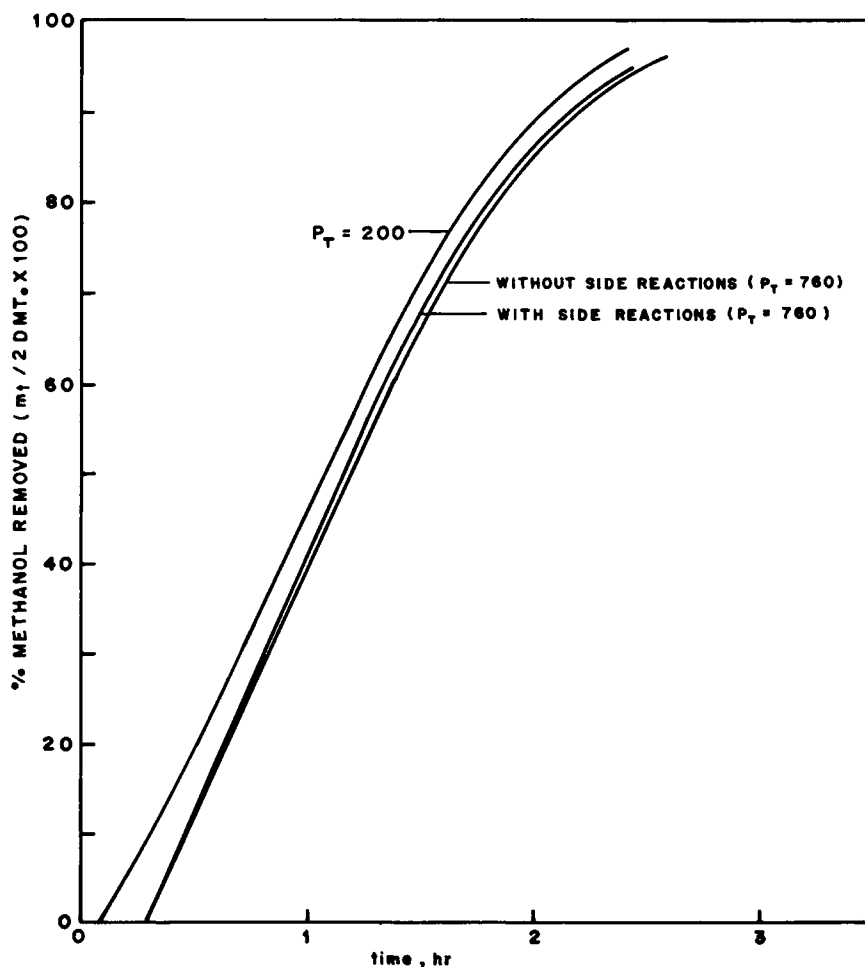
$$R_6 = \frac{k_6 e_g^2}{V^2} \tag{32}$$

Fig. 9. Effect of pressure and side reactions on the progress of reaction. $R = 2$; cat. conc. $= 5.6 \times 10^{-4}$ mol/L; temperature $= 140°C + 30°C/h$.

$$R_7 = \frac{k_7(2e_c g - (1/K_4) e_g w)}{V^2} \tag{33}$$

$$R_8 = \frac{k_8(e_c e_g - (2/K_5)zw)}{V^2} \tag{34}$$

where k_1, k_2, k_3 k_5, k_6, k_7, and k_8 are second-order rate constants and k_4 is first-order rate constant. Note that k_1–k_8 are functions of catalyst concentration; K_1–K_5 are equilibrium constants of the reactions (1)–(3), (7), and (8), respectively. Since methanol is removed continuously, the volume of the reaction mixture decreases considerably. The volume of the reaction mass at any time is defined as

$$V = V_{DMT}DMT_0 + V_{EG}EG_0 - m_t V_M - w_t V_W \tag{35}$$

where V_{DMT}; V_{EG}, V_M, and V_W are the molar volumes of DMT, EG, methanol,
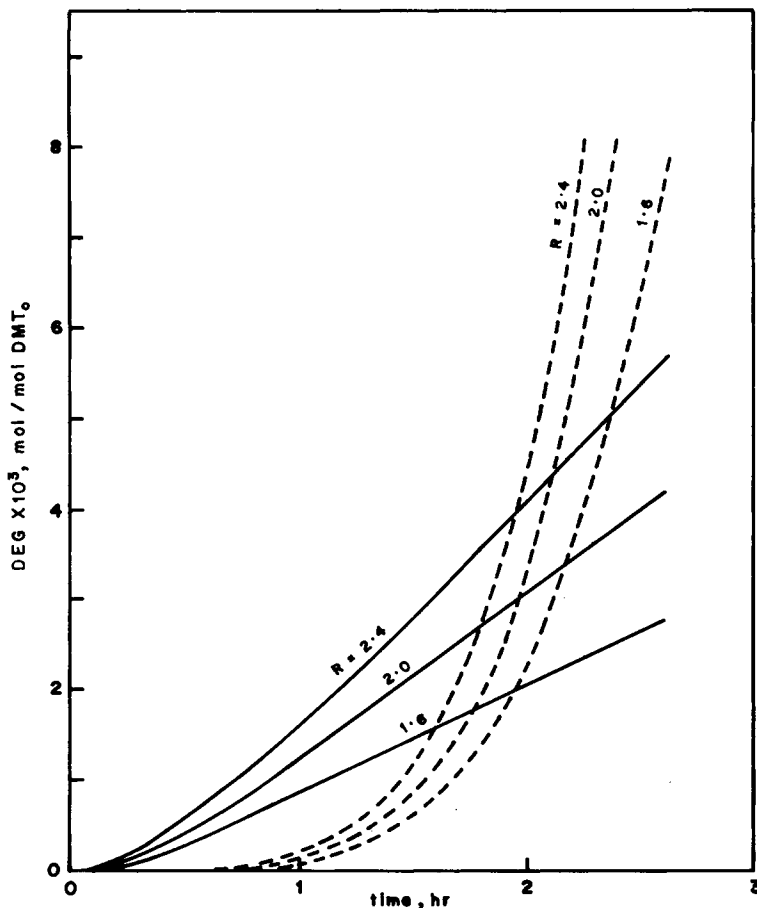
Fig. 10. Effect of EG/DMT ratio on the DEG formation rate. Cat. conc. = 5.6×10^{-4} mol/L; (- - -) 140°C + 30°C/h; (——) 180°C.

and water, respectively, as reported by Fontana.[9] DMT_0 and EG_0 are the number of moles of DMT and EG taken initially. Moles of methanol and water removed up to time t are denoted by m_t and w_t.

In writing material balance eqs. (18)–(26), it is assumed that the reactivity of DEG and E_{DEG} is the same as the reactivity of EG and E_g. In the present work, we have calculated the total content of DEG; therefore, material balance equations for free DEG and incorporated DEG were not written separately. Since the reactivity of EG and E_g is assumed to be the same as that of DEG and E_{DEG}, the rate of disappearance of EG by eq. (14) is not included in eq. (21), and the disappearance of E_g by eq. (17) is considered only once in eq. (19). The solution of these equations requires knowledge of the mass transfer functions $Q_M(t)$, $Q_W(t)$, and $Q_G(t)$. Since EG is generally refluxed back completely, $Q_G(t)$ is taken as zero.

For calculating the methanol concentration in the reaction mixture, Ault and Mellichamp[2] derived the following equation:
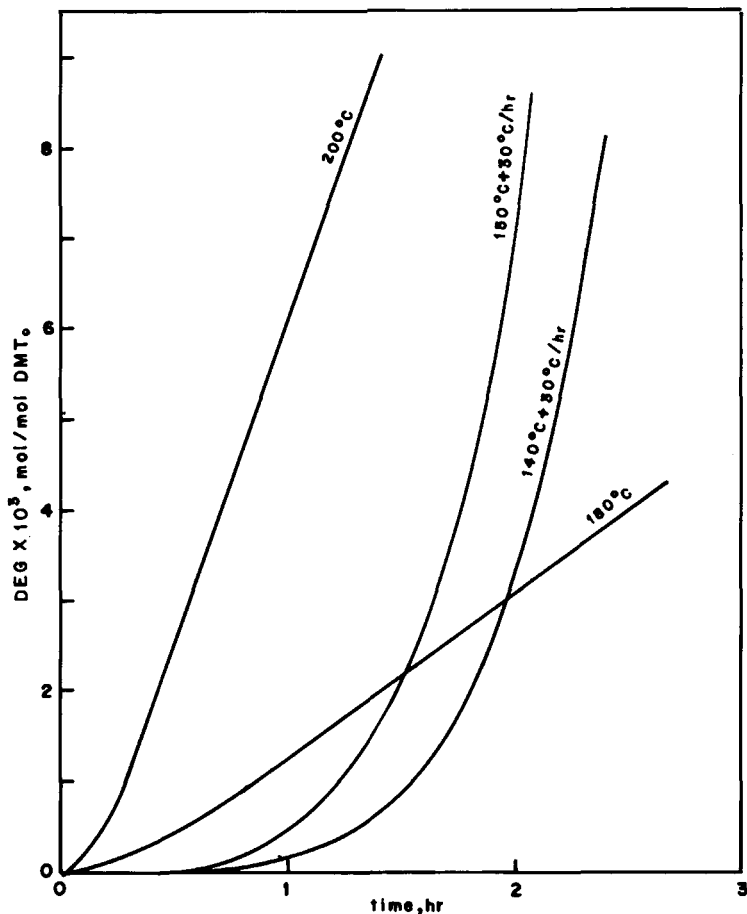
Fig. 11. Effect of EG/DMT ratio on the DEG formation rate. $R = 2$; cat conc. $= 5.6 \times 10^{-4}$ mol/ L.

$$m = \frac{(P_T - P_G^*)g + P_T(e_m + e_g)/2}{(P_M^* - P_T)} \tag{36}$$

where P_T, P_M^*, and P_G^* represent the total pressure, the vapor pressure of methanol, and the vapor pressure of EG, respectively. The values obtained from eq. (36) for methanol concentration are only approximate values, and in the initial stages of reaction eq. (36) they are negative for the first-stage operating conditions given in Table 5 by Ault and Mellichamp.[2] During the latter stages of reactions, side products such as water and acetaldehyde are formed. Therefore, eq. (36) cannot be used directly for calculating the methanol concentration in the reaction mass. We adopted a different approach for calculating the concentration of volatile species in the reaction mass. Making a quasi-steady-state assumption for small increments of time, a flash distillation process could be considered to occur. Then the concentration of volatile species and the rate of outflow of volatile species can be calculated using the following material balance equations written for a flash tank. The representative model is shown in Figure 2.
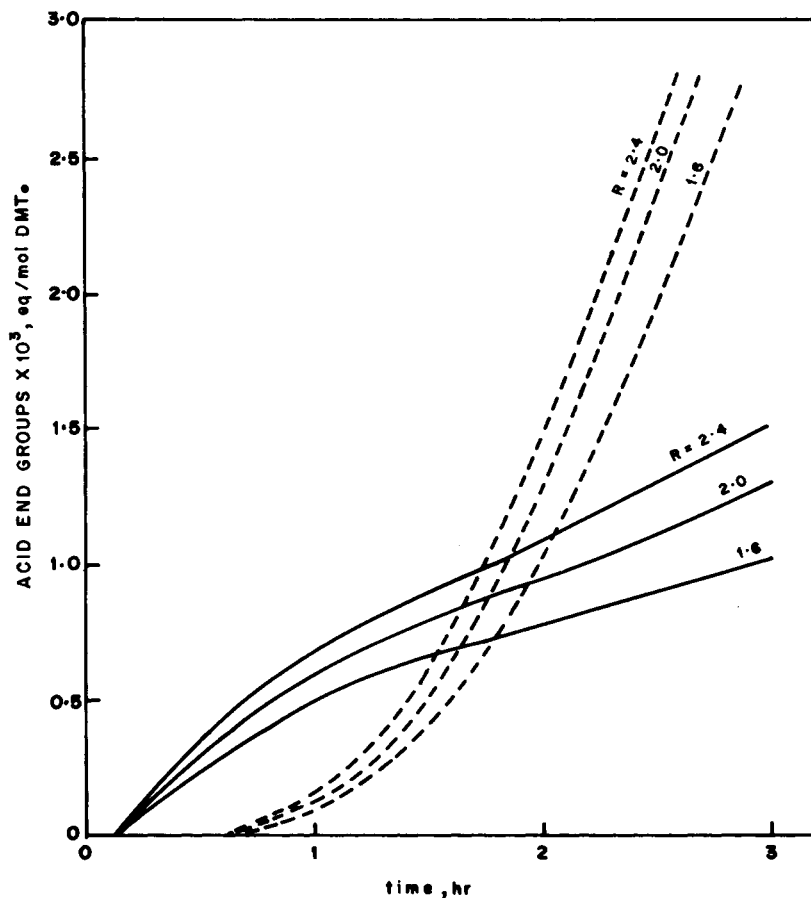
Fig. 12. Effect of temperature program on the acid end groups formation rate. Cat. conc. = 5.6 × 10⁻⁴ mol/L; (- - -) 140°C + 30°C/h; (——) 180°C.

Material Balance Equations

For the flash distillation model presented in Figure 2, we have the following material balance equations:

$$F = D + B \tag{37}$$

$$m = Dy_m + Bx_m \tag{38}$$

$$g = Dy_g + Bx_g \tag{39}$$

$$w = Dy_w + Bx_w \tag{40}$$

$$1 = y_m + y_g + y_w + y_a \tag{41}$$

where F, D, and B represents the number of moles of the feed, distillate, and liquid; y_i and x_i represent the mole fraction of the ith component in vapor and liquid, respectively. The acetaldehyde vapor pressure value is very high, and hence it is assumed that acetaldehyde leaves the reaction mixture as soon as it is formed. Higher-molecular-weight oligomers can be considered as nonvolatile.
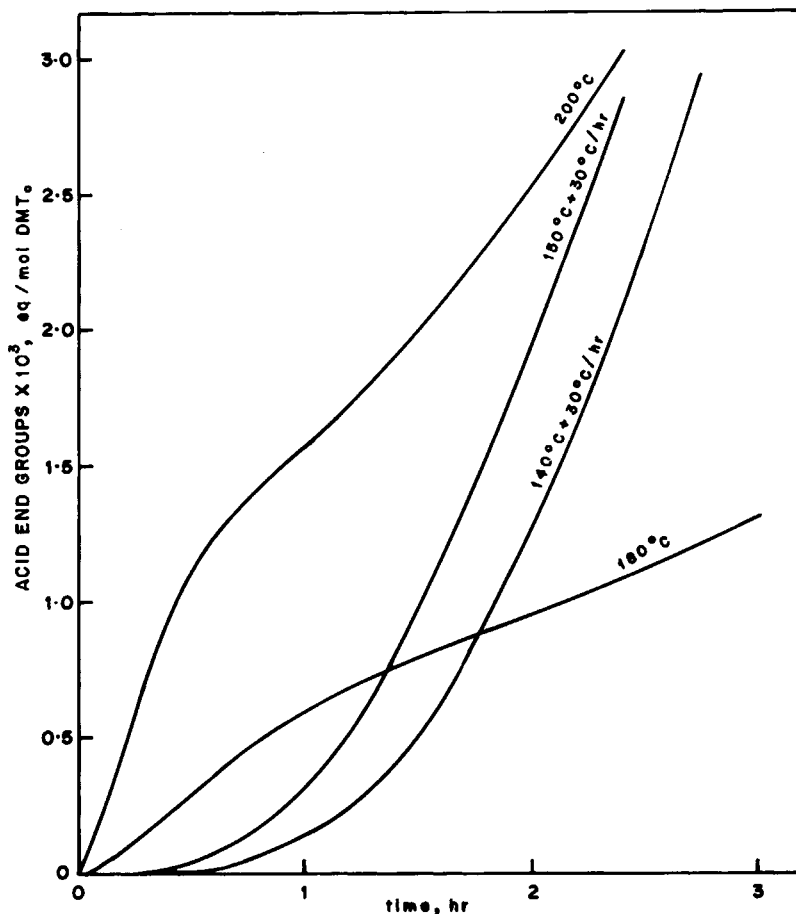
Fig. 13. Effect of temperature program on the acid end group formation rate. $R = 2$; cat. conc.
= 5.6×10^{-4} mol/L.

It is also asumed that Raoult's law is valid for all the volatile components except
for acetaldehyde:

$$y_i = P_i^* \frac{x_i}{P_T} \qquad (42)$$

where i represents the volatile component.

At the beginning of the reaction, water and acetaldehyde concentrations are
very small, but as the reaction proceeds, all these volatile components will be
formed in the reaction mixture. The numerical scheme was devised in such a
way that the sum of the partial pressures developed by all the volatile species
was greater than the reactor pressure flash calculations were done. Otherwise,
it was assumed that the vapor flow rate was zero.

Equations (18)–(26) were nondimensionalized using the initial methyl ester
end group concentration. Since the nondimensionalized governing equations
did not yield analytical solutions, these were solved numerically by using the
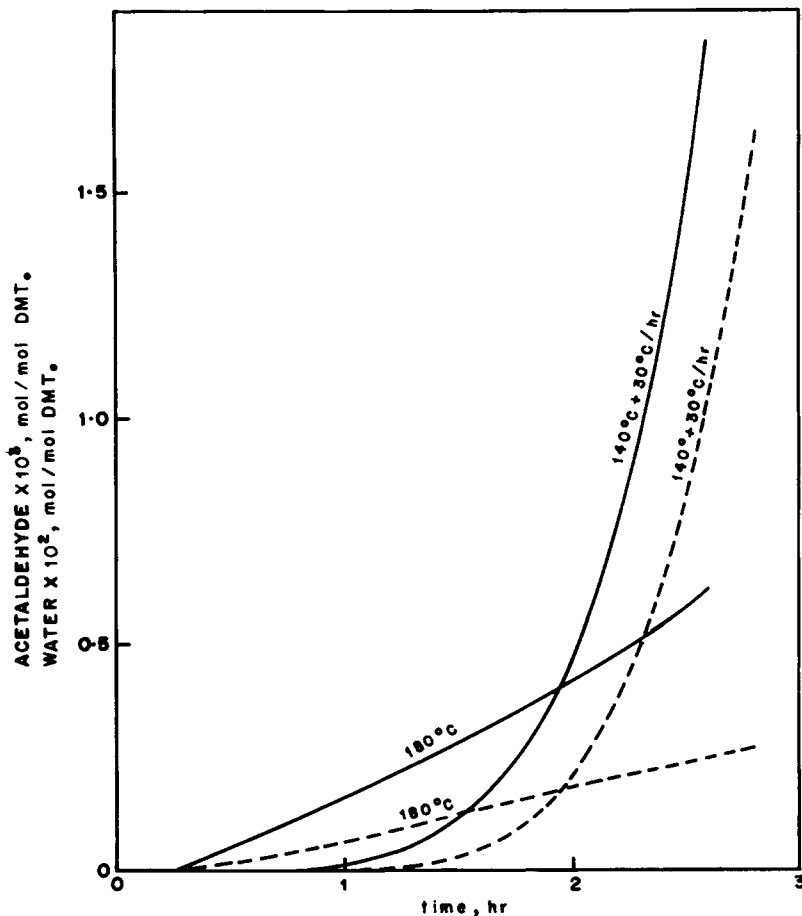modified fourth-order Runge-Kutta and Gill method. Concentrations of the

Fig. 14. Effect of temperature on the rate of formation of water and acetaldehyde. $R = 2$; cat. conc. $= 5.6 \times 10^{-4}$ mol/L; (- - -) water; (——) acetaldehyde.

volatile components in the reaction mass were calculated using eqs. (37)–(42). The effect of increase in rate constants due to the increase in catalyst concentration has been taken into account in the numerical calculations. Within the framework developed in the foregoing, we shall analyze the problem to obtain the following information: (1) percent of methanol removed (defined as $m_t/2DMT_0 \times 100$) as a function of time; (2) amount of by-products such as DEG, acetaldehyde, water, and total acid end groups formed as a function of time.

In order to obtain the results as summarized above, we need to have accurate information about the following parameters: (1) kinetic parameters appearing in eqs. (1)–(3), (12), (14), (17), (7), and (8), viz., k_1 to k_8 as a function of catalyst type, catalyst concentration, and temperature; (2) equilibrium constants, viz., K_1 to K_5; and (3) vapor pressure data for water, methanol, and EG.

Kinetic Parameters

The values of the ester interchange reaction rate constant (k_1) given by Fontana[9] were used for the numerical calculations for different catalyst (zinc acetate)
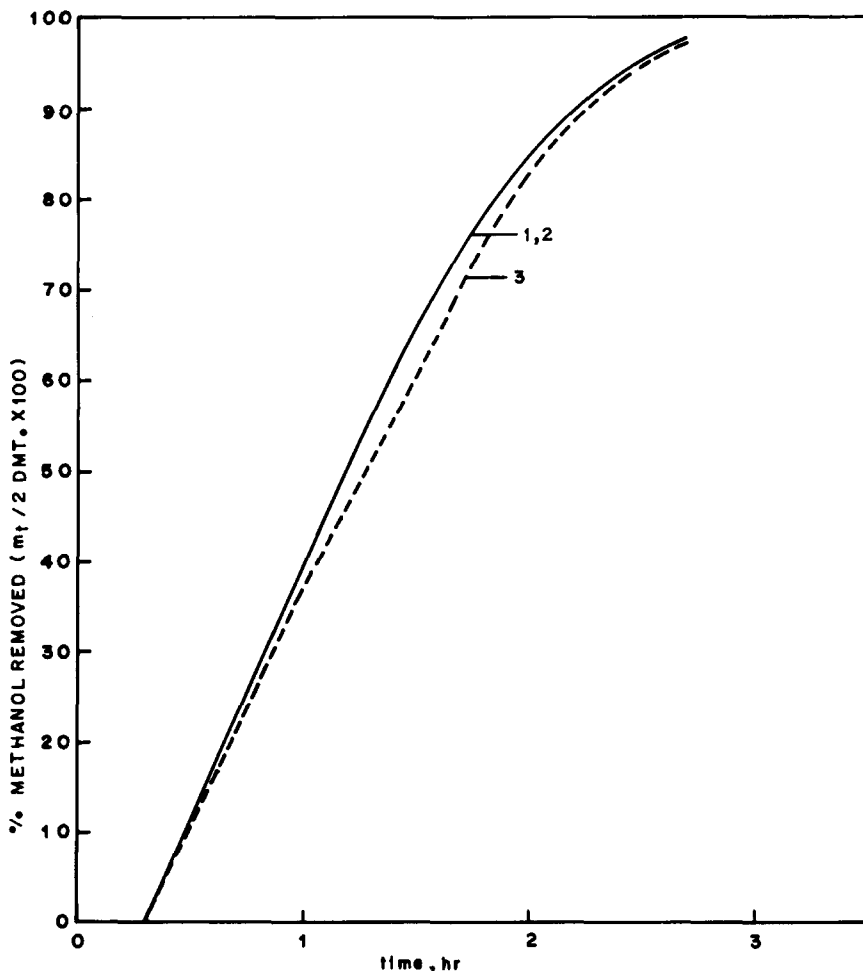
Fig. 15. Effect of EG addition process on the progress of reaction: (1), total amount of EG added in the beginning; (2), 25% of EG added continuously in the first hour; (3), 25% of EG added after 70% of initial 75% EG has been reacted. $R = 2$; cat. conc. = 5.6×10^{-4} mol/L; temperature = 140°C + 30°C/h.

concentrations. Fontana[9] assumed that the ratio of rate constants for transesterification (k_2) to ester interchange (k_1) was approximately 0.5, whereas Yamamis and Adelman[11] found that the ratio is less than 0.02. Due to this uncertainty, model results have been presented for both values. The values of k_3 given in Table I were estimated from the available data in the literature. It is shown later than the DMT conversion rate was not affected significantly by the values of k_2 and k_3 used in the calculation. Very little information is available regarding the values of k_4, k_5, and k_6, which are rate constants corresponding to the formation of acetaldehyde, free DEG, and DEG incorporated in the chain.

Hovenkamp and Munting[8] found that the rate constant for total DEG formation (i.e., k_5 and k_6) is 0.0012 kg/mol h at 270°C when a mixture of manganese acetate (0.024%) and antimony trioxide (0.04%) catalysts was used. Yokoyama et al.[12] obtained the 2-hydroxyethyl ester end group (e_g) degradation rate con-
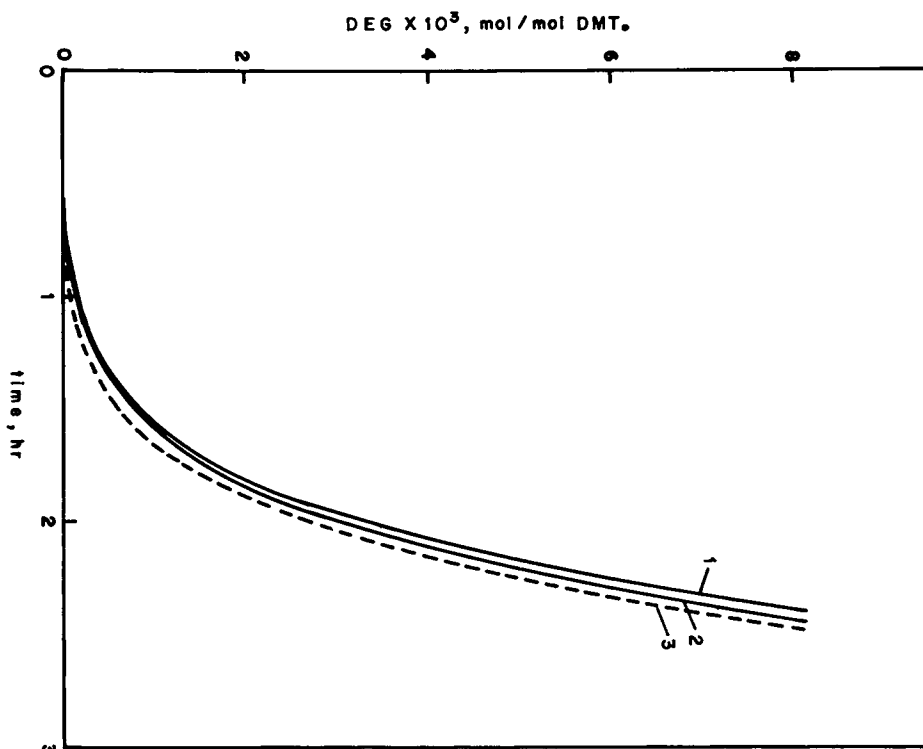
Fig. 16. Effect of EG addition on DEG formation rate (notation is the same as in Fig. 15). $R =$ 2; cat. conc. $= 5.6 \times 10^{-4}$ mol/L; temperature $= 140°C + 30°C/h$.

stants (k_4) and esterification rate constant (k_8) by simulating the batch poly-condensation experimental data. In the absence of experimental data for reactions (4), (14), and (17) and because of the similarity of the reaction mechanism in these individual reaction steps, the rate constants k_4, k_5, and k_6 were assumed to be the same as the values given by Yokoyama et al.[12] for e_g degradation rate constant k_4. The values of the rate constants k_7 and k_8 were deduced from the work of Yokoyama et al.[12] The kinetic parameters used in the present work for the purpose of computations are shown in Table I.

Equilibrium Constants

Challa[4] reported the ester interchange and polycondensation equilibrium constants to be 0.3 and 0.4, respectively. These were also found to be insensitive to temperature. The transesterification equilibrium constant K_2 can be calculated from the relationship obtained by Challa,[4] viz., $K_2 = K_1 K_3$. Many workers[9,13] have obtained polycondensation equilibrium constants, which appear to be very close to a value of 0.5. Therefore, in the present work, it was assumed that $K_1 = 0.3$, $K_2 = K_1 K_3$, and $K_3 = 0.5$. Chegolya et al.[14] studied esterification equilibrium reactions using benzoic acid–EG and benzoic acid–2-hydroxyethyl benzoate as model systems. They found that the equilibrium constants depend on the type of reaction medium. Since the reaction medium in the latter stages of reaction is very close to benzoic acid and 2-hydroxyethyl benzoate, the values

of equilibrium constants, viz., K_4 and K_5, were assumed to be 2.5 and 1.25 (Chegolya et al.[13]). The polycondensation and esterification equilibrium constants are related by $K_5 = K_3K_4$. The equilibrium constants considered in the present work are presented in Table I.

Vapor Pressure Data

The vapor pressure data for water and methanol were obtained from Perry[14] and correlated by using an equation of the following type

$$\log P_i^*(\text{mm}) = A_i - \frac{B_i}{C_i + \theta} \tag{43}$$

where θ is in °C. The values of A_i, B_i, and C_i are shown in Table II. The following equation was used[9] for calculating the vapor pressure of EG:

$$\log P_G^*(\text{mm}) = 21.61 - \frac{3729}{T} - 4.042 \log T$$

where T is in K.

RESULTS AND DISCUSSION

Using the mathematical model developed in the foregoing, the predictions of the performance of the semibatch ester interchange reactor were obtained. Certain industrial plant data on the rate of methanol generation as a function of time were available for comparison. It was found that there was a fair agreement between the model predictions and the plant data. Due to propriety reasons, such plant data cannot be reproduced in this report. However, it may be stated confidently that the overall plant performance matched quite well the model predictions.

We shall now investigate the influence of different processing and operational variables (specified in Table III) on the reactor performance in some detail.

EG-to-DMT Ratio

We shall present the data for two cases: a constant-temperature case (either 180° or 200°C) and a variable-temperature case. For the latter case, the temperature program chosen is close to that followed in industrial practice. Melted DMT and EG are charged to the reactor at 140°C, and by controlling the heat input the temperature is raised by 30°C per hour.

The industrial practice is to follow the rate of methanol removal, which gives indication of the progress of the reaction. We shall therefore present the data on the rate of methanol removal as a function of time. Note that for 100% conversion of DMT, methanol removed will be two DMT_0 moles.

In Figure 3, we have shown the changes in the reactor performance when the EG-to-DMT ratio was changed progressively from 1.6 to 2.4. It was observed that an increase in the EG-to-DMT ratio increases the methanol removal rate. It will be seen that a programmed temperature with an increase at the rate of 30°C per hour leads to improved reactor performance. In Table IV we have shown reaction time for 90% methanol removal under different conditions; it

is seen that the reaction times increase progressively with reduction in the EG-to-DMT ratio.

Another interesting observation concerns the trend in the higher time scale. It is observed that when the temperature is maintained constant at a value of 200°C, the conversion curve reaches a plateau. This is obviously due to the chemical equilibrium consideration at higher conversions. It would thus appear that it is necessary to raise the temperature at the end of the reaction to reach a higher percentage conversion.

An additional interesting observation concerns the behavior at small times. It is seen that the process of methanol removal starts almost immediately when the temperature is maintained at 200°C, whereas when a programmed temperature is used there is an induction period of approximately 17 min before any finite amount of methanol could be seen in overheads. This is obviously due to vapor–liquid equilibrium considerations since a minimum quantity needs to be built up in the liquid phase before mass transfer process can proceed to an appreciable extent.

Influence of Catalyst Concentration

In Figure 4, we show the variation of the rate constant as a function of the zinc acetate catalyst concentration at 197°C.[15] It is seen that there is a considerable increase in the rate constant at lower catalyst concentration which is not sustained at higher concentrations. It would thus intuitively appear that catalyst loading beyond a particular value is not of any significant advantage.

In Figure 5, we show the influence of catalyst concentration on the progress of the reaction for a fixed value of EG-to-DMT ratio and for given temperature programs. It is seen that an increase in catalyst concentration increases the rate of reaction; however, the advantages obtainable by using a high catalyst concentration are rather marginal, especially at higher percentage conversions, which are of interest in industrial practice.

Influence of Temperature Programs

In Figure 6 we show curves representing the progress of the reaction for different temperature programs. It is easily seen that although there is an initial advantage of higher rates of reactions when a constant temperature at high level is maintained (for example, 180 or 200°C), the trend is quite opposite at higher times. For instance, maintaining a temperature program of 140°C plus 20°C per hour leads to a final temperature of 200°C at the end of 3 h and gives 92% conversion. However, maintaining a constant temperature of 200°C throughout leads to a percentage conversion of 95%, which remains at the same level at higher times. This again is due to considerations of chemical equilibrium. It is also seen that higher initial temperatures lead to the reduction in induction times necessary for finite methanol removal at small percentage conversion.

Parametric Sensitivity

It was considered desirable to investigate in some detail the sensitivity of the results obtained to the chosen values of kinetic and equilibrium constants.

Figures 7 and 8 demonstrate this for chosen values of operational variables. A change in the values of the equilibrium constants for two sets does not show any appreciable difference. It is also seen that a change in k_2/k_1 value between 0.01 and 0.5 does not make an appreciable change in the prediction of the progress of the reaction.

Influence of Pressure

It was considered desirable to investigate the influence of pressure on the reaction. In Figure 9 we show two curves with prescribed temperature programs, one corresponding to a reactor pressure of 200 mm Hg and other to a reactor pressure of 760 mm Hg. Reduction in pressure leads to an improvement in reactor performance, as is to be intuitively expected in view of the favorable vapor–liquid equilibrium considerations at lower pressures. However, the advantages do not appear to be significant. Thus, for a fixed set of conditions, the time required for 90% methanol removal were 122 and 130 min at pressures of 200 and 760 mm Hg, respectively.

Influence of Side Reactions on Percent Methanol Removed

The numerical predictions presented so far give information about overall percentage removal of methanol which is an integral quantity. These calculations so far presented do not take into account the formation of side products. In figure 9 we present two curves wherein the influence of the side products has been investigated. It is readily seen that the influence of the side reactions on % methanol removed is not significant in general and the difference is not more than 1% at 90% conversion.

DEG Formation

For reasons outlined earlier, it is exceedingly important to control the rate of DEG formation. We therefore took up a thorough investigation of the influence of processing and operational variables on the rate of DEG formation. The results are shown in Figures 10 and 11 for different EG/DMT_0 ratios and for different temperatures. It is seen that an increase in the EG-to-DMT ratio increases the extent of DEG formation. It may be recalled that earlier we had seen that the rate of reaction became rapid when the EG-to-DMT ratio was kept at a higher value. It will thus be seen that conditions suitable for improved productivity also cause increased formation of DEG. Optimum conditions will have to be generally chosen. An interesting point can be seen from the figures that temperature plays an important role in the rate of DEG formation. Thus, for a fixed value of EG-to-DMT ratio of 2.0, the extent of DEG formed is much less at a lower temperature. The converse is true at higher temperatures.

Acid End Group Formation

In Figures 12 and 13 we show the progress of the acid end group formation rate as a function of time. It is seen again that the pattern emerging is quite similar to that in the case of DEG formation in that an increase in the EC-to-DMT ratio

and rapidly raising temperature profile results in an increase in acid end group formation. The influence of different temperature programs on the rate of acid end groups formed can be vividly seen from the data presented in Figure 13.

Formation of Other Products

Acetaldehyde and water are two other major side products of transesterification reaction. The rate of generation of acetaldehyde and water as a function of time was studied for different temperatures. The trends are seen in Figure 14. Again, the extent of acetaldehyde and water formation predicted is in good agreement with the values normally observed in industrial practice. The influence of different temperatures on the rate of acetaldehyde and water formation can be vividly seen from the data presented in Figure 14.

Continuous Ethylene Glycol Addition

In the foregoing, it has already been shown that a higher EC-to-DMT ratio is undesirable from the point of by-product formation, especially the formation of DEG. It is possible in principle to have a controlled rate of addition of EG to the ester interchange reactor. The influence of such a controlled addition was investigated, and the results on the progress of the reaction as well as DEG formation rate are shown in Figures 15 and 16, respectively. Three cases were considered. In the first, the total ethylene glycol quantity was added in the beginning. In the second instance, 75% EG was charged initially and 25% EG was added slowly in the first hour. In the third instance, 75% ethylene glycol was added in the beginning, and after completing 70% of the reaction, the rest (i.e., 25%) glycol was added.

It is readily seen that although there is no significant difference in the overall reaction, the extent of DEG formation can be reduced to a certain extent by continuous EG addition.

Nomenclature

A_i	constant in eq. (43)
a	number of moles of acetaldehyde
B	number of moles of liquid
B_i	constant in eq. (43)
C_i	constant in eq. (43)
D	number of moles of vapor
DMT_0	number of moles of DMT charged initially
EG_0	number of moles of ethyleneglycol charged initially
e_m, e_g, e_c	equivalents of methyl, glycol, and acid ester end groups
F	number of moles of feed for flash tank
g	number of moles of ethylene glycol
g^*	number of moles of diethylene glycol
$Q_G(t),$ $Q_M(t),$ $Q_W(t)$	flow rates of ethylene glycol, methanol, and water, in moles, respectively
k_1-k_3, k_5-k_8	second-order rate constants, L/mol min
k_4	first-order rate constant, in min^{-1}
K_1-K_5	equilibrium constants
m	number of moles of methanol

m_t	total number of moles of methanol removed
P_T	total pressure, in mm Hg
P_M^*, P_G^*, P_W^*	vapor pressure of methanol, ethyleneglycol, and water, respectively, in mm Hg
R	initial molar ratio of EG to DMT
R_1-R_8	reaction rates, in mol/L min
T	absolute temperature, in K
t	time, in min
V	volume of the reaction mass, in L
V_{DMT}, V_{EG}, V_W, V_M	molar volumes of DMT, ethyleneglycol, water, and methanol, respectively, in L/mol
w	number of moles of water
w_t	total number of moles of water removed
x_i	mole fraction of component i in the liquid
y_i	mole fraction of component i in the vapor
z	number of moles of diester group
θ	temperature, in °C

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