ABSTRACT

For the first time, thermal degradation of polyglycolic acid (PGA) is carried out in the presence of humid air. The thermal-oxidative-hydrolytic degradation of pure PGA is investigated in a batch reactor with reaction temperatures of 250°C, 260°C, 280°C, and 310°C. The effects of polymer loading and temperature on degradation are studied at different pressures (80 mmHg-760 mmHg). Degradation is carried out at different initial air partial pressures as well. It was found that degradation is enhanced considerably under higher pressures as well as higher air mole fractions. Empirical correlations were proposed to account for the effect of total pressure on degradation rate and found to be a parabolic form in respect to total pressure. The thermal-oxidative-hydrolytic degradation rate constants are evaluated within several experiments. Moreover, an optimum operational condition for reactor design features was obtained at P_{total}=102 mmHg under which the dimerization yield would be above 80%. The frequency factor and activation energy are also determined using Arrhenius equation considering both of the true and global degradation rate constants. It was found that in the presence of air, the polymer undergoes thermal-oxidative degradation with activation energy of 24-36 kcal/mol while the normal activation energy in absence of air and vapour was 24-26 kcal/mol.

INTRODUCTION

Polyglycolic acid (PGA), the simplest aliphatic polyester, was the first commercially successful synthetic biodegradable polymer to be used as biomedical material. Since the main advantage of PGA is its biodegradability, which makes this class of synthetic polymers more biocompatible with biological systems than those of non-biodegradable materials, it is important to understand the biological and thermal degradation phenomenon of PGA. Such an understanding could provide the basis for changing the biological and thermal degradation properties to meet some requirements in certain aspects of recons-
tractive surgery. However, the thermal sterilization is commonly utilized in medical arena due to convenience and simplicity of the process. If a polymer is needed to be thermally sterilized, its thermal stability should be known to prevent decomposition [1,2]. On the other hand it is useful to study the thermal degradation of PGA for reactor design and kinetic optimization in dimerization process so that the dimer of PGA is used to provide random and block copolymers via combination with other monomer components [3].

The degradation process has been recognized to be a single stage type at high temperature with glycolide as the main decomposition product [4]. A random chain scission has been reported [5]. From view point of mechanism circumstances, the PGA degrades by random and specific chain scissions which change the degradation rates are somehow observed. At lower temperature, the degradation is via the processes of ester interchange and decarboxylation of chain ends while at higher temperature, the increased formation of carbon dioxide in products suggests increases in formaldehyde leading to chain end scission [6]. A similar argument in changes of dominant mechanism is demonstrated for polylactic acid by Gupta et al. [7].

The major products obtained from the pyrolysis of PGA are methylglycolates, carbon dioxide, formaldehyde and ketones [6,8,9]. In case of thermal-oxidative degradation, the contribution of carbon dioxide proportion increases in products. The hydrolytic degradation occurs slowly in humid environments so that the rate of degradation is represented on day to day basis. There have been some studies carried out on hydrolytic and biodegradation of PGA [10,11,12]. However, the rate of hydrolytic degradation is much lower than the thermal and oxidative degradations. For example, the hydrolytic degradation occurs in four stages gradually proceeding by days [13,14]. In these studies the hydrolytic or biodegradation of PGA are fully investigated in different environments, but to date there have been no studies reported on thermal degradation in presence of humid air. Nevertheless, a rather comprehensive study on thermal degradation in presence of nitrogen atmosphere is reported [4]. Unfortunately, the above mentioned study has not reported the frequency factor coefficient. Because PGA is not soluble in conventional organic solvents, the measurement of average molecular weight of PGA is difficult, therefore the thermal degradation study has not been developed compared to other degradation processes.

Nonetheless, a morphological study on thermal-hydrolytic degradation of PGA is reported by Chu [15]. The dimerization process is prevalently accomplished under absolute vacuum in pilot plant, but in industrial plants, it is not practical and economical to gain the absolute vacuum condition. Consequently, the glycolide should be provided under relative vacuum and indispensably in presence of humid air, which exists in atmosphere abundantly. The nitrogen atmosphere is not recommended either. Usually the presence of oxygen as a substantial factor can aggrivate polymer degradation although it decreases the yield of dimerization. So the air partial pressure should be carefully controlled for reactor optimization considering the economical features and reaction conditions.

The major aim of present work is the characterization and definition of the thermal-oxidative degradation of PGA under relative vacuum pressures that can take into account the relevant industrial reactor design calculation. Therefore, in the present work to obtain the kinetic parameters, the kinetics of PGA thermal degradation in presence of humid air that included diverse initial air partial pressures involving pressure effect on reactor design calculation, is studied because the kinetics of the process is an important step in reactor design. The desired vacuum is usually achieved by for example a commonplace ejector capable of passing the air or vapour to induce the vacuum state. The ejector may be simulated by a water aspirator in laboratory conditions with similar function. To our knowledge, no experimental data are reported in the literature for this special thermal degradation. Also the effects of temperature, polymer loading and total pressure in course of degradation are investigated.

EXPERIMENTAL

Materials
Glycolic acid (70% aqueous solution), ethyl acetate, antimony (III) oxide (Sb$_2$O$_3$) were from Merck Company (Germany).
Method
PGA was prepared from glycolic acid (70% aqueous solution). In this way 1 g of antimony (III) oxide as catalyst was added to 1 L glycolic acid in a batch reactor at 120°C for 4 h under nitrogen atmosphere. In the next stage, the temperature was raised to 180°C for 2 h, constantly under nitrogen atmosphere, and at the end it was decreased to 140°C for 6 h under high vacuum. The preparation method was according to Gilding et al. [3]. Though the above method of PGA preparation has been modified by us for the first time, among many tests done to produce PGA with high quality, we found this method nicely obtains the best sample with anticipated physical properties like the high mechanical resistance and with a great dehydration yield [16]. Dehydration from glycolic acid which is really responsible to initiate the condensation polymerization and subsequently to generate the PGA occurs in two stages individually. In the first stage the extrinsic water is physically vapourized while in further stages the intrinsic water is chemically separated. The PGA preparation dependent flow chart marked with material balance is shown in Figure 1. The obtained crude PGA was first mechanically powdered and then was purified by refluxing in ethyl acetate for 4 h [17]. The extracted PGA was kept under vacuum for 24 h to remove all volatiles and the solvent as much as possible and then it was characterized by measurement of normal melting temperature of 219°C at 0.1 MPa. The experimental equilibrium melting temperature of PGA (molecular weight between 100,000 and 125,000) has been assessed by Nakafucu et al. as 220°C at 0.1 MPa [18]. Thus the molecular weight of the present PGA can be approximately between 100,000 and 125,000, because this property is immensely dependent on normal melting temperature. The prepared samples of pure PGA with various weights were charged into a glass batch reactor at desired degradation temperature under pressure (80-760 mmHg), repeatedly. The internal volume of the

![Figure 1. A process flow chart detailed with material balance for the PGA preparation.](image-url)
reactor equipped with an electrical heater and silicon oil bath was 100 mL. The heat of reaction was indirectly supplied by the heater equipped with a manual temperature controller and was directly transferred by the silicon oil bath which was responsible for heat transfer from the heater to the reactor. A temperature indicator was embedded into the bulk of silicon oil bath to approximate reactor temperature. Because of the high heat transfer coefficient of silicon oil, it is assumed that its temperature and reaction temperature are equal. Additionally, the temperature effects of probable heat loss due to heat resistance of thin wall of glass reactor were assumed to be negligible [19]. For controlling the reaction temperature the manual temperature controller was utilized to alter the rate of heat properly. A vacuum pump was fitted with the reactor for controlling the total pressure. The initial water partial pressure was controlled by a glass water-aspirator pump connected to the reactor. The glass water-aspirator allowed vapour to flow into reactor during the reactor operation as if the ejector was working. Consequently, the desired water partial pressure and water mole fraction were achieved. Finally, the samples were weighed and charged discretely into the reactor after attaining the desired temperature. Rest of the samples were collected after the time-hold on and then reweighed at regular time intervals recording. The samples weight for all the experiments were taken in the range of 5-10 g with an assessment uncertainty of ±0.005 g.

Because the PGA molecular weight measurement is difficult, the weight loss of PGA, instead of molecular weight, was measured in the course of thermal-oxidative degradation [4]. The PGA is more or less soluble in hexafluoro-isopropanol [20]. The absolute molecular weight would be measurable, if hexafluoro -isopropanol is available. Unfortunately, this solvent is very expensive and it was not accessible for us. Several experiments were established to study the effects of temperature, polymer loading and pressure on degradation.

KINETIC MODEL

A kinetic model was used to describe the degradation of pure PGA [21]. The rate of thermal decomposition of a reactant can be approximated via a kinetic scheme: \( \frac{dm}{dt} = f(m) \), where \( m \) is a vector of mass concentration, and \( f \) is a vector-valued function representing the degradation mechanism. The reaction order is found to be 1 for thermal degradation of polymers whether biodegradable or non-biodegradable [22]; therefore, the rate of unimolecular decomposition becomes:

\[
A \rightarrow \text{Volatile} + \text{Solid residue} \Rightarrow - \frac{dm_A}{dt} = km_A^1
\]  

(1)

where, \( k \) denotes the pseudo-unimolecular degradation rate constant. The degradation rate constant is expressed in the following form [23]:

\[
k = k_{th}(T)F_cF_p
\]  

(2)

where, \( k_{th} \) is the true thermal degradation rate constant and it is only temperature dependent. The parameters \( F_c \) and \( F_p \) in eqn (2) depend on the polymer loading and total pressure, which are temperature-independent. The correction term of \( F_p \) would make up the oxidative-hydrolytic contributions on the pseudo-unimolecular degradation rate constant, which is presented in the next section in an empirical correlation form. The integration of eqn (1) leads to:

\[
m_A = m_{A,0} \exp(-kt)
\]  

or

\[-\ln \frac{m_A}{m_{A,0}} = kt\]  

(3)

Therefore, eqn (3) could be frequently used to obtain the rate constant and activation energy of the reaction but we used a particular form of eqn (4). In eqn (3) two parameters, \( m_A \) and \( m_{A,0} \), denote polymer weight at time \( t \) and the polymer weight at initial time, respectively. The time variation of mass retained for the polymer during isothermal stage can be modelled more simplified as in the following equation [24].

\[
m_A / m_{A,0} = 1 - kt
\]  

(4)

Hence, the degradation rate constant for specific chain scission at high temperatures can unceasingly
be obtained from the slope of linear plot of \( m_A/m_{A,0} \) versus time. The kinetic parameters can be calculated from the experimental results using an integration method as we did [25]. A similar kinetic expression can be obtained from the continuous distribution of kinetic polymer degradation model using method of moment [26].

RESULTS AND DISCUSSION

The thermal degradation of PGA was investigated in the presence of humid air and the effects of temperature, polymer loading and initial water/air partial pressure were studied at specific scission. The degradation rate coefficients are determined from eqn (4), which describe the variation of the mass fraction retained with reaction time in presence of initial water/air partial pressure at any given temperature. Prior to analytical process the TGA thermogram of PGA was obtained as it is observed in Figure 2, which indicates the temperature range at which specific scission should occur between 220ºC and 350ºC [27]. Hence the desired temperatures were reached in this range. To obtain reliable values, in all experiments, the data were carefully examined and doubtful data were rejected and some uncertain tests were repeated.

To study the effect of pressure, the reaction was carried out under different total pressures as well as initial air partial pressures. The effect of total pressure on retained weight of polymer for temperature (250ºC) and polymer loading (10 g) is shown in Figure 3. The total pressures 80 mmHg, 280 mmHg, and 760 mmHg had proportions of 0.2185, 0.0624, and 0.023 as water mole fractions and 0.1565, 0.197, and 0.2052 as oxygen mole fractions, respectively. With this consideration that the partial pressure of volatile is negligible, these values were calculated with reference to phase equilibrium [28].

Oddly enough, Figure 3 reveals that with oxygen mole fraction of higher portions (at higher pressures), the degradation rate becomes faster in the last stage of degradation (sharper slope towards the end of plots), which slows down with increase in reaction time. This is in contrast with most non-biodegradable polymers such as polyethylene and polystyrene in which the degradation rates are faster at the early stage [22,29]. This fact may be due to the oxidative degradations occurring in the last stage when polymer chains are more fractured and thus the oxygen with a higher degree of selectivity can attack the chain ends carbons to produce carbon dioxide. More details are depicted in Figure 4 showing that the thermal degradation rate is relatively slow at low air partial pressure as well as low oxygen mole fraction. This is an excellent evidence to verify the previous claim about the higher rate in end stage of degradation. Effect of total pressure (80-280-760 mmHg) on degradation rate constant, temperature (250ºC) and polymer loading (10g) were studied and variation of the slope, degradation rate constant, with pressure is shown in Figure 4. In details, Figure 4 shows that the degradation rate
Figure 4. Effect of total pressure of 80, 280, and 760 mmHg on degradation rate constant under isothermal holding (250°C). The polymer loading for all plots is maintained constant as 10 g. The slopes of the fitted plots signify on degradation rate constants.

The pseudo-unimolecular degradation rate constant, \( k \), eqn (4), was calculated from the slope of the related straight line. The estimated values of the degradation rate constant show a relative increase from 0.0004064 min\(^{-1}\) to 0.001949 min\(^{-1}\) with the pressure increase.

At 250°C when any vapour or air is introduced, a vacuum state, a minimum value of the degradation rate constant is obtained to be 0.0004064 min\(^{-1}\). The square correlation coefficients (R-square) for all the three plots in Figure 4 are calculated and it is presented in Table 1. The reported R-squares, altogether, were determined by a non-linear least-square fitting routine of the Trust-Region, performed by Matlab CF Toolbox software environment.

The polymer loading effect was investigated and the results are shown in Figure 5. Three data sets in Figure 5 correspond to 5 g, 8 g, and 10 g polymer loadings. Figure 5a shows the variation of degraded polymer weight versus time with different polymer loadings. This figure also shows that at any given time, degraded polymer weight increases with the increased polymer loading. A quantitative trend is

### Table 1. A summary of experiments and investigated parameters during process, where the final results are incorporated.

<table>
<thead>
<tr>
<th>Parameters to be studied</th>
<th>Description of the test</th>
<th>Initial water mole fraction ((y_{water}))</th>
<th>Initial (\text{N}<em>2) mole fraction ((y</em>{nitrogen}))</th>
<th>Initial (\text{O}<em>2) mole fraction ((y</em>{oxygen}))</th>
<th>Total average reactor pressure ((P_{total}))</th>
<th>Temperature ((ºC))</th>
<th>Polymer loading ((g))</th>
<th>Rate constant (k) ((1/\text{min}))</th>
<th>R-square obtained from regression procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature ((ºC))</td>
<td>PGA+ air+ water</td>
<td>0.023</td>
<td>0.7710</td>
<td>0.2050</td>
<td>760</td>
<td>250</td>
<td>5.02</td>
<td>0.001873</td>
<td>0.9942</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>260</td>
<td>5</td>
<td>0.003608</td>
<td>0.9973</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>280</td>
<td>8</td>
<td>0.005361</td>
<td>0.9808</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>310</td>
<td>5</td>
<td>0.022390</td>
<td>0.9933</td>
</tr>
<tr>
<td>Pressure ((\text{mmHg}))</td>
<td>PGA+ air+ water</td>
<td>0.2185</td>
<td>0.6250</td>
<td>0.1565</td>
<td>80</td>
<td>250</td>
<td>10</td>
<td>0.0004167</td>
<td>0.9494</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0624</td>
<td>0.7407</td>
<td>0.1970</td>
<td>280</td>
<td>250</td>
<td>10</td>
<td>0.0005976</td>
<td>0.9873</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0320</td>
<td>0.7650</td>
<td>0.2030</td>
<td>550</td>
<td>250</td>
<td>10</td>
<td>0.001200</td>
<td>0.9925</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0230</td>
<td>0.7718</td>
<td>0.2052</td>
<td>760</td>
<td>250</td>
<td>10</td>
<td>0.001949</td>
<td>0.9810</td>
</tr>
<tr>
<td>Polymer loading ((g))</td>
<td>PGA+ air+ water</td>
<td>0.0230</td>
<td>0.7718</td>
<td>0.2052</td>
<td>760</td>
<td>310</td>
<td>5</td>
<td>0.022390</td>
<td>0.9933</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>310</td>
<td>8</td>
<td>0.02018</td>
<td>0.9939</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>310</td>
<td>10</td>
<td>0.01840</td>
<td>0.9976</td>
</tr>
<tr>
<td>Inert atmosphere ((\text{flow rate})) ((\text{cm}^3.\text{min}^{-1}))</td>
<td>PGA+ nitrogen</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>~ 762-770</td>
<td>250</td>
<td>10</td>
<td>0.00167</td>
<td>0.9940</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>257</td>
<td>10</td>
<td>0.00193</td>
<td>0.9850</td>
</tr>
</tbody>
</table>
Figure 5. Variation of polymer weight loss versus time with different polymer loads, temperature (310°C) (a), and effect of polymer loading on degradation rate constant, temperature (310°C) (b).

obtained for polymer loading and as it is observed from Figure 5b polymer loading has no influence on degradation rate constant. Thus the polymer loading has absolutely no effect on thermal-oxidative rate during the degradation process.

Besides, the effect of temperature (250-310°C) on degradation at 760 mmHg was studied and degradation rate constant, k, was calculated from slope of the straight line fitted on four sets of data in Figure 6. It was found that the values of degradation rate constant increases discretely with the temperature increase. Similar to Figure 4 the square correlation coefficients (R-square) for all the four plots in Figure 6 are calculated and then are tabulated in Table 1.

Figure 6. Variation of degradation rate constant with time at different temperatures under atmospheric pressure.

Since the true thermal degradation constant has to be acquired under inert atmosphere and in the absence of oxygen and vapour as well, the values of $k_{th}$ under nitrogen atmosphere at 250°C and 257°C were obtained to be 0.00167 min$^{-1}$ and 0.00193 min$^{-1}$, respectively. The true thermal degradation rate constant is useful in helping to find the pressure dependency of thermal-oxidative-hydrolytic degradation rate constant.

Figure 7 shows the variation of the degradation rate constant with varying water/oxygen mole fractions and total pressure maintaining constant degradation temperature (250°C) and polymer loading (10 g). Mathematically, the parabolic model, capable of explaining the total pressure effect on degradation.
rate, is shown to be superior to flexible fit of isotherm data although its physical meaning is arguable.

The parabolic fit is aimed at an empirical correlation due to its high accuracy, although some detailed reasons to explain why the parabolic model is a proper one have been introduced in ref [21]. The best fit equation corresponding to Figure 8 with 1.0 square correlation coefficient was obtained to account for the variation of the pseudo-unimolecular degradation rate constant, \( k \), eqn (4), with varying total pressures and is given by the following equation:

\[
k = k_{th} F_{v-inert} F_{P_{total}} = 2.802 \times 10^{-9} \ p_{total}^2 - 9.939 \times 10^{-8} \ p_{total} + 0.0004064
\]  

(5)

where \( k_{th} = 0.00167 \ \text{min}^{-1} \) (Table 1: column 9, row 5)

\[
F_{P_{total}} = \frac{k}{0.00167} = 1.678 \times 10^{-6} \ p_{total}^2 - 5.951 \times 10^{-5} \ p_{total} + 0.2433
\]  

(6)

That

\[
F_{water} = P_{total} - F_{air} = 17.48
\]  

(7)

where, value of 17.48 mmHg is the vapour pressure of water at 25ºC entered into the batch reactor. In this study, it was held constant while could vary, arbitrarily [30]. Substituting this result into eqn (6) we have:

\[
F_{P_{total}} = 1.678 \times 10^{-6} (F_{water} + F_{air})^2 - 5.951 \times 10^{-5} (F_{water} + F_{air}) + 0.2433
\]  

(8)

Eqn (8) correlates the total pressure with the initial air and water partial pressure for correcting the degradation rate. In the absence of water and oxygen, eqn (8) takes up a unit value, as long as the total pressure is higher than 760 mmHg, similar to what happened for polymer loading and eqn (3) gives the true thermal degradation rate constant. Eqn (8) is valid merely for pressures from 0 to 760 mmHg.

From view point of reactor engineering, it is a critical matter to find the optimum condition, under which the desired products are certainly formed more. For this purpose, when we depict the global degradation rate constant versus oxygen and water mole fractions simultaneously, an astonishing distribution is found as one can see in Figure 9. This figure shows that the global degradation rate constant in a special region is constant, relatively. We argue that the total degradation rate constant can be represented applying the super-position rule in this form:

\[
k_{\text{observed}} = k_{th} + k_{\text{oxy}} + k_{\text{hyd}}
\]  

(9)

Figure 8. The flexible fit to estimate the degradation rate constant in terms of total pressure, temperature (250ºC).

Figure 9. The optimum operational condition for reactor design, temperature (250ºC).
Figure 10. The dimerization yield bar plot versus total pressure.

that $k_{th}$, $k_{ox}$, and $k_{hyd}$ are the thermal degradation, the oxidative degradation and the hydrolytic degradation rates, respectively. In case of hydrolytic degradation, the relevant rate would be negligible, so eqn (9) diminishes to:

$$k_{observed} = k_{th} + k_{ox}$$

(10)

Therefore, the observed rate constant is related to the thermal-oxidative degradation. Because of the presence of oxygen, the products can be of variety kinds, but the high quality dimer is also produced in absence of oxygen with greater efficiency. Hence, it is clear that as the $k_{ox}$ and subsequently the $k_{observed}$ become smaller, the dimer product amount would be much greater, unlike the parallel products such as carbon dioxide, etc. However, the hydrolytic degradation also occurs but uselessly. The vapour mole fraction effect on mechanism, degradation rate and parallel products exactly is not transparent but somehow to optimize the dimerization process condition. The global degradation rate versus mole fraction of water must be constant and to prevent the generation of parallel products and other unknown cases influencing the overall mechanism. Based on these obvious reasons, we declare that the optimum classical condition is obtained wherever the global degradation rate takes low-constant values in terms of the oxygen and likewise water mole fractions simultaneously. This region has been discovered as it may be distinguished in Figure 9 by vertical lines. In this region, the optimum point was achieved at 0.174, for both oxygen and water mole fractions, where it corresponds to total operational pressure and the degradation rate being 102.5 mmHg and 0.0004692 min$^{-1}$, respectively.

Consequently, the dimerization procedure has to be conducted in these conditions.

A quantitative study was conducted on the yield of produced dimer to better understand the role of pressures together with nitrogen atmosphere as shown in Figure 10. From this figure it is clear that under recommended conditions, the dimerization yield is more or less higher than 80%. Inadvertently, a stable residue was formed in all the experiments, more likely due to carbonization of the polymer sample. At lower temperatures as well as higher total pressures the amount of this residue was relatively higher.

In this respect, Figure 11 is considered for determination of the frequency factor and the activation energy of the thermal-oxidative-hydrolytic degradation. An Arrhenius plot (Figure 11) is made with square correlation coefficient 0.9927 to determine the frequency factor and the activation energy of the pure PGA degradation based on the thermal-oxidative-hydrolytic degradation rate constants and found to be by average $5.0165 \times 10^5$ s$^{-1}$ and 24-35 kcal/mol, respectively.

The extensive range of the properties with a confidence bound of 0.95% may be reported as $5.0165 \times 10^5$
-5.311×10^{10} \text{ s}^{-1} and 24-36.5 \text{ kcal/mol}, respectively. However, we found that the activation energy in temperature range of 250-270°C had the higher order of magnitude than 34 \text{ kcal/mol} while the true related value under nitrogen atmosphere was 22-26 \text{ kcal/mol}. The oxygen has sensitive influence on the degradation rate and activation energy so that the activation energy is between 2-9.5 \text{ kcal/mol} up to normal condition (nitrogen atmosphere). This fact is illustrated in Figure 11. The observed activation energy in this paper is consistent with an earlier study to be 28 \text{ kcal/mol} reported by Sivalingam et al. [4] and others [6].

**CONCLUSION**

The effects of temperature, pressure and polymer loading on thermal-oxidative-hydrolytic degradation of PGA are investigated. Degradation increases with the increase in reaction temperature and total pressure whereas it remains entirely unchanged with the increase in polymer loading. A kinetic model of Kelen [21] is used to estimate the degradation rate constants. The empirical correlation is applied to account the pressure effect on thermal-oxidative-hydrolytic degradation rate constant. The optimum operational total pressure is obtained using a novel technique of supper-position principle for degradation rate. Also the yield of dimerization process is investigated and it is found that the degradation rate increases in presence of oxygen and vapour when the dimerization yield decreases. The optimum total pressure is obtained as 102.5 mmHg. Frequency factor and activation energy of ultimate degradation are also calculated from Arrhenius equation after evaluating the true thermal degradation rate constant at two different temperatures under nitrogen atmosphere with values of 5.0165×10^{5} \text{ s}^{-1} and 24-35 \text{ kcal/mol}, respectively. Presence of oxygen promoted the activation energy with surplus amount of 2-9.5 \text{ kcal/mol} compared to the normal condition. Our next work will focus on reactor design to produce PGA dimer. Also, we will endeavour to compare these results with the results of similar experiments of biodegradable polymer thermal degradation such as polylactic acid.

**ACKNOWLEDGEMENTS**

The authors thank Prof S.M. Mousavian, from the Chemical Engineering Department, Faculty of Engineering, University of Tehran, Iran for helpful discussions. Finally, the authors would like to extend their gratitude to Iran National Science Foundation for their valuable support and funding of this project.

**REFERENCES**