Apparent kinetics of high temperature oxidative decomposition of microalgal biomass

Saad Aldin M. Ali, Shaikh A. Razzak, Mohammad M. Hossain*

Department of Chemical Engineering, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia

Abstract

The oxidative thermal characteristics of two microalgae species biomass Nannochloropsis oculta and Chlorella vulgaris have been investigated. The apparent kinetic parameters for the microalgal biomass oxidation process are estimated by fitting the experimental data to the nth order rate model. Also, the iso-conversional methods Kissinger–Akahira–Sunose (KAS) and Flynn–Wall–Ozawa (FWO) were used to evaluate the apparent activation energy. The results indicate that biomass of different microalgae strains exhibit different thermal behavior and characteristics. In addition, growth parameters and medium composition can affect the biomass productivity and composition. This would have significant impact on the thermal decomposition trend of the biomass. The kinetic modeling of the oxidation reaction with direct model fitting method shows good prediction to the experimental data. The apparent activation energies estimated by KAS and FWO methods for N. oculta were 149.2 and 151.8 kJ/mol, respectively, while for C. vulgaris were 214.4 and 213.4 kJ/mol, respectively.

1. Introduction

Biomass is one of the attractive forms of renewable energy resources. It can effectively contribute to the sustainable energy for the future developments and industrialization (López et al., 2013). Conventionally biomass is used for direct heating and/or energy generation purposes (Amutio et al., 2012). It can also be further processed to produce more versatile fuels such as biodiesel and hydrogen via syngas (Razzak et al., 2013). Generally, agricultural wastes, municipal wastes and forests are considered as the major sources of biomass. On the other hand, microalgal biomass has many unique features represent by its rapid growth rate as compared to the other terrestrial plants. Microalgae culture can also be employed in CO₂ mitigation given its high carbon dioxide uptake efficiency (López-González et al., 2014). Unlike terrestrial crops, which requires vast lands, considerable amount of water and fertilizer for growth, microalgal culture can be cultivated using wastewater as a free source of nutrients (Kebelmann et al., 2013). In this way, microalgal culture can contribute to CO₂...
Regarding the thermal decomposition kinetics, only few studies have been considered based on their CO2 biofixation capabilities and wastewater treatment. Both species were acquired from Algae Depot (USA) and cultured in BBM media. Media consist of NaNO3, CaCl2,2H2O, MgSO4·7H2O, KH2PO4, KH2PO4, NaCl, EDTA, KOH, FeSO4·7H2O, H2SO4, H3BO3, ZnSO4·7H2O, MnCl2·4H2O, CuSO4·5H2O, CoCl2·6H2O, CH3N2O. The media was prepared by adding the salts in deionized water. The microalgal species samples obtained from starter culture was incubated in two different batch photo bioreactors (2 L Erlenmeyer flasks) with 1700 ml working volume of each reactor. The initial biomass concentration adjusted to 1 mg/L approximately for each flask. The culture was placed in fume hood with provision of plant culture Grolux fluorescent light. After filtration, the ambient air was mixed with CO2 using gas mixing device. The CO2 concentration of 4% was mixed with air fed to the reactor. Fluorescent light was provided at the surface of reactors. Cultures were set for 10 days, samples were analyzed during the growth to determine the optimal cell density, cell concentration, and dry weight, effect of CO2 utilization by two different species, pH changes, and growth rate measurements were made. The biomass harvested using centrifugation with 9000 RPM for 3 min and then farther dried using freeze dryer.

2.2. Thermogravimetric experiments

The high temperature thermal decomposition of the microalgal biomass samples were evaluated using TGA (SDTG 600, TA Instruments, USA). For each experimental run, 6–6.2 mg biomass sample were placed on the sample holder. The samples were heated at an air flow rate of 100 ml/min. The weight loss of the sample was recorded from ambient temperature to 800 °C with heating rates of 5, 10, 15, 20 °C/min. Each experiment was repeated 2–4 times in order to confirm the minimum standard deviation of the percentage weight loss.

2.3. Proximate and ultimate analysis

In order to determine the moisture content, the samples were exposed to constant temperature of 105 °C until stabilized their sample weight (Keibelmann et al., 2013). Following the moisture
removal, the ash and other volatile matter fractions were estimated by modifying the traditional standard methods for biomass as described by Cantrell et al. (2010). For ash measurement, the sample was heated at 600 °C under air flow with heating rate of 11 °C/min and held at isotherm temperature for 10 min. In order to determine the amount of the volatile substance, the sample equilibrated at 110 °C then heated to 950 °C with 100 °C/min heating rate in nitrogen atmosphere and held for 7 min. The gas flow rate for both test were kept at 80 ml/min. The fixed carbon content was calculated by difference. The elemental composition represented by the percentage weight of the carbon, hydrogen and oxygen were determined using correlations developed by Parikh et al. (2007), while the corresponding higher heating value calculated using correlation developed by Parikh et al. (2005). All correlations are based on proximate analysis.

2.4. Kinetic modeling

The high temperature non-isothermal degradation of biomass is a function of temperature and the fractional amount of the remnant solid. Thus, the reaction rate can be described by the following equation.

\[ \frac{dx}{dt} = k(T)f(x) \] (1)

where \( t \) is the reaction time (in min); \( T \) is absolute temperature (in K); \( x \) is the fractional conversion and is defined as:

\[ x = 1 - W_f \] (2)

Since \( W_f \) represents the remnant weight fraction of the sample, \( k(T) \) is the reaction rate constant which is function of temperature. Using the Arrhenius expression for the reaction rate constant, the overall rate of reaction becomes,

\[ \frac{dx}{dt} = k_o \exp \left( -\frac{E_a}{RT} \right)f(x) \] (3)

where \( R \) is universal gas constant (in kJ/mol K); \( E_a \) is the apparent activation energy (in kJ/mol); \( k_o \) is the frequency factor (in 1/min); and \( n \) is the overall order of degradation.

The apparent activation energy \( (E_a) \) can be obtained by two approaches. The first approach required to specify \( f(x) \) depending on the proposed reaction mechanism, and by direct fitting procedure \( E_a \) and other reaction kinetic parameters can be estimated. While the second approach is independent of the reaction mechanism and it is called model-free methods.

2.4.1. Direct model fitting

We assume \( f(x) \) as the \( n \)th order reaction rate model, then the overall rate of degradation can be expressed as follows, (Lu et al., 2013; Peng et al., 2001; Rizzo et al., 2013)

\[ \frac{dx}{dt} = k_o \exp \left( -\frac{E_a}{RT} \right)(1 - x)^n \] (4)

The kinetics parameters of Eq. (4) which are \( E_a \), \( k_o \) and \( n \), were evaluated by fitting Eq. (4) to the experimental data. FindFit and NonlinearModelFit commands in Mathematica 9 software were used to evaluate the unknown parameters for each heating rate. Maximum 1000 iterations was used to achieve a specified

Fig. 1. (a) TG curve for Nannochloropsis oculta for different heating rate. (b) DTG curve for Nannochloropsis oculta for different heating rate. (c) TG curve for Chlorella vulgaris for different heating rate. (d) DTG curve for Chlorella vulgaris for different heating rate.
precision, since that the fitting commands generate many solutions and the selection was based on the highest coefficient of determination $R^2$. The coefficient of determination was estimated using “RSquared” command.

In order to compare between the thermogravimetric (TG) profile of the model and the experiments, we need a relationship between $a$ and $T$ to obtain the TG curve for the model after substitution of the estimated parameters. Therefore, we must firstly expressing Eq.(4) to be as a function of temperature only and then solving it. This was done by replacing the time differential according to the given relation between temperature, time and the heating rate ($\beta = dT/dt$), where $\beta$ is the heating rate (°C/min).

Thus, Eq.(4) becomes

$$\frac{da}{dT} = \frac{k_0}{\beta} \exp \left( -\frac{E_a}{RT} \right) (1 - \alpha)^n$$

Eq. (5) can be solved by two procedure, either by the approximate analytical solution or by the numerical solution.

Approximate analytical solution

Firstly, Eq. (5) was arranged, followed by taking the integral of the both side of the equation

$$\int_0^T \frac{dx}{(1 - \alpha)^n} = \frac{k_0}{\beta} \int_{T_{in}}^{T} \exp \left( -\frac{E_a}{RT} \right) dT$$

where $T_{in}$ refers to the initial experiment temperature (in K). And the left hand sight of was defined as $g(\alpha)$.

$$g(\alpha) = \int_0^\alpha \frac{dx}{(1 - \alpha)^n} = \frac{1 - (1 - \alpha)^{1-n}}{(1 - n)}$$

Although, the right hand side of Eq. (6) has no analytical solution (Ebrahimi-Kahrizsangi and Abbasi, 2008), the Coats–Redfern approximation could be used (Coats and Redfern, 1964).

Given that the value of $E_a/RT \approx 1$, then the right hand side of Eq. (6) could be approximated as follow (López et al., 2013).

$$\int_{T_{in}}^{T} \exp \left( -\frac{E_a}{RT} \right) dT \approx \frac{R}{E_a} T^2 \exp \left( -\frac{E_a}{RT} \right)$$

After substitution of Eq. (7) and Eq. (8) in Eq. (6), and by taking the natural logarithmic for both sides we get

$$\ln \left( \frac{1 - (1 - \alpha)^{1-n}}{(1 - n)T^2} \right) = \ln \left( \frac{k_0 R}{\beta E_a} \frac{E_a}{RT} \right)$$

The same results of Eq. (9) is obtained by (Lu et al., 2013), further rearrangement of Eq. (9) yields;

$$W_f = (1 - \alpha) = \left[ 1 - (1 - n)T^2 \cdot \frac{k_0 R}{\beta E_a} \exp \left( -\frac{E_a}{RT} \right) \right]^{1/n}$$

Then, TG curve from model was plotted after substituting the estimated parameters values in Eq.(10).

For thermogravimetric (TG) and differential thermogravimetric (DTG) profiles modeling, data were selected from experimental results, starting from temperature of 30 °C and with increment of 10 °C the total number of point selected were in the range of (65–78 points), for plotting of the experimental data for Fig. 2 and Fig. 3 half of the points are chosen in order to get a clear and neat graphs.

Numerical solution

Numerical solution for $a$ as a function of temperature was obtained by solving Eq.(5) using NDSolve command in Mathematica.
9 software. The boundary condition is \( x \) \([298 \text{ K}] = 0\), which at the initial experimental temperature (normally 298 K) the sample weight loss not started.

2.4.2. Model-free methods

These methods are used to determine the unknown apparent activation energy \( (E_a) \) without specifying a model to describe the reaction mechanism, there is no need to define \( f(x) \) or \( g(x) \). The following two iso-conversional methods are commonly used (Slopiecka et al., 2012):

**Kissinger–Akahira–Sunose (KAS) method**

This methods is briefly described as (Zhao et al., 2013).

\[
\ln \left( \frac{\beta}{T^2} \right) = \ln \left( \frac{k R}{E_a g(x)} \right) - \frac{E_a}{RT} \tag{11}
\]

According to this method, the plots of \( \ln \left( \frac{\beta}{T^2} \right) \) versus \( 1/T \) for different \( x \) values is a straight line and the \( E_a \) can be calculated from the slope of the line. Though, there is an \( E_a \) value at each fractional conversion \( x \).

**Flynn–Ozawa–Wall (FWO) method**

The alternative linearized form of the model equation (Zhao et al., 2013)

\[
\ln [\beta] = \ln \left( \frac{0.0048 k_0 E_a}{R g(x)} \right) - 1.0516 \frac{E_a}{RT} \tag{12}
\]

Again, \( \ln [\beta] \) versus \( 1/T \) gives straight line. The \( E_a \) can be calculated from the slope of the line. Also, there is an \( E_a \) value at each fractional conversion \( x \).

3. Results and discussion

3.1. Biomass yields

For this investigation \( N. \) *oculta* and \( C. \) *vulgaris* microalgae samples were collected after 10 days of cultivation in batch processes. The biomass yields of \( N. \) *oculta* and \( C. \) *vulgaris* are 0.86 g/L and 0.9 g/L. The corresponding biomass productivities are 0.0859 g/L/day and 0.0899 g/L/day, respectively. The biomass productivities was determined from the difference between initial and final culture concentration in (g/L) divided by the culture duration. One can consider the biomass productivity for the both the algae species are in the lower side. The possible reason for this low biomass productivity may be due to the low starting concentration of the culture (1 mg/L). According to Chiu et al. (2008) the biomass yields is get affected by the initial cell concentration, however when high density inoculums is used the biomass yield will be significantly greater than when low density used for culturing.

3.2. Thermal characteristics of microalgae strains

Table 1 shows the approximate and ultimate analysis of \( N. \) *oculta* and \( C. \) *vulgaris*. Approximate analysis is found that the moisture content, ash, volatile matter, fixed carbon and heating values are different for \( N. \) *oculta* than those of \( C. \) *vulgaris* in the culture product. It can be even more confirmed that the elemental carbon, hydrogen and oxygen content also higher for \( N. \) *oculta*.

TG and DTG profiles show in Fig. 1 for \( N. \) *oculta* and \( C. \) *vulgaris* at different heating rates 5, 10, 15 and 20 °C/min. Fig. 1 shows the TG and DTG profiles of both the \( N. \) *oculta* and \( C. \) *vulgaris* algae species considered for this study. One can see both the microalgae species
shows similar thermal behavior in the first burning stage up to temperature of 220 °C. In case of C. vulgaris a small change in trend was observed just before the maximum peak while this change not recorded clearly for N. oculta. Also, N. oculta shows high decomposition rate at the last peaks than C. vulgaris confirmed from DTG plots for both strains.

In general, the thermal decomposition processes can be classified into three stages, first stage where the devolatilization of volatile compounds and moisture occur, at the second sages most of the weight loss is observed, and the last stage wherein weight loss is limited heat transfer from the furnace pan to the sample, and thermal conductivity, so with increasing the heating rate the temperature of 220 °C, the weight loss decreases slowly and this stage is associated with the decomposition of the solid residual (Wu et al., 2014).

Moreover, the maximum peak temperature (Tpeak) for N. oculta is slightly higher than C. vulgaris for all heating rates. Also, the corresponding maximum decomposition rates (dx/dt)max and (dx/dT)max is higher in N. oculta than C. vulgaris as shown in Table 2. If these temperatures at the maximum peak temperature (Tpeak) for microalgae biomass decomposition compared to other biomass like corncob, sawdust, palm shell and coconut shell as described by Chaiwong et al. (2013), we found that N. oculta and C. vulgaris have the lowest temperatures.

Ash is considered as byproduct for biomass thermal decomposition, however in real operation like in pyrolysis and gasification high values of ash content is undesirable and its would influence the process design and operation since it decreases the final products quality and consequently the need for purification process (Bi and He, 2013). Ashes in microalgae mainly formed by metal compounds, however different pre-treatment processes such as washing before the combustion processes are suggested by several researches to reduce the mineral content (López-González et al., 2014). In this study, C. vulgaris showed slightly high ash content than N. oculta and in term of heating value N. oculta is better as recorded in Table 1.

### 3.3 Effects of heating rate

Generally, when the heating rate increased the temperature at the maximum peak is tend to be delayed, a similar results was reported by Chen et al. (2011) and Chen et al. (2013) for C. vulgaris decomposition.

Gai et al. (2013) postulate that since the biomass has poor thermal conductivity, so with increasing the heating rate the temperature gradient inside the biomass is increased resulting into limited heat transfer from the furnace pan to the sample, and

### Table 1
Approximate analysis and ultimate analysis.

<table>
<thead>
<tr>
<th>Approximate analysis (%)</th>
<th>Nannochloropsis oculta</th>
<th>Chlorella vulgaris</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>6.71 ± 0.29</td>
<td>6.89 ± 0.44</td>
</tr>
<tr>
<td>Ash</td>
<td>6.40 ± 0.47</td>
<td>6.86 ± 1.41</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>78.94 ± 2.61</td>
<td>78.40 ± 2.05</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>7.95</td>
<td>7.85</td>
</tr>
<tr>
<td>Heating value (MJ/kg)</td>
<td>15.07</td>
<td>14.94</td>
</tr>
</tbody>
</table>

#### Ultimate analysis (%)

<table>
<thead>
<tr>
<th></th>
<th>Nannochloropsis oculta</th>
<th>Chlorella vulgaris</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>40.98</td>
<td>40.67</td>
</tr>
<tr>
<td>H</td>
<td>5.31</td>
<td>5.27</td>
</tr>
<tr>
<td>O</td>
<td>39.99</td>
<td>39.70</td>
</tr>
</tbody>
</table>

The standard deviation calculated using STDEV in Microsoft Excel 2010.

Fixed carbon calculated by difference.

### Table 2
Maximum peak characteristics.

<table>
<thead>
<tr>
<th>β</th>
<th>Nannochloropsis oculta</th>
<th>Chlorella vulgaris</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tpeak</td>
<td>(dx/dt)max</td>
<td>(dx/dT)max</td>
</tr>
<tr>
<td>5</td>
<td>278.20 ± 0.15</td>
<td>3.42 ± 0.01</td>
</tr>
<tr>
<td>10</td>
<td>283.47 ± 0.16</td>
<td>6.78 ± 0.04</td>
</tr>
<tr>
<td>15</td>
<td>285.50 ± 0.02</td>
<td>10.82 ± 0.21</td>
</tr>
<tr>
<td>20</td>
<td>287.24 ± 0.23</td>
<td>15.26 ± 0.01</td>
</tr>
</tbody>
</table>

The standard deviation calculated using STDEV in Microsoft Excel 2010.

T in (°C), (dx/dt)max in (wt%/min), (dx/dT)max in (wt%/K).

### Table 3
Estimated reaction kinetic parameters using the nth order model fitting.

<table>
<thead>
<tr>
<th>β, °C/min</th>
<th>Nannochloropsis oculta</th>
<th>Chlorella vulgaris</th>
</tr>
</thead>
<tbody>
<tr>
<td>k0, min⁻¹</td>
<td>n</td>
<td>Ea, kJ/mol</td>
</tr>
<tr>
<td>5</td>
<td>3.37748 × 10⁰</td>
<td>6.06432</td>
</tr>
<tr>
<td>10</td>
<td>4.2576 × 10⁰</td>
<td>6.48867</td>
</tr>
<tr>
<td>15</td>
<td>9.1346 × 10⁰</td>
<td>6.79387</td>
</tr>
<tr>
<td>20</td>
<td>1.04168 × 10¹</td>
<td>6.97765</td>
</tr>
</tbody>
</table>

### Table 4
Comparison between average reaction kinetics parameters evaluated using nth order model from previous studies and this work.

<table>
<thead>
<tr>
<th>Microalgae</th>
<th>β, °C/min</th>
<th>Atmosphere</th>
<th>Ea, kJ/mol</th>
<th>k0, min⁻¹</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorococcum humicola</td>
<td>5, 10, 20 and 80</td>
<td>Nitrogen</td>
<td>189.99</td>
<td>2.4359 × 10¹⁰</td>
<td>Kirtania and Bhattacharya (2013)</td>
</tr>
<tr>
<td>Nannochloropsis oculta</td>
<td>5, 10, 15 and 20</td>
<td>Air</td>
<td>106.87</td>
<td>6.8011 × 10⁹</td>
<td>Present work</td>
</tr>
<tr>
<td>Chlorella vulgaris</td>
<td>5, 10, 15 and 20</td>
<td>Air</td>
<td>92.36</td>
<td>3.8216 × 10⁸</td>
<td>Present work</td>
</tr>
</tbody>
</table>
Apparent activation estimated using KAS and FWO methods.

![Graph](image)

Fig. 4. The plot of \( \ln( \frac{\alpha}{T^2} ) \) versus \( 1/T \) for different \( \alpha \) values for KAS method for (a) \textit{Nannochloropsis oculta} and (b) \textit{Chlorella vulgaris}.

therefore shifting the decomposition temperatures, on other words delay will occur in the sample temperature due to the rapid change in the furnace temperature. Also they argued that when heating rate is increased the residence time of the sample inside the combustion furnace is shorten and as consequences the corresponding initial and final decomposition temperatures are get affected (delayed). This evidences supported again by Liang et al. (2014) for the thermal decomposition process of smooth cordgrass, affected (delayed). This evidences supported again by Liang et al. (2014) for the thermal decomposition process of smooth cordgrass, affected (delayed). This evidences supported again by Liang et al. (2014) for the thermal decomposition process of smooth cordgrass, affected (delayed).

![Graph](image)

Table 5
Apparent activation estimated using KAS and FWO methods.

<table>
<thead>
<tr>
<th></th>
<th>KAS</th>
<th>FWO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Slope</td>
<td>( E_a ), kJ/mol</td>
</tr>
<tr>
<td><strong>Nannochloropsis oculta</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>21939</td>
<td>182.4</td>
</tr>
<tr>
<td>0.4</td>
<td>26602.6</td>
<td>221.1</td>
</tr>
<tr>
<td>0.6</td>
<td>-12919.6</td>
<td>107.4</td>
</tr>
<tr>
<td>0.8</td>
<td>-10334.7</td>
<td>85.9</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td>149.2</td>
</tr>
<tr>
<td><strong>Chlorella vulgaris</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>-28873.2</td>
<td>240.0</td>
</tr>
<tr>
<td>0.4</td>
<td>-38656.4</td>
<td>321.0</td>
</tr>
<tr>
<td>0.6</td>
<td>-19607.9</td>
<td>163.0</td>
</tr>
<tr>
<td>0.8</td>
<td>-15990.9</td>
<td>132.9</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td>214.3</td>
</tr>
</tbody>
</table>

mass when high heating rates is used. In addition, Idris et al. (2010) reported that when heating rate is decreased, residual of the thermal decomposition reaction decreased too.

3.4. Evaluation of the model-fitting method

Experimental and modeling TG curves at (a) \( \beta = 5 \ ^\circ \text{C}/\text{min} \), (b) \( \beta = 10 \ ^\circ \text{C}/\text{min} \), (c) \( \beta = 15 \ ^\circ \text{C}/\text{min} \) and (d) \( \beta = 20 \ ^\circ \text{C}/\text{min} \) for \textit{N. oculta} shown in Fig. 2 and for \textit{C. vulgaris} in Fig. 3. The fitting of the thermal weight loss with the nth order rate model described by Eq. (4) shows excellent prediction to the experimental values of the decomposition processes for both species. However, model-fitting enables using of just one single heating rated each time for determination of reaction kinetics parameters including the activation energy, and actually this is considered as drawback, since the activation energy is get affected by the heating rate due to mass and heat transfer consequences (López et al., 2013).

Table 3 shows the estimated reaction kinetic parameters using the nth order rate model described by Eq. (4). Although, the proposed model shows best fitting the experimental data but the coefficient of determination \( (R^2) \) values from Table 3 are to some extent much lesser than unity. This because for such nonlinear model is misleading to use the coefficient of determination \( R^2 \). Therefore, the coefficient of determination \( R^2 \) is an inappropriate measure for the goodness of fit in case of nonlinear models (Spiess and Neumeyer, 2010). More discussions about fitting data to nonlinear models, \( R^2 \) determination and its suitability, and about nonlinear methods for regression are provided by (Filzmoser, 2008; Spiess and Neumeyer, 2010). Other statistical expression to examine the fitting accuracy for nonlinear modeling of the thermal decomposition of biomass is used by Vamvuka et al. (2003) which is based on the deviation between the observed and calculated \( (dx/dt) \) with respect to the maximum observed \( (dx/dt) \).

The estimated average reaction kinetic parameters described in Table 4, shows high value of reaction order \( (n) \), since the reaction orders were 6.58 and 5.76 for \textit{N. oculta} and \textit{C. vulgaris}, respectively. A similar result of such high value of \( (n) \) for nth order reaction model was reported by Kirtania and Bhattacharya (2013) in pyrolysis kinetics of fresh water alga strain \textit{Chlorococcum humicola}.

In addition, the approximate analytical solution developed by Coats–Redfern method gave identical TG curve to those evaluated by the numerical solution generated using NDSolve command in Mathematica 9 software, which is mean that the Coats–Redfern method is misleading to use the coefficient of determination \( R^2 \) extent much lesser than unity. This because for such nonlinear models \( \alpha = 0.8 \), \( \alpha = 0.6 \), \( \alpha = 0.4 \), and \( \alpha = 0.2 \) shown in Fig. 2 and for \( C/min \), (c) \( C/min \) for \textit{N. oculta} and \textit{C. vulgaris}, respectively. A similar result of such high value of \( (n) \) for nth order reaction model was reported by Kirtania and Bhattacharya (2013) in pyrolysis kinetics of fresh water alga strain \textit{Chlorococcum humicola}.

In addition, the approximate analytical solution developed by Coats–Redfern method gave identical TG curve to those evaluated by the numerical solution generated using NDSolve command in Mathematica 9 software, which is mean that the Coats–Redfern method is an accurate approximation, and it can be used safely.

3.5. Evaluation of the iso-conversional methods

Using iso-conversional models KAS and FWO the activation energy was determined using different heating rate experimental data, hence the evaluation of apparent activation energy was done...
by the same methods described before, and the values listed for $E_a$ and $k_o$ calculated from $\text{KAS}$ and $\text{FWO}$ methods is very sensitive towards small changes in the experimental data than the model fitting techniques described before, however a considerable change are noticed in the average activating energy if experiments replicated. For all reviewed studies the difference between the average values of activation energy estimated by $\text{KAS}$ and $\text{FWO}$ are in significance for various microalgal biomass under different atmosphere with different heating rate used (Table 6).

Although, the apparent activation energy is not constant and it varies during the conversion as clear in Fig. 6, which means there is more than single reaction mechanism for the biomass thermal decomposition process (Słopiecka et al., 2012). Therefore, single reaction mechanism at each thermal decomposition stage can be used to evaluate the activation energy and other reaction parameters instead of single mechanism for the whole process (López-González et al., 2014).

To analyze the trend of activation energy versus reaction conversion we found that for all decomposition stage $\alpha = 0.2$, $0.4$, $0.6$, and $0.8$ the average estimated activation energy by $\text{KAS}$ and $\text{FWO}$ methods for $N. \text{oculta}$ is lower than that for $C. \text{vulgaris}$. A general trend is that at small $\alpha$, activation energy increase with increasing the reaction conversion till reaching the maximum at almost a middle conversion, then the value of activation energy decreases sharply until the end of combustion process as shown in Fig. 6. Therefore, the facts that apparent activation energy change during the decomposition indicates the present of different reaction mechanisms throughout the thermal decomposition process, since these iso-conversational methods do not depend on a reaction mechanism for activation energy determination (Słopiecka et al., 2012).

Multi stages kinetics modeling are normally being used for this purpose, since the thermal decomposition process is divided into devolatilization stage and oxidation stage which also includes the
devolatilization stage and oxidation stage which also includes the

Table 6
Comparison between reaction kinetics parameters evaluated $\text{KAS}$ and $\text{FWO}$ from previous studies and including this work.

<table>
<thead>
<tr>
<th>Microalgae</th>
<th>$\beta$, °C/min</th>
<th>Atmosphere</th>
<th>$E_a$, kJ/mol $\text{KAS}$</th>
<th>$E_a$, kJ/mol $\text{FWO}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Chlorella vulgaris}$</td>
<td>10, 20 and 40</td>
<td>$\text{O}_2$: $\text{N}_2$ (20:80)</td>
<td>134.53</td>
<td>134.03</td>
<td>Chen et al. (2011)</td>
</tr>
<tr>
<td>$\text{Chlorella vulgaris}$</td>
<td>10, 20 and 40</td>
<td>$\text{O}_2$: $\text{N}_2$ (50:50)</td>
<td>163.49</td>
<td>165.74</td>
<td>Chen et al. (2011)</td>
</tr>
<tr>
<td>$\text{Chlorella vulgaris}$</td>
<td>10, 20 and 40</td>
<td>$\text{O}_2$: $\text{N}_2$ (60:40)</td>
<td>211.24</td>
<td>209.92</td>
<td>Chen et al. (2011)</td>
</tr>
<tr>
<td>$\text{Chlorella vulgaris}$</td>
<td>10, 20 and 40</td>
<td>$\text{O}_2$: $\text{N}_2$ (80:20)</td>
<td>242.33</td>
<td>241.04</td>
<td>Chen et al. (2011)</td>
</tr>
<tr>
<td>$\text{Macrocystis pyrifera}$</td>
<td>5, 10, 20, and 30</td>
<td>$\text{Ar}$</td>
<td>221.4</td>
<td>219.7</td>
<td>Zhao et al. (2011)</td>
</tr>
<tr>
<td>$\text{Potaengeton crispus}$</td>
<td>10, 30 and 50</td>
<td>$\text{N}_2$</td>
<td>143.2</td>
<td>145.3</td>
<td>Li et al. (2012)</td>
</tr>
<tr>
<td>$\text{Sargassum thunbergii}$</td>
<td>10, 30 and 50</td>
<td>$\text{N}_2$</td>
<td>185.6</td>
<td>185.4</td>
<td>Li et al. (2012)</td>
</tr>
<tr>
<td>$\text{Tetraselmis sueca}$</td>
<td>5, 10, and 15</td>
<td>$\text{O}_2$: $\text{N}_2$ (21:79)</td>
<td>70.09</td>
<td>75.81</td>
<td>Tahmasbeh et al. (2013)</td>
</tr>
<tr>
<td>$\text{Chlorella vulgaris}$</td>
<td>10, 20 and 40</td>
<td>$\text{O}_2$: $\text{N}_2$ (20:80)</td>
<td>37.58</td>
<td>42.11</td>
<td>Chen et al. (2013)</td>
</tr>
<tr>
<td>$\text{Chlorella vulgaris}$</td>
<td>10, 20 and 40</td>
<td>$\text{O}_2$: $\text{CO}_2$ (20:80)</td>
<td>46.13</td>
<td>50.22</td>
<td>Chen et al. (2013)</td>
</tr>
<tr>
<td>$\text{Chlorella vulgaris}$</td>
<td>10, 20 and 40</td>
<td>$\text{O}_2$: $\text{CO}_2$ (50:50)</td>
<td>53.75</td>
<td>57.31</td>
<td>Chen et al. (2013)</td>
</tr>
<tr>
<td>$\text{Chlorella vulgaris}$</td>
<td>10, 20 and 40</td>
<td>$\text{O}_2$: $\text{CO}_2$ (80:20)</td>
<td>56.27</td>
<td>59.50</td>
<td>Chen et al. (2013)</td>
</tr>
<tr>
<td>$\text{Nannochloropsis oculata}$</td>
<td>5, 10, 15 and 20</td>
<td>$\text{Air}$</td>
<td>149.23</td>
<td>151.78</td>
<td>Present work</td>
</tr>
<tr>
<td>$\text{Chlorella vulgaris}$</td>
<td>5, 10, 15 and 20</td>
<td>$\text{Air}$</td>
<td>214.35</td>
<td>213.44</td>
<td>Present work</td>
</tr>
</tbody>
</table>

* Macroalgae.
last step of carbonate decomposition and metal volatilization (López-González et al., 2014). Multi-zone pyrolysis analysis was also involved in study done by Wu et al. (2014) for the thermal analysis and modeling of aquatic biomass decomposition including Dunaliella tertiolecta microalgal.

4. Conclusions

The TGA analysis shows that decomposition profiles are different for the two studied microalgal species (N. oculta and C. vulgaris). The TGA study also reveals that the biomass culture conditions have significant influences on the produced biomass compositions and their thermal decomposition characteristics. The thermal decomposition kinetics analysis shows that the thermal degradation of the studied microalgae biomass follows different mechanisms. The estimated values of activation energy for C. vulgaris (215 kJ/mol) is significantly higher than that of N. oculta (150 kJ/mol).

Acknowledgements

King Abdulaziz City for Science and Technology (KACST) – Saudi Arabia through the Science & Technology Unit at King Fahd University of Petroleum & Minerals (KFUPM) is acknowledged for funding this work through project No. KACST ARP# A-T-32-62.

References


Filizmoor, P., 2008. Linear and Nonlinear Methods for Regression and Classification and applications in R.