

Modeling of Poly(ethylene Terephthalate) Reactors.

II. A Continuous Transesterification Process*

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Synopsis

A comprehensive mathematical model for a continuous transesterification process has been built so as to enable prediction of the influence of different process and operational variables on productivity and by-product formation. The influence of temperatures and temperature profiles, of residence time and residence time distribution, and also of the number of reactors in series has been investigated. The modeling has been done as close to the industrial practice as possible. Important pragmatic implications from the point of view of operation of continuous transesterification are highlighted.

INTRODUCTION

We have launched a comprehensive program on modeling poly(ethylene terephthalate) reactors. As a first step in this endeavor, we developed a mathematical model for a semibatch ester interchange reactor.¹ We investigated the effect of various process and operating variables on the DMT conversion rate as well as the by-product formation rate. We reached definite conclusions concerning the choice of desirable range of process and operational variables to maximize the productivity and to minimize by-product formation.

Although a number of semibatch plants are in operation throughout the world, the recent trends appears to be toward continuous processes. Thus, a series of reactors are used for the transesterification process as well as the polycondensation process. The obvious advantage in the continuous process is a significant energy saving. We therefore thought that it would be desirable to develop a mathematical model for continuous transesterification process so as to enable a prediction of the influence of different process and operational variables on productivity and by-product formation. There is no previous effort in this direction in the literature, except for the work of Dijkman and Duvekot.² Unfortunately the effort by Dijkman and Duvekot is not very comprehensive with regard to the influence of important variables such as residence time distribution, temperature distribution, and the number of reactors in series. Indeed, the important point concerning the influence of various operating and process variables on by-product formation has not been dealt with at all.

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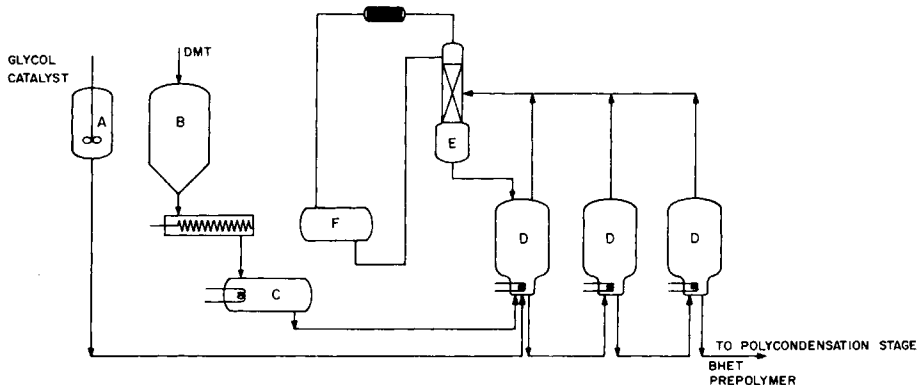


Fig. 1. Process flow diagram for the continuous transesterification process.

Transesterification Process

A process flow diagram for a continuous transesterification process or ester interchange process is shown in Figure 1. Ethylene glycol (EG) is passed batchwise from storage tank to the preparation vessel (A), where one or more catalysts are added. Dimethyl terephthalate (DMT) is continuously fed to the melter (C) from the DMT storage tank (B). Melted DMT and EG are fed to the ester interchange reactor (D). The reaction mass is passed through a fixed number of reactors before proceeding to the polycondensation stage. For simplicity, only three reactors are shown in Figure 1. The vapors coming out of the ester interchange reactors are passed through a rectification column (E), and EG is completely refluxed back to the first ester interchange reactor. Methanol is collected in tank F, and part of it is used as reflux for the rectification column E.

There is an alternate way of refluxing EG back to the system. If each reactor has a separate rectification column, then vapors coming out of a particular reactor are fractionated in the respective rectification columns and EG is refluxed back to the reactor. This does not appear to be particularly advantageous and hence has not been considered in this work. The prepolymer coming out of the last reactor of the first stage contains mainly bis(2-hydroxyethyl) terephthalate (BHET) and its linear oligomers. The waste methanol collected in tank F contains small amounts of EG, diethylene glycol (DEG), water, and ketones.

Reaction Scheme

Various reactions occurring in the transesterification process have been discussed by Ravindranath and Mashelkar.¹ For detailed information, the reader is referred to this work. However, we shall present a summary pertinent to the development of a model for a continuous reactor. (In the discussion here, we shall use the symbols shown in Table I). The main reactions are

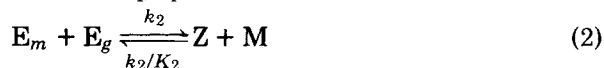


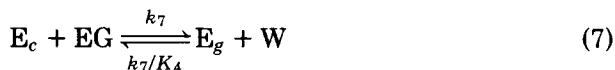
TABLE I
Key to Symbols

E_m	$\sim\sim\sim\text{C}_6\text{H}_4\text{—COOCH}_3$	methyl ester end group
E_g	$\sim\sim\sim\text{C}_6\text{H}_4\text{—COOC}_2\text{H}_4\text{OH}$	hydroxyethyl ester end group
Z	$\sim\sim\sim\text{C}_6\text{H}_4\text{—COOC}_2\text{H}_4\text{OOC—C}_6\text{H}_4\sim\sim\sim$	diester group
Z^*	$\sim\sim\sim\text{C}_6\text{H}_4\text{—COOC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OOC—C}_6\text{H}_4\sim\sim\sim$	DEG-incorporated diester group
E_c	$\sim\sim\sim\text{C}_6\text{H}_4\text{—COOH}$	acid end group
E_{DEG}	$\sim\sim\sim\text{C}_6\text{H}_4\text{—COOC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OH}$	DEG ester end group
EG	$\text{HOC}_2\text{H}_4\text{OH}$	ethylene glycol
M	CH_3OH	methanol
W	H_2O	water
DEG	$\text{HOC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OH}$	diethylene glycol
A	CH_3CHO	acetaldehyde
$\sim\sim\sim$		polymer chain

In eqs. (1)–(3), it is assumed^{3,4} that the reactivity of the methyl ester end groups on DMT and on half-esterified DMT are the same and that the reactivity of the hydroxyl groups on EG and on half-esterified EG are different. There are a number of side reactions taking place in the transesterification process. Important side reactions are the reactions leading to the formation of acetaldehyde, DEG, and water. Ravindranath and Mashelkar¹ have discussed in detail the reaction mechanisms of the side reactions proposed by various investigators.^{5–8} It was concluded that the formation of acetaldehyde and DEG can be best represented by the following reactions:



Acid end groups formed in reactions (4)–(6) can react with hydroxyl groups of EG and E_g as shown in (7) and (8):



The side reactions involving diester groups Z and E_{DEG} are not considered in the present model; k_1 – k_3 and k_5 – k_8 are second-order rate constants and k_4 is a first-order rate constant. Note that k_1 – k_8 are functions of the catalyst type and concentration used; K_1 – K_5 are equilibrium constants.

DEG and E_{DEG} can react with E_m , E_c , and E_g , as in the case of EG and E_g . The reaction of E_{DEG} with E_g involves four polycondensation reactions. These are





For simplicity, reactions of DEG and E_{DEG} with E_m and E_c are not shown in the above reaction scheme. Because of the complexity of the reactions involving DEG and E_{DEG} , and because of the limitations of the available kinetic data, we have calculated the total DEG content (i.e., free DEG and incorporated DEG in polymer chain) in the present work rather than calculating the two values separately.

Mathematical Model for Continuous Transesterification Process

The reaction mixture of the transesterification process contains mainly methanol, EG, DEG, water, and linear polymer molecules having methyl, hydroxyl, and acid end groups. Assuming that the reactivity of the functional groups does not depend on the polymer chain length, material balance equations for a steady-state continuous stirred tank reactor (CSTR) can be written as

$$F_i e_m^i - F_0 e_m + \rho V R_{E_m} = 0 \quad (13)$$

$$F_i e_g^i - F_0 e_g + \rho V R_{E_g} = 0 \quad (14)$$

$$F_i m^i - F_0 m + \rho V R_M - F_v m^v = 0 \quad (15)$$

$$F_i g^i - F_0 g + \rho V R_{\text{EG}} - F_v g^v = 0 \quad (16)$$

$$F_i z^i - F_0 z + \rho V R_Z = 0 \quad (17)$$

$$F_i e_c^i - F_0 e_c + \rho V R_{E_c} = 0 \quad (18)$$

$$F_i w^i - F_0 w + \rho V R_W - F_v w^v = 0 \quad (19)$$

$$F_i g^{*i} - F_0 g^* + \rho V R_{\text{DEG}} = 0 \quad (20)$$

$$\rho V R_A - F_v a^v = 0 \quad (21)$$

Where R_{E_m} , R_{E_g} , R_M , R_{EG} , R_Z , R_{E_c} , R_W , R_{DEG} , and R_A represent the rate formation of E_m , E_g , M, EG, Z, E_c , W, DEG, and A respectively; F_i , F_0 , and F_v represent the flow rates of input, output, and vapor, respectively; e_m , e_g , m , z , e_c , and w represent the output concentration of the respective species shown in Table I (with capital letters); g and g^* are the concentration of EG and DEG; ρ and V are the density and volume of the reaction mixture, respectively; m^v , g^v , w^v , and a^v are the concentrations of methanol, EG, water, and acetaldehyde in vapor, respectively, and e_m^i , e_g^i , m^i , g^i , z^i , e_c^i , w^i , and g^{*i} represent the input concentration of the respective species. The vapor pressure of acetaldehyde is very high; and hence in eq. (21), it is assumed that acetaldehyde leaves the reaction mixture as soon as it is formed. In the present work, the total content of DEG (i.e., free DEG and DEG incorporated in the polymer chain) is calculated on the basis of eq. (20), and therefore material balance equations for free DEG and incorporated DEG in the polymer chain have not been written separately. The rate of formation of each species can be written as

$$R_{E_m} = -R_1 - R_2 \quad (22)$$

$$R_{E_g} = R_1 - R_2 - 2R_3 - R_4 - R_5 - R_6 + R_7 - R_8 \quad (23)$$

$$R_M = R_1 + R_2 \quad (24)$$

$$R_{\text{EG}} = -R_1 + R_3 - R_7 \quad (25)$$

$$R_Z = R_2 + R_3 + R_8 \quad (26)$$

$$R_{E_c} = R_4 + R_5 + R_6 - R_7 - R_8 \quad (27)$$

$$R_W = R_7 + R_8 \quad (28)$$

$$R_A = R_4 \quad (29)$$

$$R_{DEG} = R_5 + R_6 \quad (30)$$

where R_1 – R_8 represent the reaction rates. Assuming that order and molecularity of the reactions are same, reaction rates for reactions (1)–(8) can be written as

$$R_1 = k_1 \left(2e_m g - e_g \frac{m}{K_1} \right) \quad (31)$$

$$R_2 = k_2 \left(e_m e_g - 2z \frac{m}{K_2} \right) \quad (32)$$

$$R_3 = k_3 \left(e_g^2 - 4z \frac{g}{K_3} \right) \quad (33)$$

$$R_4 = k_4 e_g \quad (34)$$

$$R_5 = 2k_5 e_g g \quad (35)$$

$$R_6 = k_6 e_g^2 \quad (36)$$

$$R_7 = k_7 \left(2e_c g - e_g \frac{w}{K_4} \right) \quad (37)$$

$$R_8 = k_8 \left(e_c e_g - 2z \frac{w}{K_5} \right) \quad (38)$$

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 reaction (5) is not included in eq. (25), and the disappearance of E_g by reaction (6) is considered only once in eq. (23). For a constant reactor volume V , the following relation holds:

$$F_i = F_0 + F_v \quad (39)$$

For solving the mass balance equations (13)–(19) and (21), the concentration of each species in the vapor phase must be known. They are related to the mole fractions x_i in the liquid phase through eq. (40):

$$\text{concn of } j\text{th component in the vapor phase (mol/kg)} = \frac{x_j P_j^*}{\sum_j x_j M_j P_j^*} \quad (40)$$

where M_j and P_j^* represent the molecular weight and vapor pressure of species j , respectively. In eq. (40) it is assumed that the vapor above the melt is ideal and physical equilibrium exists between the components in the liquid and the vapor phases. With this assumption, the total pressure P_T will be the sum of the partial pressures, and therefore

$$1 = \frac{P_m^*}{P_T} x_M + \frac{P_G^*}{P_T} x_G + \frac{P_W^*}{P_T} x_W + \frac{a^v}{m^v + w^v + g^v + a^v} \quad (41)$$

The commercial practice is to carry out the transesterification process in a chain

of reactors, where the feed to the next reactor in the chain is the product from the previous reactor. In the continuous transesterification process, EG in the vapor coming out of the reactors is refluxed back. Specifically, vapors emerging from all reactors are fractionated in a single fractionating column, and EG is refluxed back into the first reactor. This means that the mass balance equations for each reactor are not independent but are coupled. Hence, mass balance equations for all the reactors have to be solved simultaneously. Here, we adopted an iterative method (using initially an approximate value of EG reflux) to solve the mass balance equations for each reactor.

The objective now is to solve the governing equations to obtain the following information:

- (1) Percentage of DMT conversion in each reactor. This enables one to follow the course of reaction to its designed state of completion.
- (2) Ratio of EG to methanol flow rates to the fractionating column. This ratio should be minimized in an industrial operation, since large values of this ratio indicate wasteful utilization of energy in vaporizing and condensing EG.
- (3) Amount of side products formed such as DEG, acetaldehyde, and water. These, apart from indicating wasteful utilization of raw materials, determine the product quality such as dyeability and tensile strength (DEG) and color (acetaldehyde).

In order to obtain the results summarized above, we need information about the following parameters:

- (1) Kinetic parameters k_1 – k_8 as a function of temperature, catalyst type, and concentration.
- (2) Equilibrium constants, viz., K_1 – K_5 .
- (3) Vapor pressure data of methanol, EG, and water.

Ravindranath and Mashelkar¹ have discussed the available information on the pertinent kinetic, thermodynamic, and physicochemical data. The parameter values used in the present work are shown in Table II.

The following processing and operating variables were used in this study: initial molar ratio of EG to DMT = 2; zinc acetate catalyst concentration = 5.6×10^{-4} mol/L; temperature = 180, 200, and 220°C; number of compartments = 1, 3, 6, and 9; total residence time = 3 h; pressure = 760 mm Hg.

While solving the mass balance equations, the change in catalyst concentration because of the change in the flow rates is also considered.

Numerical Computation Procedure

The governing equations are highly nonlinear in nature. For solution of these equations, the feed conditions and initial guesses are needed. The method suggested by Brown⁹ was employed to solve these equations. Good initial guess values are a prerequisite for convergence. Therefore, an objective function consisting of sums of absolute values of L.H.S. of eqs. (13)–(19) and (41) was formed. This objective function was then minimized with respect to the variables using the multivariable optimization technique of Box.¹⁰ It was found that even approximately valid initial guess values could be used in this optimization procedure. The guess values obtained by using the optimization procedure were then used as the initial guess values for solving the nonlinear equations using Brown's method.

TABLE II
Kinetic Parameters Used in the Present Work

Reaction	Ester inter-change eq. (1)	Trans-esterification eq. (2)	Poly-condensation eq. (3)	Acetaldehyde formation eq. (4)	Free DEG formation eq. (5)	Incorporated DEG formation eq. (6)	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	4.0×10^4	2.0×10^4	6.8×10^5	2.17×10^9 a	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.

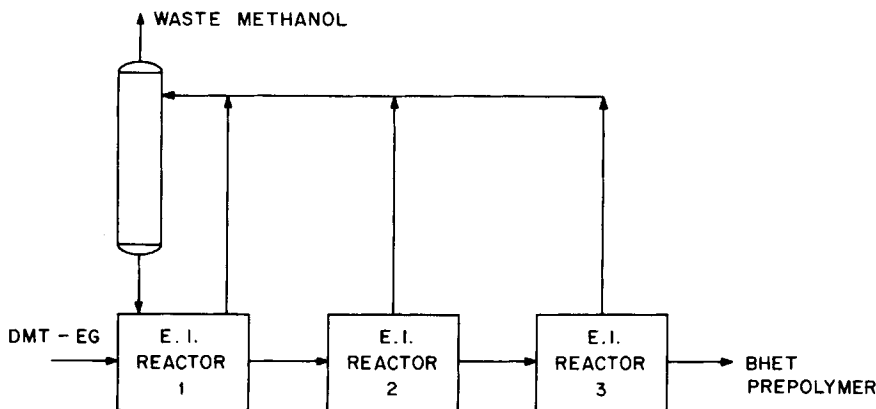


Fig. 2. Model of a continuous transesterification process.

RESULTS AND DISCUSSION

Using the mathematical model developed (see Fig. 2), the role of various processing and operating variables on the performance of the ester interchange process was investigated. We shall now discuss the results of the theoretical investigation in a systematic manner.

Single reactor: Influence of Residence Time and Temperature

The results in this case were computed for two fixed temperatures, viz., 180 and 200°C, and also for a fixed value of $R = 2$. Figures 3 and 4 indicate the influence of residence time on (a) DMT conversion, (b) amount of EG refluxed back when compared with the amount of methanol, and (c) the side products such as DEG, acetaldehyde, water, and acid end groups formed.

It is seen that as the residence time increased from 1 h to 6 h, DMT conversion increased and also the amount of EG refluxed back increased. It is easily seen that both these variables reached an asymptote after a particular residence time. In our previous investigation¹ on the semibatch reactor, we had shown that operation of a semibatch reactor at a constant temperature does not enable the percentage conversion to exceed a particular value due to chemical equilibrium consideration. Similar considerations apply here. It is also seen that the amount of side products formed keep on increasing with increasing residence time, as is to be expected.

As regards the influence of temperature at a fixed residence time, it can be seen that increased temperature helps in increasing DMT conversion and in increasing the amount of EG refluxed back.

It will be of interest to compare the performance of a single CSTR and a single semibatch reactor. A comparison of the performance of a semibatch reactor and a CSTR for $R = 2$ and reactor temperature of 180°C is shown in Table III. The comparison has been made under conditions wherein the cycle time for the batch reactor and the residence time for CSTR are kept equal. The essential difference between the two cases arises from the fact that in the case of a semibatch reactor, the concentrations of reactive species and the product change as a function of time; whereas in the case of CSTR, perfect mixing implies that the concentration values at any point in CSTR are held at the exit concentration value. The

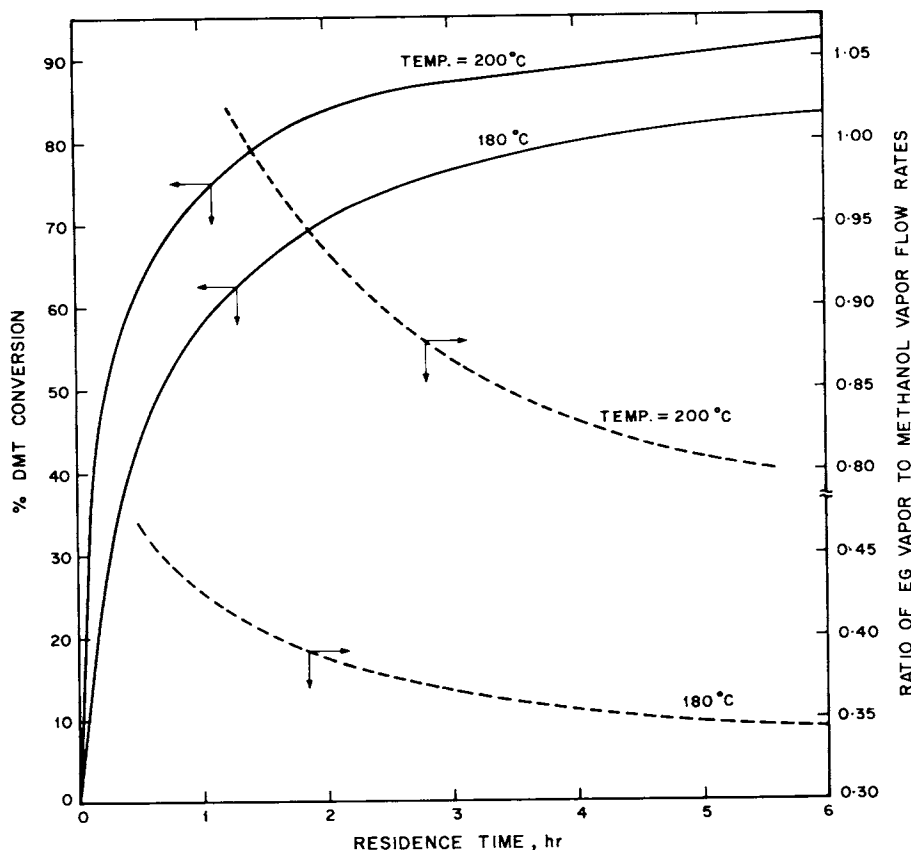


Fig. 3. Effect of residence time on percentage of DMT conversion and on ratio of EG vapor to methanol vapor flow rates for a single reactor.

concentration histories therefore in both cases are different, and these will obviously reflect on the performance.

The comparison shown in Table III shows clearly that DMT conversion in the case of a semibatch reactor is higher than in the CSTR. As regards by-product formation, DEG, acetaldehyde, and water formation rates are less in a semibatch reactor than in the CSTR. However, more acid end groups are formed in a semibatch reactor than in a continuous reactor.

Influence of Number of Reactors in Series

It is obvious that in industrial practice it will be unproductive to carry out the entire transesterification process in a single reactor since an extremely large residence time will be required in order to reach the required percentage conversion of DMT. Therefore, in industrial practice usually three to four reactors are used in series. We shall now investigate systematically the influence of increasing the number of reactors in series. Numerical computations were carried out for two temperatures, viz., 180 and 200°C. The total residence time was fixed at 3 h. The number of compartments was increased discretely from 1 to 3, 6, and 9. Figures 5 and 6 show the influence of change of number of compartments on

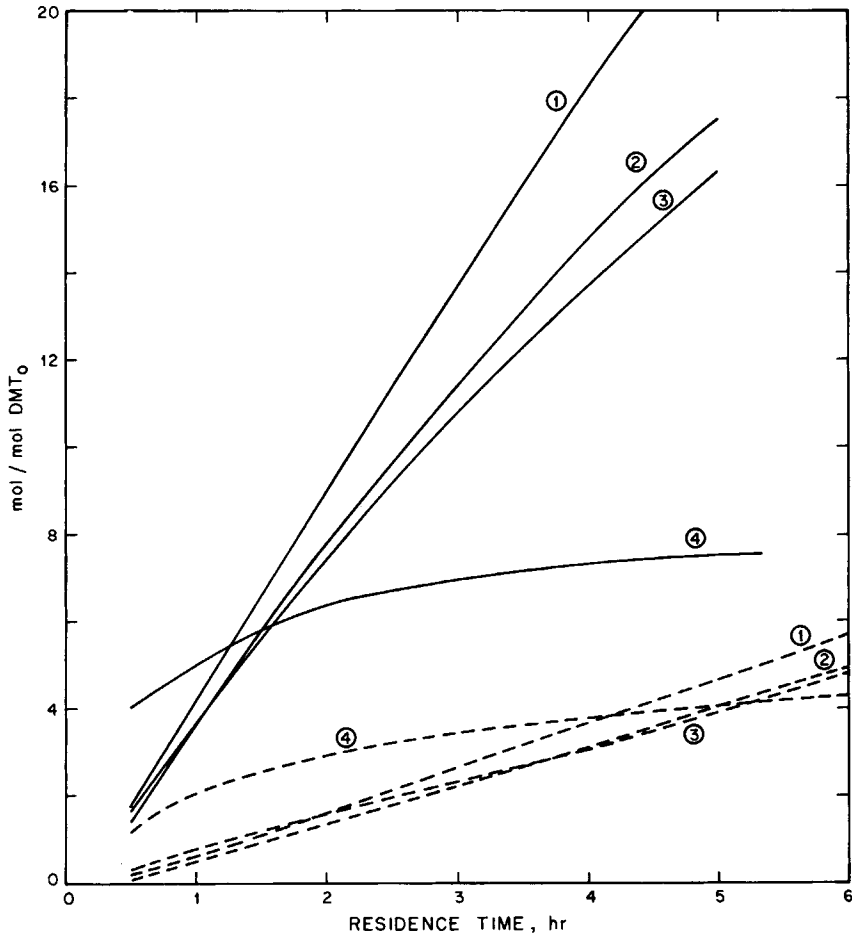


Fig. 4. Effect of residence time on formation of side products for a single reactor: 1, acetaldehyde $\times 10^3$; 2, water $\times 10^2$; 3, DEG $\times 10^2$; 4, acid end groups $\times 10^3$; (—) 200°C; (---) 180°C.

the percentage of DMT conversion, ratio of EG vapor to methanol vapor flow rate, and also the side products formed. It is seen that increasing the number of reactors in series helps in increasing the percentage DMT conversion and also

TABLE III
Comparison of a Semibatch and a Continuous Transesterification Process

	Reaction time			
	Batch cycle time = 1 h	CSTR residence time = 1 h	Batch cycle time = 3 h	CSTR residence time = 3 h
DMT conversion	70.60	58.08	91.70	76.43
Acetaldehyde $\times 10^3$, mol/mol DMT ₀	0.46	0.66	2.12	2.63
DEG $\times 10^2$, mol/mol DMT ₀	0.46	0.66	1.75	2.35
Water $\times 10^2$, mol/mol DMT ₀	0.25	0.53	1.44	2.28
Acid end groups $\times 10^3$, mol/mol DMT ₀	2.56	2.07	5.2	3.37

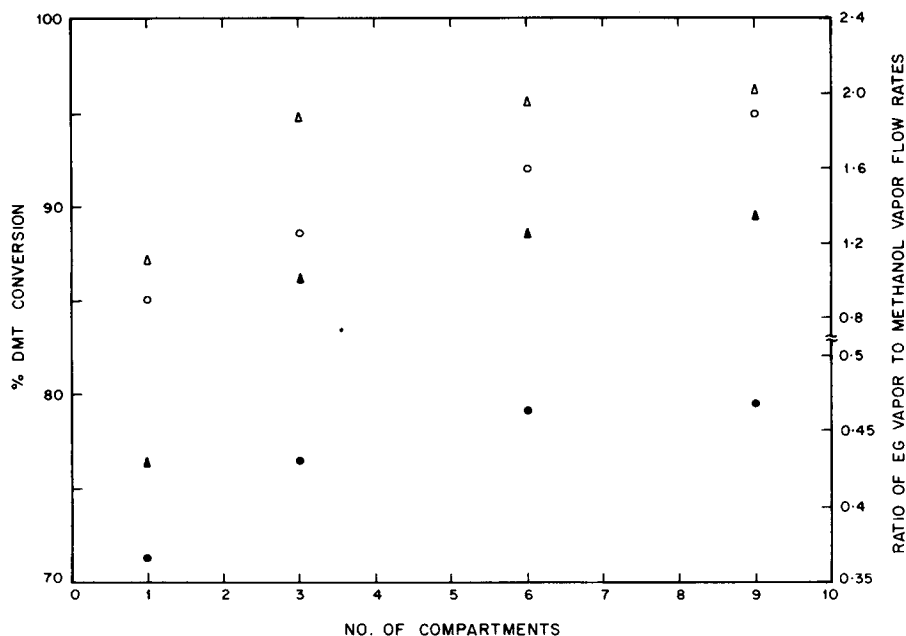


Fig. 5. Effect of number of compartments on percentage of DMT conversion and on ratio of EG vapor to methanol vapor flow rates. Solid symbols, 180°C; open symbols, 200°C; (Δ , \blacktriangle) percentage of DMT conversion; (O, \bullet) ratio of EG vapor to methanol vapor flow rates.

in increasing the EG vapor flow rate. As regards the side products formed concentrations of DEG, acetaldehyde, and water decrease but the concentration of acid end groups increases. Note that in this case the temperatures of all the individual reactors have been assumed constant, and the residence times in all reactors are assumed to be equal.

The conclusions reached above can be explained on the basis of the consideration of mixing or residence time distribution. It is well known that increase in the number of reactors in series brings us to a situation which is close to plug flow. Indeed, for elementary reactions and reasonably low conversion levels, optimal performance of the plug flow reactor is reached when the number of reactors in series approaches approximately five. It can therefore be concluded that the comparison shown in Figures 5 and 6 reflects the influence of mixing, i.e., the influence of moving from a perfectly mixed flow situation to an almost plug flow situation.

Effect of Unequal Residence Times for Sequence of Three Reactors

Constant Temperature

It is obvious that in industrial practice it will be unattractive to use more than three or four reactors to carry out the entire transesterification process. Additionally, in industrial practice the residence times of individual reactors are not maintained at equal values but are distributed. Since a number of possibilities of distributing these residence times exist, we have considered only some specific cases where simple discrete variation could be made.

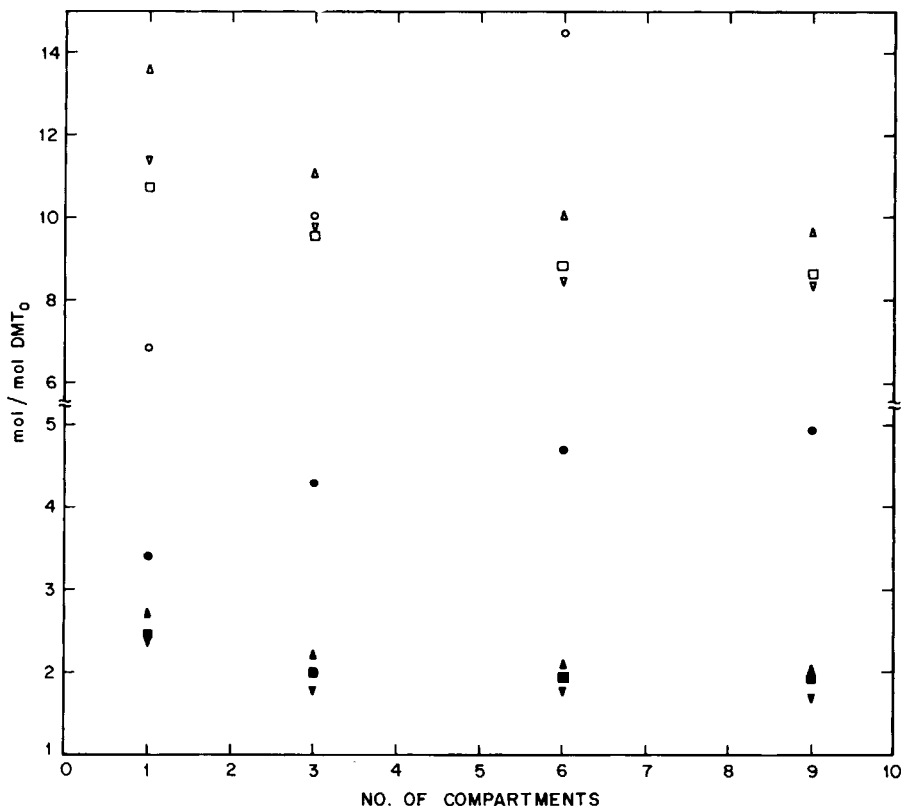


Fig. 6. Effect of number of compartments on formation of side products. Solid symbols, 180°C; open symbols, 200°C; (Δ , \blacktriangle) acetaldehyde $\times 10^3$; (∇ , \blacktriangledown) water $\times 10^2$; (\square , \blacksquare) DEG $\times 10^2$; (\circ , \bullet) acid end groups $\times 10^3$.

Tables IV and V show some of the results obtained. Essentially three cases are considered. In the first case, the residence time in the three reactors have been changed from 1.5 h to 1 to 0.5 h. In the second case, the residence times are kept at equal values viz., 1 h each; whereas in the third case, the residence times have been changed from 0.5 h to 1 to 1.5 h. Computations have been done for temperatures of 180 and 200°C. It is seen that the distribution does not affect the final percentage DMT conversion but the amount of EG refluxed back is less for the first case. It increases, however, the formation of the side products.

Variable Temperature

We similarly examined the possibility of changing the temperature distribution along with the residence time distribution. Again, due to the large number of possibilities we selected only some discrete values which were representative of the industrial practice. Table VI shows the results. It is seen that in the case of distribution of residence time and temperature shown in case 1, a reasonably good percentage conversion is reached, which is close to the other cases but which distinctly shows reduced formation of side products and also EG reflux. It would thus appear that it is useful to maintain a residence time and temperature distribution pattern in a continuous transesterification process as depicted in Table VI.

TABLE IV
Effect of Residence Time Distribution on DMT Conversion for Constant Temperature

Case no.	Residence time distribution, h			% DMT conversion at 180°C			Ratio of EG to methanol flow rates at 180°C	% DMT conversion at 200°C			Ratio of EG to methanol flow rates at 200°C
	First reactor	Second reactor	Third reactor	First reactor	Second reactor	Third reactor		First reactor	Second reactor	Third reactor	
1	1.5	1	0.5	66.97	81.31	85.50	0.41	82.78	92.25	94.50	1.15
2	1	1	1	59.57	78.46	86.20	0.43	78.43	91.09	94.96	1.29
3	0.5	1	1.5	44.73	73.10	85.76	0.45	68.38	88.66	94.88	1.56

TABLE V
Effect of Residence Time Distribution on the Formation of Side Products for Constant Temperature

Case no.	Residence time distribution			Side products at 180°C, mol/mol DMT ₀				Side products at 200°C, mol/mol DMT ₀			
	First reactor	Second reactor	Third reactor	Acetaldehyde × 10 ³	DEG × 10 ²	Water × 10 ²	Acid end groups × 10 ³	Acetaldehyde × 10 ³	DEG × 10 ²	Water × 10 ²	Acid end groups × 10 ³
	1	1.5	1	0.5	2.30	2.18	1.99	4.18	11.90	10.50	10.72
2	1	1	1	2.21	2.09	1.88	4.34	11.10	9.76	9.86	10.09
3	0.5	1	1.5	2.17	2.02	1.80	4.35	10.30	8.99	9.00	10.18

TABLE VI
Effect of Residence Time and Temperature Distribution on DMT Conversion and on Side Products Formed

Case No.	Residence time distribution, h			%DMT conversion			Ratio of EG to methanol flow rates	Side products, mol/mol DMT ₀			
	First reactor	Second reactor	Third reactor	First reactor 180°C	Second reactor 200°C	Third reactor 220°C		Acetaldehyde × 10 ³	DEG × 10 ²	Water × 10 ²	Acid end groups × 10 ³
1	1.5	1	0.5	71.02	90.72	96.14	0.96	11.20	9.96	9.91	11.79
2	1	1	1	63.73	89.69	97.07	1.17	17.30	14.00	14.43	12.66
3	0.5	1	1.5	47.28	87.14	97.14	1.44	23.50	17.50	19.07	12.96

CONCLUSIONS

In this work we have attempted to develop a mathematical model for the continuous transesterification process. The modeling was done as close to industrial practice as possible.

It must be emphasized that the number of processing and operational variables that affect the process are many, and therefore a true optimization would be fairly involved. Additionally, a number of factors will have to be taken into account before a true optimization strategy could be evolved. For instance, it was seen earlier that increasing the number of reactors in series improves the percentage DMT conversion but also increases EG vapor flow rate and the majority of the by-products. Increased percentage conversion means a smaller cumulative reactor volume but a larger number of reactors. Furthermore, increased EG vapor flow rate requires larger energy input. Formation of fewer side products means better utilization of raw materials and improved product quality.

Thus, the overall optimization strategy will need to be such that all of the above factors are carefully incorporated. The present analysis is indicative of the directions in which industrial operations should be carried out to obtain maximum productivity and better product quality.

Nomenclature

a^v	concentration of acetaldehyde in vapor, mol/kg
DMT ₀	initial number of moles of DMT taken
e_c, e_g, e_m	concentration of acid, hydroxyl, and methyl ester end groups, respectively; superscript i indicates input concentration equiv/kg
F_i, F_o, F_v	input, output, and vapor flow rates, respectively, kg
g, g^i, g^v	concentration of ethylene glycol in output, input, and vapor, respectively, mol/kg
g^*	concentration of DEG, mol/kg
k_1-k_3	second-order rate constants, L/mol min
k_5-k_8	first-order rate constant, min ⁻¹
k_4	equilibrium constants
K_1-K_5	concentration of methanol in output, input, and vapor, respectively, mol/kg
m, m^i, m^v	molecular weight of j th species, kg/mol
M_j	total pressure, torr
P_T	vapor pressure of methanol, ethylene glycol and water, respectively, torr
P_M^*, P_G^*	vapor pressure of j th species, torr
P_W^*	initial molar ratio of EG to DMT
P_j^*	rates of formation of the respective species as shown in Table I, mol/L min
P_j^*	
R	
$R_{E_m}, R_{E_g},$	
$R_M,$	
$R_{EG},$	
$R_A,$	
$R_Z, R_{E_c},$	
$R_W,$	
R_{DEG}	
R_1-R_8	reaction rates, mol/l min
V	volume of the reaction mixture, L
w, w^i, w^v	concentration of water in output, input, and vapor, respectively, mol/kg
x_j	mole fraction of j th species in the liquid
z, z^i	concentration of diester group in output and input, respectively, equiv/kg
ρ	density of the reaction mixture, kg/L

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