Kinetics of the transesterification of dimethyl terephthalate with 1,4-butanediol

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The kinetics of transesterification of dimethyl terephthalate with 1,4-butanediol have been studied in a semi-batch reactor under non-isothermal conditions. Also, the kinetics of tetrahydrofuran production by side reactions were studied. Models were fitted by using an algorithm of parameter estimation in differential equations based on the Gauss–Newton method. It was found that the transesterification reaction had an overall order of three, with one order each for dimethyl terephthalate (DMT), 1,4-butanediol (BD) and catalyst concentration, whereas the formation of tetrahydrofuran (THF) involved reactions with fractional reaction order.

(Keywords: kinetics; transesterification; dimethyl terephthalate; 1,4-butanediol; tetrahydrofuran)

INTRODUCTION

Poly(1,4-butylene terephthalate) (PBT) is produced by polycondensation of bis(4-hydroxybutyl)terephthalate (BHBT). Although BHBT may be synthesized by both transesterification of dimethyl terephthalate (DMT) with 1,4-butanediol (BD) and by direct esterification of BD and terephthalic acid, a substantial proportion of BD converted to tetrahydrofuran (THF) during esterification makes the transesterification process preferred.

Despite the increasing importance of PBT, to our knowledge no kinetic study of transesterification of DMT with BD has been carried out. In the present work, the kinetics of transesterification of DMT with BD in a semi-batch reactor were studied taking into account the non-isothermal character of the reaction and the formation of THF by side reactions.

EXPERIMENTAL

Reactions were carried out in the apparatus presented in *Figure 1*. The system was provided with a rectification column and mechanical agitation. DMT (0.5 mol) was introduced into the reaction vessel and electrically heated until its melting point ($\simeq 140°C$), BD and catalyst titanium isopropoxide) were then added and the reaction mixture heated until the temperature reached its final value. The internal reactor temperature was continuously measured and recorded. A controlled flow of nitrogen ($120\,cm^3\,min^{-1}$) was made to flow throughout the reaction vessel to help methanol and THF removal. These two compounds were collected in a cold trap. The temperature of the effluent in the cold trap was measured to determine the amount of methanol and THF not retained in the trap. Methanol and THF collected in the cold trap were analysed by gas chromatography, using a Carbowax-400 column 2 m in length, at 50°C. A BD/DMT ratio of 2:1 and $Ti[OCH(CH_3)_2]_4$ 0.009% w/w DMT as catalyst were used throughout the work.

RESULTS

The effect of temperature on the rates of production of BHBT, measured as methanol withdrawn from the reactor, and THF is presented in *Figure 2*. An increase in temperature led to increased production of methanol and THF. It is worth noting that both the methanol and THF data presented in *Figure 2* included a correction due to

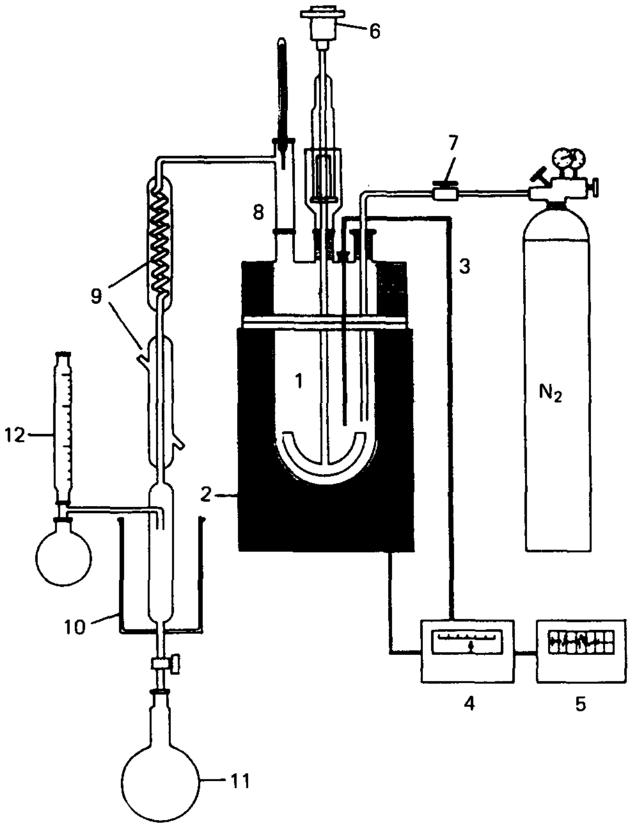

Figure 1 Reaction equipment. 1, Reactor ($500\,cm^3$); 2, heater; 3, thermocouple; 4, temperature controller; 5, recorder; 6, stirrer; 7, needle valve; 8, rectification column; 9, condenser; 10, cold trap; 11, collecting vessel; 12, soap-bubble flow meter

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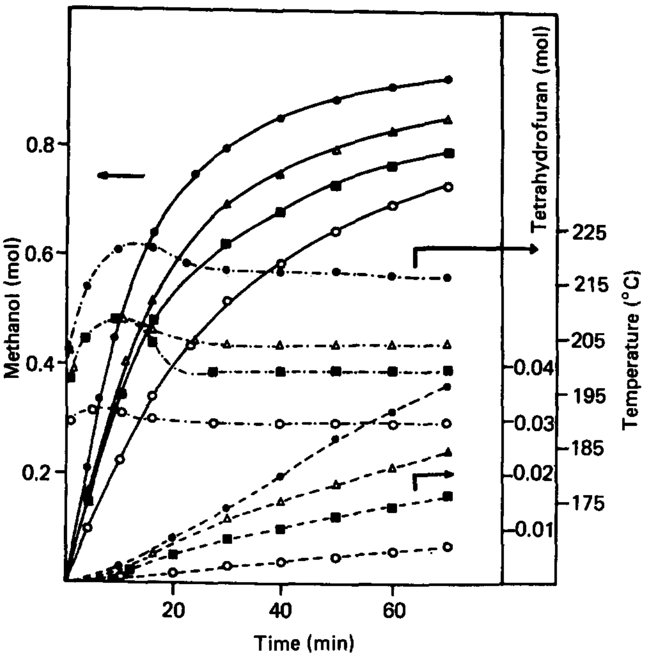


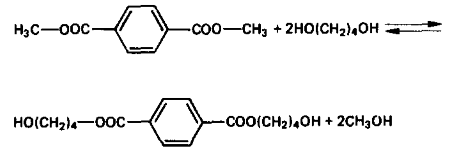
Figure 2 Effect of the temperature profile (—·—·—) on the rates of production of methanol (———) and THF (– – –) (DMT = 0.5 mol; BD/DMT = 2:1; titanium isopropoxide: 0.009% w/w DMT). ○, ■, △, ●: different temperature profiles

methanol and THF not retained in the cold trap. *Figure 2* shows that most of the reaction was carried out under non-isothermal conditions and the temperature reached a constant value only after about 20 min.

KINETIC ANALYSIS

Material balance

Transesterification reaction may be represented by the equation:



(1)

This reaction is always accompanied by the formation of THF. This compound may be formed by both BD dehydration catalysed by acid groups and from hydroxybutyl end-groups[1,2].

$$\mathrm{HO(CH_2)_4OH} \xrightarrow{\mathrm{—COOH}} \mathrm{THF + H_2O} \tag{2}$$

$$\mathrm{—COO(CH_2)_4OH} \longrightarrow \mathrm{—COOH + THF} \tag{3}$$

The whole set of reactions may be written in terms of participating functional groups:

$$\mathrm{E_m + BD \xrightarrow{k_1} E_g + M} \tag{4}$$

$$\mathrm{BD \xrightarrow[E_a]{k_2} THF + H_2O} \tag{5}$$

$$\mathrm{E_g \xrightarrow{k_3} THF + E_a} \tag{6}$$

where $\mathrm{E_m}$ = —$\mathrm{COOCH_3}$, the methyl ester end group; $\mathrm{E_g}$ = —$\mathrm{COO(CH_2)_4OH}$, the 4-hydroxybutyl ester end group; M = methanol and $\mathrm{E_a}$ = —COOH, the carboxyl end group.

The following assumptions were made in writing the material balance: methanol and THF were removed from the reactor as soon as they were formed; BD was not withdrawn from the reactor; the reactor volume changed continuously during the reaction; the reactor was well mixed; and reaction rates were first-order with respect to participating functional groups and catalytic species.

According to these assumptions the material balances were:

$$(1/V)\cdot(\mathrm{d}e_\mathrm{m}/\mathrm{d}t) = -k_1(c/V)\cdot(e_\mathrm{m}/V)\cdot(2b/V) \tag{7}$$

$$(1/V)\cdot(\mathrm{d}e_\mathrm{g}/\mathrm{d}t) = k_1(c/V)\cdot(e_\mathrm{m}/V)\cdot(2b/V) - k_3(e_\mathrm{g}/V) \tag{8}$$

$$(1/V)\cdot(\mathrm{d}b/\mathrm{d}t) = -k_1(c/V)\cdot(e_\mathrm{m}/V)\cdot(2b/V) - k_2(e_\mathrm{a}/V)\cdot(b/V) \tag{9}$$

$$m = e_{\mathrm{m}0} - e_\mathrm{m} \tag{10}$$

$$e_\mathrm{a} = e_\mathrm{m} - e_{\mathrm{m}0} - e_\mathrm{g} \tag{11}$$

$$\mathrm{THF} = b_0 - b - e_\mathrm{g} \tag{12}$$

where e_m, e_g, e_a, b and m are the number of moles of $\mathrm{E_m}$, $\mathrm{E_g}$, BD and M, respectively; the subscript 0 refers to initial conditions; c is moles of catalyst and V the reactor volume given by:

$$V = V_\mathrm{DMT}e_{\mathrm{m}0}/2 + V_\mathrm{BD}b_0 - V_\mathrm{M}m - V_\mathrm{THF}\mathrm{THF} \tag{13}$$

where V_i is the molar volume of compound i.

PARAMETER ESTIMATION

Parameter estimation was carried out by means of an extended Gauss–Newton method proposed by Hwang and Seinfeld[3] for ordinary differential equations. In order to achieve convergence, reparametrization was used to write the parameters in an equivalent mathematical form, but with different parameters:

$$k_i = k_{i0}\cdot\exp(-E_i/RT) = k_i^*\cdot\exp[-E_i(1/T - 1/T^*)/R] \tag{14}$$

where T^* is the mean temperature of all experiments and k_i^* is given by:

$$k_i^* = k_{i0}\cdot\exp[-E_i/RT] \tag{15}$$

The approximate confidence intervals of the estimates were calculated by:

$$k_i \pm t(n-p,\ 1-\alpha/2)\cdot S(k_i) \tag{16}$$

where n is the number of experimental points, p the number of parameters, $t(n-p, 1-\alpha/2)$ the $\alpha/2$ percentage point of the t-distribution with $n-p$ degrees of freedom; and $S(k_i)$ the square root of the ith diagonal element of the covariance matrix of estimates[4,5]. All the experimental points ($\simeq 70$) were analysed together.

Once the parameter estimation had been carried out, good agreement between experimental methanol data and the predictions of the model was observed. *Figure 3* shows that, in agreement with experimental results, the model predicted increasing production of THF with

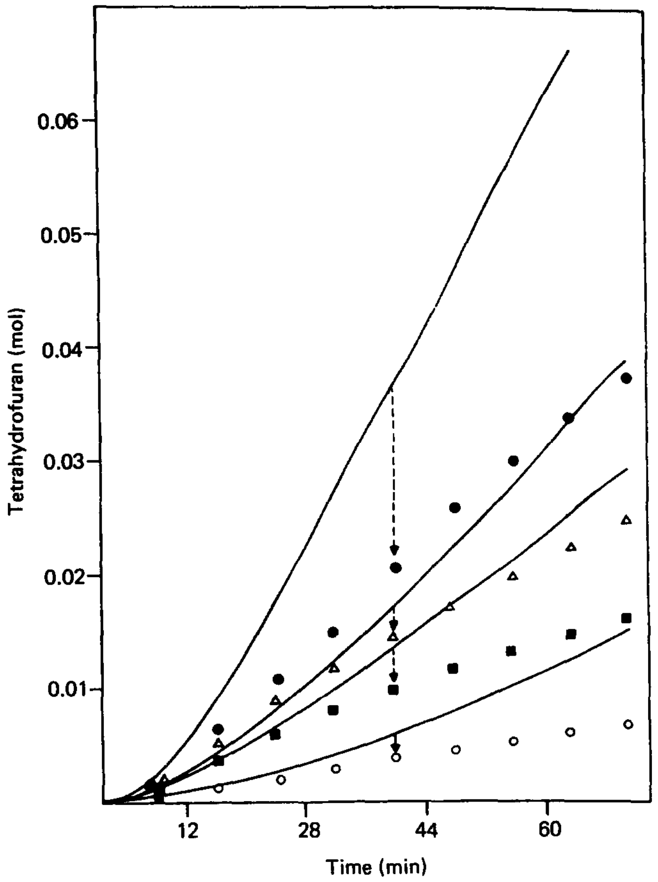


Figure 3 Comparison between THF experimental data obtained for the temperature profiles of *Figure 2* and the predictions of the model (———) including first order with respect to E_g groups. Same legend as *Figure 2*

increasing temperature. However, much higher THF values than the experimental ones were obtained. These results suggest that the reaction order with respect to E_g groups should be smaller than one. Therefore, equation (8) was modified to:

$$(1/V)\cdot(de_g/dt)=k_1(c/V)\cdot(e_m/V)\cdot(2b/V)-k_3(e_g/V)^h \quad (17)$$

Parameter estimations with different values of h were carried out and the $\chi 2$ test[6] was used to discriminate between models. It was found that values of h ranging between 0.15 and 0.35 were statistically equivalent (95% probability). However, $h=0.25$ was retained because it gave the smallest sum of square of error. The rate constants obtained with $h=0.25$ were:

$$k_1^*=0.38\times10^2\pm0.82\times10^{-1}\ (\mathrm{l^2\,mol^{-2}\,min^{-1}})$$

$$k_2^*=0.20\times10^{-5}\pm0.51\times10^{-6}\ (\mathrm{l\,mol^{-1}\,min^{-1}})$$

$$k_3^*=0.11\times10^{-4}\pm0.33\times10^{-3}\ (\mathrm{mol^{0.75}\,l^{-0.75}\,min^{-1}})$$

Figures 4 and *5* show that good agreement between experimental data and model predictions were obtained by using these parameters.

CONCLUSIONS

It has been shown that the reaction rate of the transesterification of DMT with BD had an overall order of three, with one order each for DMT, BD and catalyst concentration. Also it was found that production of THF could be explained through a model including the formation of THF by both BD dehydration catalysed by acid groups and from hydroxybutyl end-groups. A fractional reaction order was found for the last reaction.

NOMENCLATURE

BD	1,4-butanediol
BHBT	bis(4-hydroxybutyl)terephthalate
b	amount of 1,4-butanediol (mol)

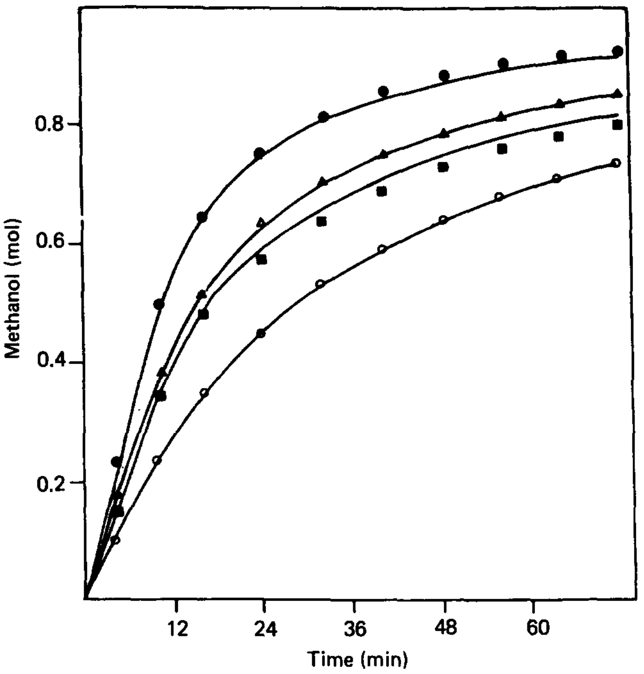


Figure 4 Comparison between methanol experimental data obtained for the temperature profiles of *Figure 2* and the model predictions (———) with $h=0.25$. Same legend as *Figure 2*

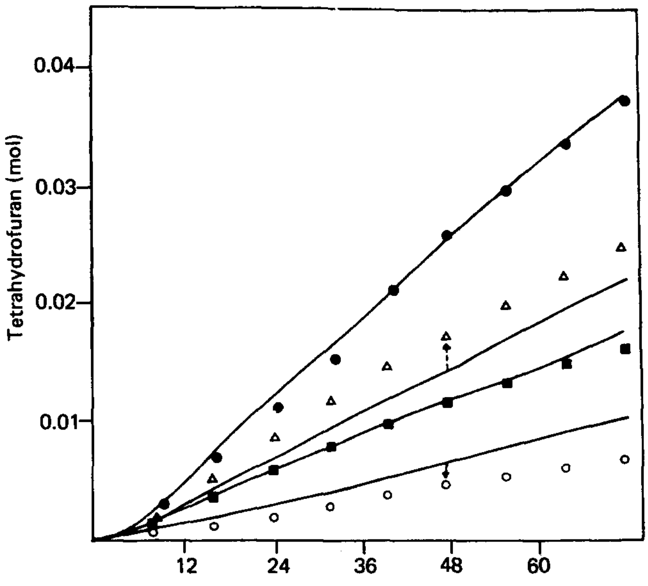


Figure 5 Fit of THF experimental data obtained for the temperature profiles of *Figure 2* by the model including a reaction order with $E_g=0.25$. Same legend as *Figure 2*

c	catalyst content in the reactor (mol)
DMT	dimethyl terephthalate
E_a	carboxyl end-group, $-COOH$
E_g	4-hydroxybutyl ester end-group, $-COO(CH_2)_4OH$
E_m	methyl ester end-group, $-COOCH_3$
E_i	activation energy of reaction i (cal mol^{-1})
e_a	amount of carboxyl end-group (mol)
e_g	amount of 4-hydroxybutyl ester end-group (mol)
e_m	amount of methyl ester end-group (mol)
h	reaction order with respect to E_g groups
k_i	rate constant of reaction i
k_i^*	reparametrizated rate constant of reaction i
k_{i0}	frequency factor of reaction i
M	methanol
m	amount of methanol (mol)
n	number of experimental points
PBT	poly(1,4-butylene terephthalate)
R	gas constant
T	reactor temperature (K)
T^*	mean temperature (K)
THF	tetrahydrofuran
V	reactor volume
V_i	molar volume of compound i

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