Study on kinetics of polymerization of dimer fatty acids with ethylenediamine in the presence of catalyst

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Abstract

A generally applicable stoichiometric and kinetic model was developed for the polymerization of dimer fatty acids with ethylenediamine in the presence of phosphoric acid as catalyst. Rate equation used is based on second order and the temperatures are between 405 and 475 K with mixing rate of 75 rpm. The parameters of the rate equations are determined using nonlinear regression analysis. Comparison of the model predictions with the experimental data show that the approach is useful in predicting the polymerization kinetic. Equilibrium constant changes from 2.432 to 17.765. Frequency factor and activation energy for forward rate constant are 362306102.681 $kg\,mol^{-1}\,min^{-1}$ and 83.24 $kJ\,mol^{-1}$, respectively. The equilibrium constant is independent of temperature with frequency factor and activation energy values of 17317.97 and 28.65 $kJ\,mol^{-1}$, respectively.
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1. Introduction

Dimer fatty acids have been traditionally used to synthesize and formulate hot-melt adhesives, flexographic inks, functional coatings, and other engineering materials [1]. Kale et al. [2] studied the kinetics of the reaction between ethylenediamine and dimeric fatty acids in melt phase in the temperature range of 399–465 K and found that reaction was second order with activation energy of 76.44 $kJ\,mol^{-1}$ for conversion of up to 90%. For higher conversion the reaction was overall third order with an activation energy of 68.88 $kJ\,mol^{-1}$. In another work Kale et al. [3] carried out a kinetic study on the reaction between C_{36} dimer acids and diethylenetriamine and triethylenetetramine in the temperatures range between 420 and 465 K and found that reactions followed overall second order kinetics with activation energies of 60.8 and 51.7 $kJ\,mol^{-1}$, respectively. These polyamides are known as reactive polyamides because they can be crosslinked with other resins such as epoxy resins and they are not linear.

To assist the condensation reaction, a catalyst, such as phosphoric acid, may be added to the reaction mixture [4]

in catalytic proportion. The catalyst employed in the condensation reaction may be charged to the reaction mixture either at the beginning of the reaction or added slowly just prior to the point at which the reaction rate slowing. The preferred concentration of the catalyst is within the range of 0.001–3 wt.% and more preferably from about 0.01–1.0% by weight of the total materials charged [4].

In industry, the water produced during reaction should be purged out to minimize reverse reaction. Besides, evaporation of ethylenediamine during reaction is another important factor that need to be considered [5] because if the evaporation becomes high, the loss in ethylenediamine will cause imbalance in acid and amine values and this will affect the final product. To obtain the reverse rate constant and the amount of evaporation with temperature and time, an appropriate model is needed.

All the above study however did not consider the catalytic reaction and evaporation of diamine during reaction in the presence of catalyst. Besides, water that evaporated during reaction was not modeled and the reverse reaction was not cognized.

In this work, kinetics of polyamidation reaction of ethylenediamine and dimer fatty acid in the presence of catalyst is modeled using MATLAB, EXCEL, and EASY-FIT softwares and the results generated are compared with the experimental data. The study also includes reverse reaction and evaporation of water and amine. The same

Nomenclature

A_E	frequency factor ($kg\,mol^{-1}\,min^{-1}$)
$A–E$	empirical parameters
$A_1, B_1, C_1, D_1,$	the temperature dependency of
A_2, B_2, C_2, D_2	empirical parameters
c_i'	the concentration in the distillate ($mol\,kg^{-1}$)
C_i	concentration ($mol\,kg^{-1}$)
E_{aE}	activation energy ($kJ\,mol^{-1}$)
e_1	sum of residual squares
k	rate constant: ($kg\,mol^{-1}\,min^{-1}$)
K	equilibrium constant
m'	distillate mass (kg)
$\dot{m}'$	distillate mass flow (kg/min^{-1})
m_0	total mass (initial) (kg)
M	molar mass ($kg\,mol^{-1}$)
n	amount of substance (mol)
$\dot{n}$	flow of substance (mol/min^{-1})
r	generation rate of a functional group ($mol\,kg^{-1}\,min^{-1}$)
r'	generation rate of an analytical quantity ($mol/kg\,min^{-1}$)
R	gas constant
t	time (min)
T	temperature (K)
w	dimensionless weight fraction
Z	dimensionless mass of distillate

Subscripts and superscripts

i	component index
j	time index

Greek letters

ρ	liquid density

model used for noncatalytic reaction in our previous work [6].

1.1. Mathematical model of the polyamidation stage

Reactor model for the kinetics was based on work of Juha et al. [7] for polyesters.

In the derivation of reactor model, some fundamental assumptions were introduced. The liquid phase in the reactor was presumed to be basically in batch, however some volatilization of the compounds, particularly water and diamine, was assumed to take place. The reaction rates were described with respect to the mass of the liquid—not with respect to volume, as traditionally done. However, the rates used in the present work (r_i) are related to the volume-based rates (r_i') by $r_i' = r_i \rho$, where ρ is the liquid density. The analytical concentrations of carboxylic groups, and amount of distillate were measured during the reaction.

Based on these assumptions, the mass balance for a component (i) in the liquid phase can be written as follows:

$$r_i m = n_i' + \frac{dn_i}{dt} \tag{1}$$

where m is the mass of the liquid phase and n_i' is the amount of substance leaving the reactor in the gas phase in the distillate. This amount of substance is expressed with the mass of liquid and the concentration,

$$n_i = c_i m \tag{2}$$

After differentiation of n_i with time and rearrangement, the mass balance is transformed to

$$\frac{dc_i}{dt} = r_i - \frac{c_i}{m}\left(\frac{dm}{dt}\right) - \frac{n_i'}{m} \tag{3}$$

The flow leaving the reactor is expressed as the concentration in the distillate (c_i') and the distillate mass flow ($\dot{m}'$):

$$\dot{n}_i = c_i' \dot{m}' \tag{4}$$

For the mass remaining in the reactor (m) and in the distillate (m'), the total balance is applied

$$m + m' = m_0 \tag{5}$$

where m_0 is the total (initial) mass. For the distillate collected, the total mass balance is given by

$$\dot{m}' = \frac{dm'}{dt} \tag{6}$$

Since the total mass (m_0) is constant and the discrete sampling method is carried out, differentiation of Eq. (5) gives the simple relation

$$\frac{dm}{dt} + \frac{dm'}{dt} = 0 \tag{7}$$

Relation (7) is emphasized in the definition of $\dot{n}_{ii}$, Eq. (4), after which the expression for $\dot{n}_i$

$$\dot{n}_i = c_i' \frac{dm'}{dt} \tag{8}$$

is included in the mass balance (3), which becomes

$$\frac{dc_i}{dt} = r_i + \frac{c_i - c_i'}{m}\frac{dm'}{dt} \tag{9}$$

The total mass balance (9) is divided by m_0, which gives for m

$$\frac{m}{m_0} = 1 - \frac{m'}{m_0} \tag{10}$$

The following dimensionless quantities are introduced:

$$Z = \frac{m'}{m_0} \tag{11}$$

After inserting (10) and (11) in Eq. (9), the final form of the mass balance is obtained:

$$\frac{dc_i}{dt} = r_i + \frac{c_i - c_i'}{1 - Z}\frac{dZ}{dt} \tag{12}$$

This approach would in principle be applicable also for the cumulative mass of distillate (Z). It turned out, however, that an efficient way to describe the time evaluation of the distillate is to fit an empirical model to the experimental data. The function for Z was chosen to [7]:

$$Z = A(1 - e^{-Bt}) \qquad (13)$$

The empirical parameters A and B were assumed to have the following temperature dependencies: $A = A_1 T + A_2$ and $B = B_1 e^{B_2 T}$. The distillate was analyzed chemically, i.e., the weight fractions (w_i) of water and diamine in the distillate were obtained. The concentrations c_i' were calculated from the experimentally observed weight fractions (w_i) and the molar masses (M_i):

$$c_i' = \frac{w_i}{M_i} \qquad (14)$$

The only components of global importance in the distillate were water and diamine. For the weight fraction of diamine the following empirical function was introduced:

$$w_{NH_2} = Ce^{-Dt} + E \qquad (15)$$

Where the parameters C–E have the following temperature dependence: $C = C_1 T + C_2$, $D = D_1 T + D_2$ and $E = E_1 T + E_2$. The water weight fraction can be calculated as follows:

$$w_{H_2O} = 1 - w_{NH_2} \qquad (16)$$

The parameters included in Eqs. (13) and (15) were determined simultaneously from the experiments using nonlinear regression analysis. The objective function was minimized using the EXCEL solver (2002). The solver option is based on reduced gradient method (GRG).

The equation for rate of reaction for amine and acid is as follow:

$$r_i = k_1 C_{COOH} C_{NH_2} - k_2 C_{CONH} C_{H_2O} \qquad (17)$$

and for water the right hand side should multiply by -1.

Eq. (17) is applied based on second order reaction. C_{COOH}, C_{NH_2}, C_{CONH}, and C_{H_2O} are concentrations of acid, amine, linkage (reacted acid and amine), and water respectively. The amount of water and diamine condensed is used in the empirical equations, the empirical constants are estimated from these data. These empirical equations were then used in Eq. (3) which consists of four equations. i.e. acid, amine, water and polymer for estimation of rate constants. The estimation is based on acid concentration of experimental data which means that the equations also include water and amine concentration because it contains in the empirical equations. The estimation of the rate parameters was performed in stage wise. The mass balances were solved numerically during the objective function minimization with the Runge–Kutta method available in EASY-FIT software [8] and simultaneously SQP-based Gauss-Newton/Quasi Newton method was used for optimization that is also available in the software. By comparing

these data to the experimental data, the rate constants for forward and reverse reaction can be obtained. The objective function was minimization of:

$$e_1 = \sum (COOH_{j,cal} - COOH_{j,exp})^2 \qquad (18)$$

For polyesters as shown in reference [7] the exponential empirical equations give good fit with the experimental data. This means that the stream of condensate with time that leaves the reactor have exponential relation with time, this means that, at first, it will increase with time and then approaches constant value. This is because initially, the concentrations of reactants are high, hence reaction rate is high and so the rate of production of water is high. However, after sometimes, the rate of production of water will become low. For fatty polyamides, almost similar behavior is predicted.

For polyesters, with the above mentioned exponential empirical equation the reverse rate constant could be easily measured, in our case, before the experiment is performed it is not possible to know how much water will come out from reactor and how much will remain inside the reactor to determine the reverse rate constant. In addition it is not known that the condensate that came out from reactor obeys exponential equations or not, and this includes the weight fraction of evaporated monomer in the stream of condensate. The same problem existed about evaporated monomer, since it is not known how much will evaporate and whether the evaporated monomer obeys the same trend as polyesters. Because it involves high temperature of reaction (more than boiling point of monomer).

The parameters of the empirical Eqs. (12), (13) and (15) for each experiment, k_1, k_2, A–E were estimated. It is likely that the parameters are correlated, so for each experiment statistical correlation analysis between A and B, between C–E was performed. For obtaining correlation between parameters the TableCurve 2D Version 5 software is used, it has nonlinear Robust fitting technique [9] and the software generated the covariance matrix for estimated parameters for curve fitting, using these covariance matrix the correlation between parameters are obtained using the following formula:

$$\text{correlation}\,(a, b) = \frac{\text{covariance}\,(a, b)}{[\text{variance}\,(a) \times \text{variance}\,(b)]^{1/2}} \qquad (19)$$

In the above formula, a and b are the empirical parameters that been obtained from the curve fitting, the correlation between them is obtained using the above formula. The same software used for obtaining 95% confidence intervals for estimated empirical parameters, and for rate constants the Easy-Fit software is used for obtaining 95% confidence intervals.

2. Experimental

2.1. Materials

Dimer fatty acid (PRIPOL 1013 From Uniqema, Netherlands) with 97% purity (monomer 0.1%, dimmer 97%, and trimer 3%) and acid value of 195 was used. Ethylenediamine was of laboratory reagent grade having purity of above 98% as determined by titration with standard acid. Ortho-phosphoric acid was also of laboratory reagent grade with 85% purity. All other materials used were of reagent grade.

2.2. Method

The experimental set up as shown in Fig. 1 consists of a 1.5 l stainless steel reactor, equipped with a variable stirrer, nitrogen inlet tube and connected to two condensers. A cooling coil was placed inside reactor, and the reactor temperature was controlled using an automatic temperature controller. The equipment is connected to a computer for monitoring the variation of temperature and motor speed with time. In a typical operation, 240 g of dimeric fatty acids was charged into the reactor and 1% by weight of phosphoric acid based on total stoichiometric amount of monomers added to it and heated 10 K below the desired temperature. An extra molar amount of ethylenediamine (based on mole of dimmer fatty acid) was preheated to 391 K and added to the reactor. Extra amine was used to compensate the amount evaporated during the preheating process. The amount of ethylenediamine charged at each temperature is given in Table 1 and it can be calculated from initial amine numbers. The stirring speed was set at 75 rpm (rotation per minute). Low mixing rate was used to prevent the occurrence of foaming. The reaction was carried out at five different temperatures in the range of 405–465 K. Within this range the materials remain in molten state. The water generated during the reaction and evaporated diamine were purged out of the reactor using nitrogen at a rate of 20 ml min^{-1}. These materials were later condensed and collected in a prepared container for analysis. The temperature of the condenser cooling water was kept at 279 K. The amount of distillate collected with time was measured, and the sample refractometery index was analyzed using a refractometer (model NAR-1T). Before that a calibration curve was established by measuring several samples of known weight fraction of ethylenediamine in water. The weight fraction of ethylenediamine in the condensate was measured based on the established calibration curve.

Several samples were taken out of the reactor via the sampling port at several intervals for analysis of acid and amine
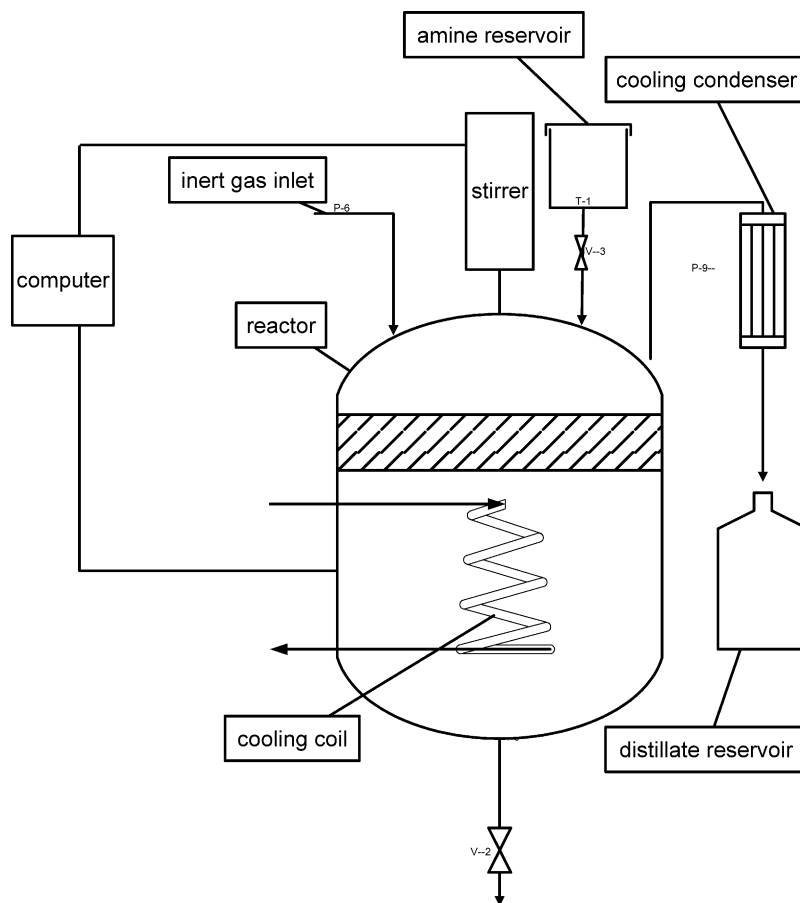

Fig. 1. Diagram for melt polymerization of fatty polyamides.

Table 1
Empirical parameters for the distillates and 95% confidence interval for them (Eqs. (13)–(15))

T (K)	A	95% confidence interval for A	B	95% confidence interval for B	C	95% confidence interval for C	D	95% confidence interval for D	E	95% confidence interval for E
405	0.026536	0.0211430–0.0319298	–	–	0.451932	0.306614–0.597250	0.018111	0.000655–0.035567	0.547793	0.422891–0.672695
420	0.017014	0.0147726–0.0192546	–	–	0.685223	0.099551–1.270895	0.342231	−2.256679–2.941140	0.314777	0.021931–0.607623
435	0.051534	0.043933–0.059135	0.051461	0.017401–0.085521	0.624457	−0.061207–1.310121	0.623231	−55.23088–56.477345	0.375543	0.032711–0.718375
450	0.054995	0.051623–0.058367	0.137821	0.086034–0.189608	0.621654	0.374311–0.868999	0.149542	−0.025845–0.324929	0.378342	0.266633–0.490051
475	0.115608	0.113883–0.117333	0.349627	0.265192–0.434062	0.954555	−3.192942–5.102052	0.186976	−2.530231–2.904182	0.045445	−2.360900–2.451790

values. The acid value was determined based on ASTM D-1980–67 using a neutral solution (1:1 v/v) of *n*-butanol and xylene for dissolving the samples. The amine value was determined using ASTM D-2074-62T using the same solvent as for determining the acid value.

3. Results and discussion

3.1. Modeling of the distillate

Obtaining a good model for the polymerization of fatty polyamides in the presence of catalyst that gives good fit of the experimental data, and from which forward and reverse rate constants and evaporation of ethylenediamine at any temperature can be obtained, and also the reversibility of reaction can be verified is very useful in manufacturing of these fatty polyamides, and this is the aim of this research. Fig. 2 shows the change in the amine values against time at different temperatures. For all the temperatures, the significant decrease of ethylenediamine at the initial part of reaction could be attributed to evaporation and high rate of reaction. It was observed that at each temperature at the initial stage of the reaction, some evaporated ethylenediamine, did not condensed, even though two condensers were used. However, for water it can be easily condensed, so to measure the total amount of evaporated ethylenediamine, the samples were drawn out of the reactor to be analyzed for the amine and acid values, based on that, the amount of evaporated amine was obtained [6].

An example of dimensionless mass of distillate (Z), the weight fraction of the ethylenediamine (w_{NH_2}) and the fit of a model for 435 K are shown in Figs. 3 and 4, respectively. The general conclusion is that the exponential function applied is suitable for the description of the amount of distillate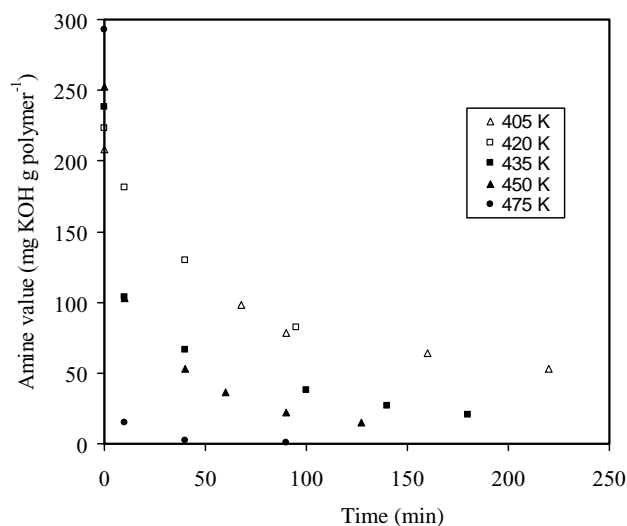, and the weight fraction of diamine in the stream of condensate. As it can be seen from Fig. 3, the amount of distillate initially increases rapidly and then it becomes constant. This is attributed to the high reaction rate at the beginning due to high concentration of reactants, thus releasing a lot of water. From Fig. 4, it is observed that at the beginning, the weight fraction of diamine is high, however, after a period of time the weight fraction becomes low and this could be due to the fact that, evaporation of excess free amine at the beginning of reaction as compared to the later part of the reaction. Juha et al. [7] concluded that, for polyesters the analytical data are less accurate to measure the composition of distillate. In some cases, at the end of reaction the weight fraction approaches zero, but exponential equation does not approach to zero. The evaporation at the end of reaction is not affective on the model, because at this time interval the flow of stream of condensate is almost zero, thus weight fraction will not affect the model, and this fact can be seen in Fig. 3 after 50 min. The weight fraction of evaporated monomer in stream of condensate have exponential relation with time because at the beginning all of condensate is amine so $w = 1$. However, after sometimes because of production of water, weight fraction will reduce and for polyesters it decreases exponentially to a constant value. For fatty polyamides, because of salt formation it will decrease exponentially but it approaches to zero as explained above.
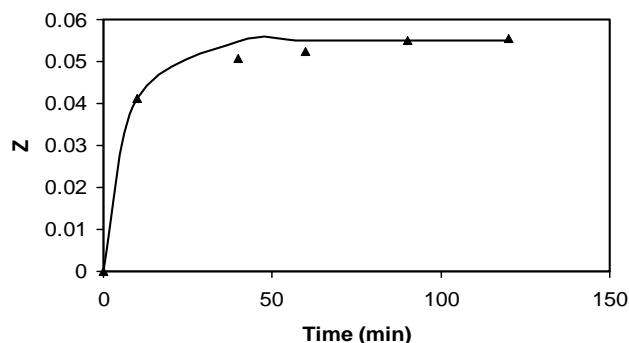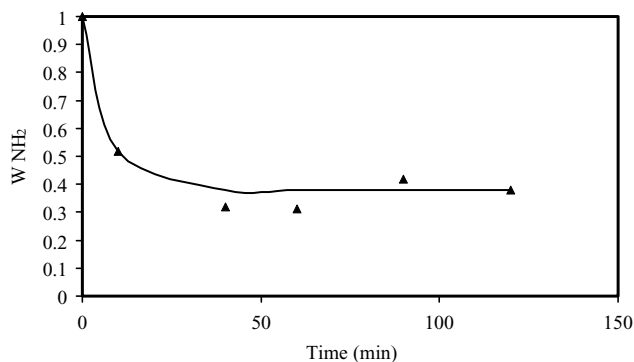

Fig. 3. Amount of produced condensate with time at 450 K, solid line predicted and (▲) are calculated with experimental.

Fig. 2. Amine values with time for different temperatures.

Fig. 4. Weight fraction of ethylenediamine w_{NH_2} with time in stream of distillate at 450 K, solid line predicted and (▲) are experimental.

A list of the empirical parameters is given in Table 1 which shows that by increasing the temperature, A and B also increase and this is attributed to higher rate of evaporation of both diamine and water at higher temperatures and also because of more initial ethylenediamine at higher temperatures For *C–E* with increasing temperature there is a fluctuation. For the temperatures of 405 and 420, $A = B$ and this is due to results of statistical correlation analysis because it was found that they are correlated as will be explained later. The empirical parameter A decrease from 405 to 420 K because at 405 K the rate of reaction is very low and there is more free ethylenediamine for evaporation at the beginning so *A* and *B* at this temperature are more than *A* and *B* at 420 K, but above this temperature, *A* and *B* increases as expected. The same results obtained for non catalytic reaction [6]. The same Table shows the 95% confidence intervals for estimated parameters. The results show that, except the temperature 435 K for *D* the confidence intervals are narrow and this indicates good fit between experimental data and empirical equations. At 435 K, because the distribution of experimental data which is a bit far from the model curve for weight fraction of amine in stream of distillate the confidence interval for *D* is not narrow.

In general the results indicate that, the experimental data and the model show a good agreement and the empirical functions used are sufficient to correct the liquid phase mass balance. The evaporation of amine and water are directly related to geometry of reactor. At the beginning of reaction some ethylenediamine will evaporate due to temperature difference between temperature of reaction and boiling point of amine and this evaporation is directly related to the surface area of reaction mass which is related to geometry of reaction, also large surface area will cause more evaporation of water. The change in the geometry will affect on the empirical equations. Besides the removal of the water from the reactor free space using N_2 will affect the reaction. In this work, N_2 bubbling inside reaction mass was not used in order to measure the reversibility of reaction due to water presence in the reaction mass.

Table 2 shows the statistical correlation analysis between *A* and *B* and also between *C–E* for different temperatures. For temperatures of 405 and 420 K, $A = B$, and number of empirical parameters for *Z* equation will reduce from two parameters to one because the results of statistical correlation analysis showed that they are correlated. Results show that, there is a weak negative correlation between *A* and *B* in
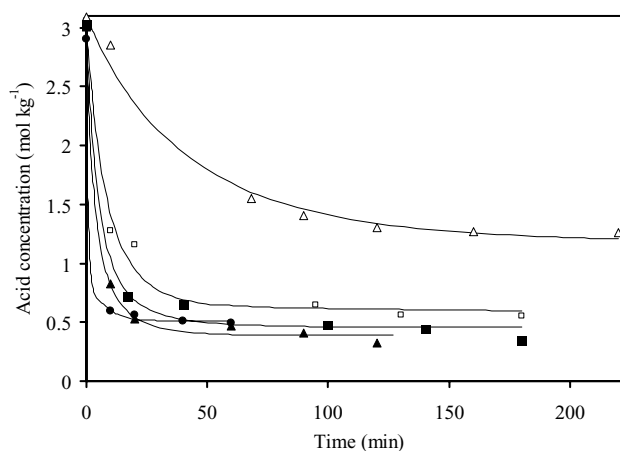

Fig. 5. Concentration of the carboxylic acid with time. The continuous lines represent the complete kinetic model: 405 K(△); 420 K (□); 435 K (■); 450 K (▲); 475 K (●).

all temperatures, because the correlation constant is almost greater than -0.57 and they are not near -1. For *C* and *D* the correlation is also negative and greater than -0.42 so again the correlation between them is weak. For *C* and *E* the correlation is negative, except 405 K the correlation is not strong and also at 405 K it is not considerable. In the same way, for *D* and *E* the correlation is positive and except 405 K which is not so considerable the correlation is weak and less than 0.52 which is far from 1.

The fit for the change in acid concentration with time is presented in Fig. 5 and it shows that, the rate of reaction is strongly influenced by the reaction temperature. For the acid values, since evaporation did not take place, the decrease in the acid value comparison to amine is marginal. The results also indicate the reaction obeys the model well. The acid and amine values are nearly the same at the later stage and this indicates the correct amounts of extra amine have been added to compensate the evaporated amount at the beginning. At 475 K due to high evaporation rate of amine and high rate of reaction the amine was almost completely consumed in less than 10 min, thus almost terminating the reaction. Fig. 6 shows the change in amine concentration at 475 K and it also obeys the model. For amine concentrations similar results are obtained for other temperatures. Fig. 7 shows the variation in the concentration of water with time that remains inside the reactor and it reveals that, the concentration reaches a constant value after sometime and

Table 2
The statistical correlation analysis between empirical parameters

T (K)	Correlation between *A* and *B*	Correlation between *C* and *D*	Correlation between *C* and *E*	Correlation between *D* and *E*
405	–	−0.4188451577	−0.7235702745	0.812930372829
420	–	−0.2190726616	−0.5000156514	0.487482381
435	−0.5246072430	−0.2481562641	−0.4999998031	0.49926242546
450	−0.3826537076	−0.0122158876	−0.4480574043	0.37678600745
475	−0.5655707704	−0.1937366201	−0.5792210409	0.51789624906

Table 3
The kinetic value of the rate constants and equilibrium constants and 95% confidence intervals for rate constants

T (K)	k_1 (kg mol^{-1} min^{-1})	95% Confidence interval for k_1	k_2 (kg mol^{-1} min^{-1})	95% Confidence interval for k_2	Absolute deviation percentage	K_E
405	0.0043499183	0.002983314–0.005910205	0.0017885284	$-0.1974382 \times 10^{-3}$ to 0.003475324	1.77	2.432
420	0.027150420	0.01651953–0.03778131	0.0046377233	0.6490792×10^{-3} to 0.008626367	6.47	5.854
435	0.044401941	0.01737479–0.07142910	0.0076882096	0.41942×10^{-4} to 0.01533448	5.27	5.775
450	0.062853302	0.05192357–0.07378303	0.0035380525	0.002080379 to 0.004995727	3.37	17.765
475	0.23887297	-0.04573171–0.5234777	0.033338116	-0.01814006 to 0.08481630	1.25	7.165

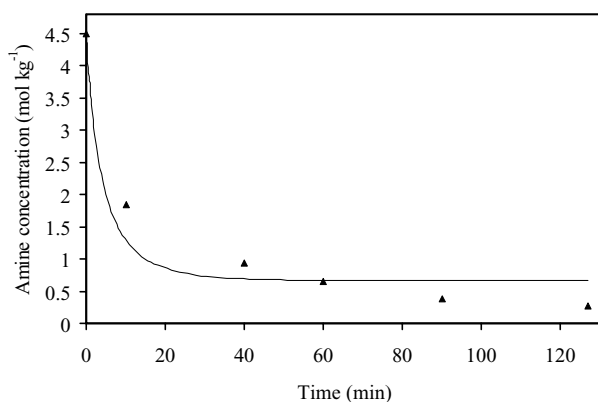

Fig. 6. Experimental and predicted concentrations of the amine groups at 450 K, solid line predicted and (▲) are experimental.

Fig. 7. Simulated liquid phase concentration of water at 435 K.

that is attributed to lower rate of production of water due to lower concentration of reactants at the end part of reaction. The numerical values of the rate constants for forward and reverse rate constants and equilibrium constant are given in Table 3. The results indicate that, reverse rate constant and forward rate constant increase with increasing temperature as expected, except for 435 K which reverse rate constant shows slight deviation, however the absolute percentage of deviation of each of them is below 6.47%, which means the deviation from experimental value is marginal. In comparison to non catalytic reaction [2 and 6] by using catalyst, the rate constants increase for both forward and reverse reac-
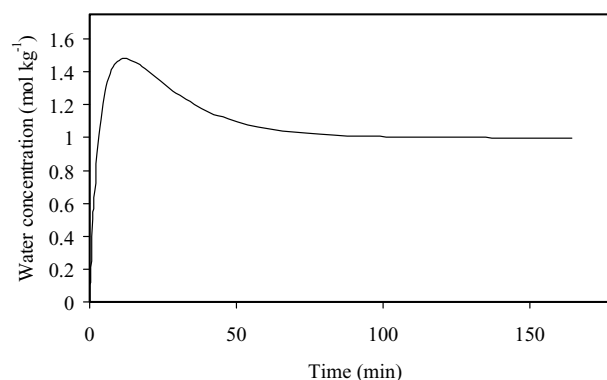
tion. Therefore, it can be concluded that, the use of catalyst has increased both forward and reverse rate constants. The results above depict that, equilibrium constant varies randomly with temperature. The same Table shows the results of 95% confidence intervals for forward and reverse rate constant, it is clear that the confidence intervals are narrow and this shows the good fit of model and experimental data.

The temperature dependence of rate parameters for forward rate constant were tested with Arrhenius plots. Fig. 8 shows that, the rate parameters obey the Arrhenius law. Table 4 shows the Arrhenius parameters for rate constants and equilibrium constant and by comparing with noncatalytic reaction [2], the activation energy is 1.089 times
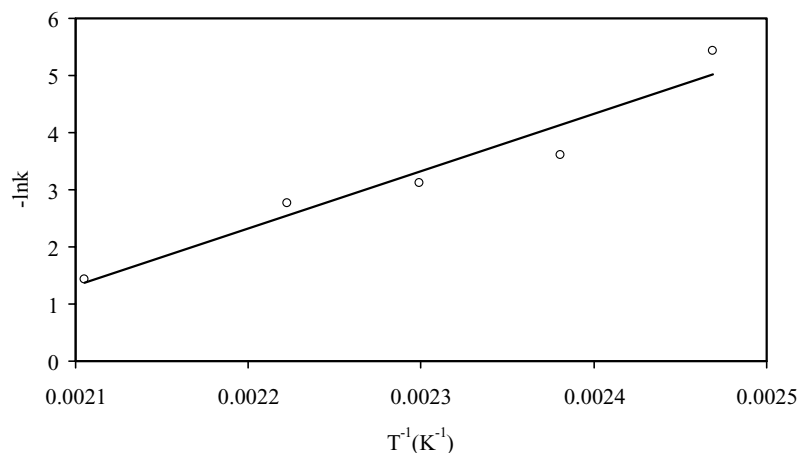

Fig. 8. The temperature dependencies of the rate parameters.

Table 4
The Arrhenius parameters for rate constants and equilibrium constants

Rate constant	A_E	E_{aE} (kJ mol^{-1})
k_1	362306102.681 (kg mol^{-1} min^{-1})	83.239768
K_E (equilibrium constant)	17317.97	28.645887

increases and frequency factor is 687.1 times increases. For equilibrium constant, because of the fact that polyamidation reaction is slightly exothermic and the heat of reaction is very low [8], so it can be concluded that the equilibrium constant is independent of temperature and this can be seen from Table 4 where the activation energy is very low. By comparing the values obtained with the published values [2,3,6,10] of non-catalytic reaction, the rate constants and Arrhenius parameters for forward catalytic reaction is higher than non-catalytic one. For reverse reaction and equilibrium constants there are no published literature values to make comparison.

4. Conclusions

A kinetic model was proposed for homogeneous polyamidation of dimer fatty acids and ethylene diamine in presence of catalyst. Rate laws for these reactions, were derived and the kinetic model was tested by determining the kinetic parameters using nonlinear regression analysis. A comparison between the model predictions with actual experimental data shows that the approach is useful and reliable in predicting the progress in polyamidation process. The activation energy for forward rate constant is 66.7 kJ mol^{-1}. Forward and reverse rate constant increase with increasing temperature and the equilibrium constant is independent of temperature.

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