

Modeling of Poly(ethylene Terephthalate) Reactors. VIII. A Modified Continuous Transesterification Process*

Recently, Ravindranath and Mashelkar¹ developed a mathematical model for a continuous transesterification process. The influence of various operating and processing variables (such as residence time distribution, temperature distribution, and the number of reactors) was investigated. In particular, their influence on the dimethyl terephthalate (DMT) conversion and the side products formation was examined critically. The mathematical model developed by us is valid only when a single fractionating column is used for all the reactors and when ethylene glycol (EG) is refluxed completely to the first reactor (see Fig. 1). This is the industrial practice in new continuous plants.² However, there appear to be a number of instances when the old semibatch plants are being converted into continuous plants where the practice differs³ (see Fig. 2). In such cases, each reactor has a separate fractionating column, and EG will be refluxed to the individual reactor immediately. We shall refer to this as the "modified process." It is obvious that these two different arrangements are likely to produce different concentration profiles, thereby changing the levels of conversion as well as those of side products formation. It is not very clear *a priori* as to what changes such difference in industrial practice should bring in, and yet the problem seems to be of immediate industrial importance. We therefore decided to extend the model built previously to answer this question. During the course of this investigation, we have also examined the influence of different process and operating variables on DMT conversion and side products formation in the modified process, since our previous work does not provide this information.

The framework of the mathematical model to be used has been described in detail by Ravindranath and Mashelkar.¹ The reactors in the train are assumed to be completely backmixed. The kinetic parameters, equilibrium constants, and the vapor pressure data for volatile components were taken from our earlier work.¹ We shall not provide the details of the mathematical model, except to state the major difference between this work and our earlier work.¹ These lie mainly in the calculation of the vapor flow rates and the composition of the reaction mixture. The vapors emerging from the fractionating column in the modified plants contain mainly methanol, water, and acetaldehyde, since EG is refluxed immediately. No reactions occur in the fractionating column. Furthermore, it is assumed that complete separation of the mixture occurs in the fractionation column. Therefore, eqs. (15), (16), (19), and (21) in Ref. 1 are now modified as follows:

$$F_i m^i - F_0 m + \rho^2 V R_M - F_0 m^{v'} = 0 \quad (1)$$

$$F_i g^i - F_0 g + \rho^2 V R_{EG} = 0 \quad (2)$$

$$F_i w^i - F_0 w + \rho^2 V R_W - F_0 w^{v'} = 0 \quad (3)$$

$$\rho^2 V R_A - F_0 a^{v'} = 0 \quad (4)$$

$m^{v'}$, $w^{v'}$, and $a^{v'}$ represent the concentration of methanol, water, and acetaldehyde in the vapor emerging from the fractionating column. Notation for all other symbols is defined in our earlier work. $m^{v'}$, $w^{v'}$ and $a^{v'}$ can be calculated from

$$m^{v'} = m^v/c \quad (5)$$

$$w^{v'} = w^v/c \quad (6)$$

$$a^{v'} = a^v/c \quad (7)$$

where

$$c = m^v M_M + w^v M_W + a^v M_A \quad (8)$$

Here m^v , w^v , and a^v represent the concentration of methanol, water, and acetaldehyde in the vapor emerging from the reaction mixture. M_M , M_W , and M_A represent the molecular weights of methanol, water, and acetaldehyde, respectively. Equations (5)–(8) are obtained from material balance considerations, when one of the components (*viz.*, EG) is removed from the vapor.

The numerical computational procedure suggested by Ravindranath and Mashelkar¹ is used for solving eqs. (13), (14), (17), (18), (19), (22)–(41) in Ref. 1 and eqs. (1)–(8) of this work.

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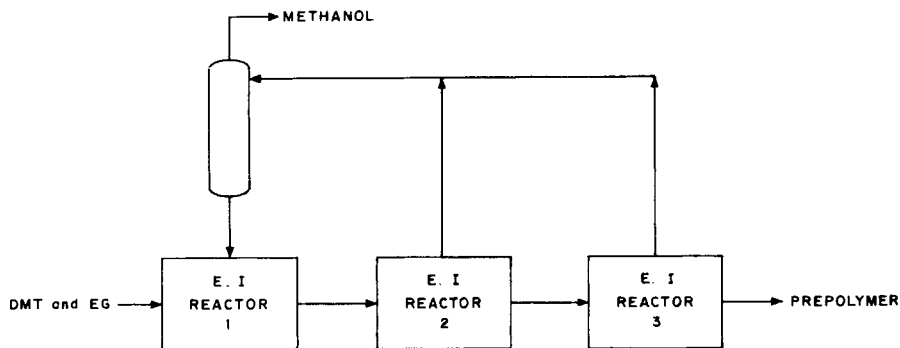


Fig. 1. Model for a continuous transesterification process.

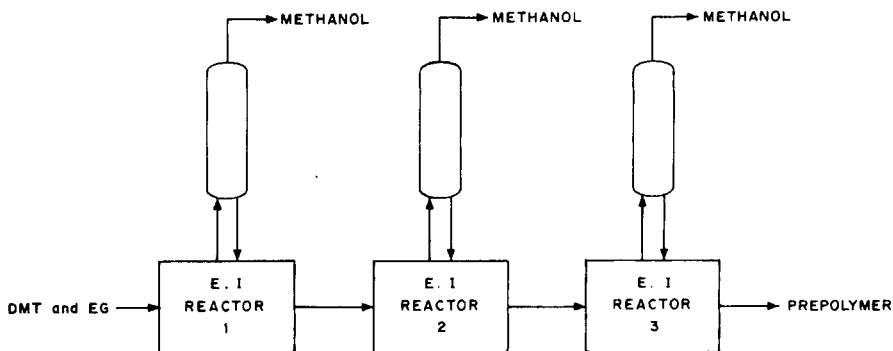


Fig. 2. Model for a modified continuous transesterification process.

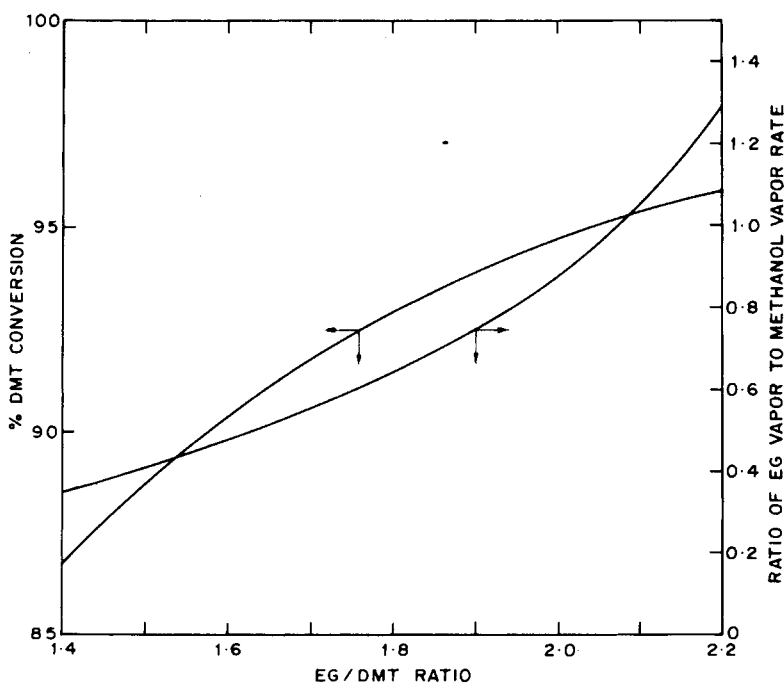


Fig. 3. Effect of EG-to-DMT ratio on DMT conversion and EG vapor-to-methanol vapor flow rate for a train of three reactors.

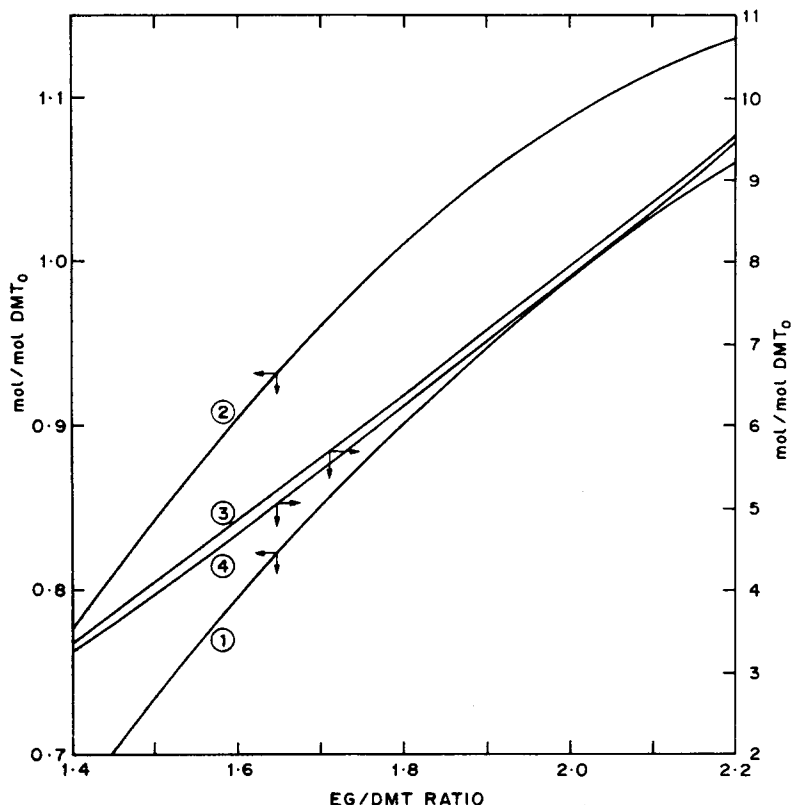


Fig. 4. Effect of EG to DMT ratio on the formation of side products for a train of three reactors: (1) acetaldehyde $\times 10^2$; (2) acid end groups $\times 10^2$; (3) DEG $\times 10^2$; (4) water $\times 10^2$.

RESULTS AND DISCUSSION

Using the mathematical model, the results are obtained for a train of three reactors. The temperatures in the three reactors have been changed discretely from 180°C to 200°C to 220°C, which appears to be close to the current industrial practice. Table I shows the results. The figures in brackets show the scheme depicted in Figure 1.

Effect of Residence Time Distribution

Three cases are considered here. Case 1 corresponds to the reduction of residence time from 1.5 to 1 to 0.5 h in successive reactors. Case 2 corresponds to equal residence times (viz., 1 h) in each of the reactors. The third case corresponds to an increase in the residence time from 0.5 to 1.0 to 1.5 h in successive reactors. Table I shows the effect of residence time distribution on DMT conversion and the side products formed. For comparison the results obtained for a single fractionating column (the case considered in Ref. 1 under otherwise identical conditions) are also shown in Table I. DMT conversion is approximately 95% for all the cases considered here compared to the value of 97% for the single fractionating column. The side products formation is found to be less for case 1 as compared to that in cases 2 and 3 (see Table I) in the modified process. Again the side products and the EG-to-methanol flow rates are less in the case of the modified process as compared to that in the previous case.¹ The model calculations therefore indicate that provision of separate fractionating columns with individual EG recycle will be advantageous in improving the product quality and reducing the input energy. However, such a provision for new continuous plants will increase the fixed capital cost, and one will have to strike a proper balance between these two opposing factors.

TABLE I
Effect of Residence Time and Temperature Distribution on DMT Conversion and on the Side Products Formed^a

No.	Residence time distribution			DMT conversion			Side products (mol/mol DMT ₀)				Ratio of EG-to-methanol flow rates
	First reactor	Second reactor	Third reactor	First reactor (180°C)	Second reactor (200°C)	Third reactor (220°C)	Acetaldehyde (× 10 ²)	DEG (× 10)	Water (× 10)	Acid end groups (× 10 ³)	
1	1.5	1.0	0.5	64.20 (71.02)	86.60 (90.72)	94.64 (96.14)	0.99 (1.12)	0.79 (0.99)	0.785 (0.99)	10.87 (11.79)	0.873 (0.96)
2	1.0	1.0	1.0	56.31 (63.73)	84.44 (89.69)	95.80 (97.07)	1.51 (1.73)	1.15 (1.40)	1.184 (1.44)	11.61 (12.66)	1.016 (1.17)
3	0.5	1.0	1.5	41.46 (47.28)	80.63 (87.14)	95.98 (97.14)	2.03 (2.35)	1.47 (1.75)	1.558 (1.91)	11.87 (12.96)	1.199 (1.44)

^a The figures in brackets refer to the scheme shown in Figure 1.

Effect of EG-to-DMT Ratio

The effect of EG-to-DMT ratio as investigated. The DMT conversion and EG-to-methanol flow rate increases as EG-to-DMT ratio increases as shown in Figure 3. Similarly the side products formation increases with an increase in EG-to DMT ratio, as shown in Figure 4. The optimum value of EG-to-DMT ratio depends on the maximum DMT conversion to be obtained and the allowable limit of side products in the product.

CONCLUSIONS

We have modeled a modified process (see Fig. 2), which is operated currently, when semibatch transesterification plants are converted to continuous transesterification plants. Our model calculations show that this procedure is marginally advantageous in terms of improving the product quality; however, the DMT conversion is shown to be reduced marginally. Although the present case refers to a transesterification process with some minor extent of polycondensation, it is instructive to remark here about a similar result reached by Teaney and Anthony,⁴ who show that, in the case of a free radical polymerization, the influence of intermediate monomer feed is that of a reduction in conversion.

References

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