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Isothermal and non-isothermal torrefaction characteristics and kinetics of microalga Scenedesmus obliquus CNW-N

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Highlights

- The pyrolysis of S. obliquus CNW-N is characterized by four-stage decomposition.
- Non-isothermal torrefaction gives more severe pretreatment than the isothermal one.
- Increasing the heating rate of non-isothermal torrefaction intensifies the pretreatment severity.
- The activation energy of isothermal is 57.52 kJ mol$^{-1}$.
- The activation energy of non-isothermal torrefaction is between 40.14 and 88.41 kJ mol$^{-1}$.

Graphical Abstract

Abstract

Isothermal and non-isothermal torrefaction characteristics and kinetics of microalga Scenedesmus obliquus (S. obliquus) CNW-N are studied using thermogravimetric analysis. The pyrolysis of S. obliquus CNW-N with increasing temperature is characterized by four-stage decomposition. Depending on the torrefaction temperature, light, mild, and severe torrefaction from the weight loss and the maximum decomposition rate of the microalga can be classified. Under the same average temperature and torrefaction duration, non-isothermal torrefaction gives more severe pretreatment than the isothermal one. Increasing the heating rate of non-isothermal torrefaction also intensifies the pretreatment severity. Therefore, microalgae can be torrefied via non-isothermal torrefaction in a shorter time under the same pretreatment extent. The atomic H/C ratio in the microalga decreases with increasing torrefaction severity, whereas the atomic O/C ratio rises. The analysis suggests that the activation energy of isothermal torrefaction is 57.52 $\times$ 10$^3$ J mol$^{-1}$, while it is between 40.14 $\times$ 10$^3$ and 88.41 $\times$ 10$^3$ J mol$^{-1}$ for non-isothermal torrefaction.

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1. Introduction

Biomass energy or bioenergy is a potential renewable energy and is also the fourth largest primary energy in the world, next to oil, coal and natural gas (Chen et al., 2012). While biofuels, such as bioethanol, biodiesel, and biogas, are developed as alternative fuels to fossil fuels, microalgae have been considered as good substitutes for fuel production because of their advantages.

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of abundant distribution, fast growth, high photosynthetic or carbon fixing efficiency, and high biomass production when compared to lignocellulosic materials (Peng et al., 2001a,b). Unlike lignocelluloses which are mainly composed of cellulose, hemicellulose, and lignin (Chen et al., 2010), microalgae mainly contain carbohydrates, proteins, and lipids (Ho et al., 2010).

Regarding the conversion processes of biomass to energy from microalgae, as a whole, the technologies can be categorized into two pathways with one the thermochemical way and the other the biochemical route (Rizzo et al., 2013). In the thermochemical route, the methods consist of combustion, gasification, liquefaction, and pyrolysis; the biochemical methods include anaerobic digestion and alcoholic fermentation process, utilizing microalgal biomass (mainly the carbohydrates) as feedstock. In addition to the aforementioned pathways, transesterification can also be used to covert microalgal lipids into biodiesel (Mata et al., 2010). Pyrolysis is a method to produce bio-oil where biomass or microalgae are thermally degraded in inert or oxygen-free environments at temperatures ranging from 350 to 750 °C (Elliott, 2007; Zhang et al., 2007). If the reaction temperature is lowered to the range of 200–300 °C, the thermal decomposition extent of biomass is reduced and solid residues rather than condensable liquids are the prime products. This thermal process is called torrefaction (Lu et al., 2012).

Raw biomass is characterized by hygroscopic nature, high moisture content, large volume, low density, low calorific value, and low grindability. The properties of biomass undergoing torrefaction can be improved greatly. For example, torrefied biomass becomes hydrophobic in nature, and its calorific value and grindability are substantially enhanced (Chen and Kuo, 2010; Rouset et al., 2011; Peng et al., 2012; Sabir et al., 2013; Tran et al., 2013). As a result, the storage and delivery of torrefied biomass are easier than those of its parent biomass. In addition, the utilization efficiency of torrefied biomass (e.g., gasification) would be higher (Chen et al., 2013).

Many studies concerning the conversion of microalgae to bio-oil, biodiesel, and bioethanol have been carried out (Amin, 2009; Brennan and Owende, 2010; Ahmad et al., 2011; Chen et al., 2011a; John et al., 2011). However, very little research has been performed to investigate the impact of torrefaction upon microalgae for solid fuel production. A recent study by Wu et al. (2012) might be the only research reporting that the higher heating value of microalgae from the torrefaction at 300 °C for 30 min was increased by 26.7% and the Hardgrove grindability index (HGI) of the torrefied microalgal residue exceeded that of sub-bituminous coal when the torrefaction temperature was up to 250 °C. So far there is no information in the literature concerning the study of torrefaction kinetics on microalgae. Moreover, the non-isothermal torrefaction process of biomass has not yet been explored.

In light of this, the present study was undertaken to investigate isothermal and non-isothermal torrefaction characteristics and kinetics of microalgae using a thermogravimetric analyzer. Although the amount of a sample in a thermogravimetric analyzer is usually by far less than those in a reactor or oven, their reaction environments are similar to each other (Chen and Kuo, 2011). Using a thermogravimetric analyzer for the analysis of biomass torrefaction is preferable since the weight loss dynamics of biomass can be measured precisely (Peng et al., 2001b; Agrawal and Chakraborty, 2013). In addition, the reaction dynamics of both isothermal and non-isothermal heating can be determined from the thermogravimetric analysis (TGA).

2. Methods

2.1. Microalgae and analyses

The microalga studied in this work was Scenedesmus obliquus (S. obliquus) CNW-N, which was isolated from freshwater in southern Taiwan (Ho et al., 2010). The microalga consumes CO2 efficiently while it grows. Hence, it is appropriate to cultivate S. obliquus CNW-N for simultaneous CO2 capture and solid fuel production via torrefaction. Detailed information of S. obliquus CNW-N and of the photobioreactor operations for the microalgal growth can be found elsewhere (Ho et al., 2010).

The basic properties of raw microalgae were measured through composition, proximate, elemental, and calorific (IKA C2000 Basic) analyses. In the composition analysis, crude protein, crude lipid, and carbohydrates were determined by Kjeldehl method, Soxhlet-extract method, and phenol–sulfuric acid method, respectively (Peng et al., 2001a). The proximate analysis was performed in accordance with the standard procedure of American Society for Testing and Materials (Chen et al., 2011b). The elemental analysis was carried out using an elemental analyzer (PerkinElmer 2400 Series II CHNS/O Elemental Analyzer) to measure the weight percentages of C, H, and N in the microalgal biomass. The calorific value of the sample was detected by a bomb calorimeter (IKA C5000).

2.2. Thermogravimetric analysis

The thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) analysis of the microalgae were carried out by use of a thermogravimetric analyzer (TG, PerkinElmer Diamond TG/DTA). In TGA, the particle sizes of sieved microalga powder were controlled between 100 and 200 mesh (i.e. 75–150 μm) and around 5 mg of the sample was used for each experimental run. The flow rate of carrier gas (i.e. N2) was fixed at 100 cc min−1 (STP).

The operation of TGA was cataloged into three different modes: (1) constant heating rate; (2) isothermal torrefaction; and (3) non-isothermal torrefaction. The first mode was for investigating the microalga pyrolysis, and the heating rate in the TG was controlled at 20 °C min−1. Once the heating temperature in the TG reached 105 °C, it was held for 5 min to completely remove moisture and
provide a basis for analysis. The heating process in the second mode was made up of two dynamic heating periods and an isothermal heating period after the temperature in the TG was beyond 105 °C, whereas it comprised three dynamic heating periods in the third mode. To reduce the impact of heating process before reaching 105 °C on microalgae torrefaction, the heating rate in the second and third modes was controlled at 40 °C min⁻¹ prior to commencing torrefaction. In all the operating modes, the heating temperature was in the range of 25–800 °C. Detailed heating processes of the three operating modes are listed in Table 1.

As mentioned earlier, torrefaction is a thermal pretreatment process at temperatures between 200 and 300 °C. Therefore, five different torrefaction temperatures of 200, 225, 250, 275 and 300 °C were taken into account for isothermal torrefaction. Considering non-isothermal torrefaction, three different heating rates of 0.5, 1.0, and 1.5 °C min⁻¹ during torrefaction were performed. In both isothermal and non-isothermal torrefaction, the duration was fixed at 1 h. To ensure the measured quality of the TGA, the TG was periodically calibrated and the experiment under any given condition was usually carried out more than twice. The relative error among the measurements of TGA was controlled within 3%.

2.3. Torrefaction kinetics

The reaction rate of a sample is typically given as follows (Lu et al., 2013):

\[
\frac{dX}{dt} = k(1 - X)^n \quad (1)
\]

where \(k\) is the reaction rate constant and \(n\) is the order of reaction. \(X\) is the conversion of the sample and is defined by

\[
X = \frac{W_i - W}{W_i - W_f} \quad (2)
\]

where \(W, W_i,\) and \(W_f\) designate the instantaneous sample weight, initial sample weight, and final sample weight, respectively. To provide a standard of analysis, the initial and final sample weights are identified at 105 and 800 °C, respectively (Chen and Kuo, 2011).

2.3.1. Isothermal torrefaction

For isothermal torrefaction, the conversion of a sample is expressed as (Chen and Kuo, 2011):

\[
\begin{align*}
\ln \left( \frac{1 - X}{1 - X_0} \right) &= k(t - t_0) & \text{if } n = 1 \\
(1 - X)^{1-n} - (1 - X_0)^{1-n} &= k(n - 1)(t - t_0) & \text{if } n \neq 1
\end{align*}
\]

where \(X_0\) is the conversion of the sample at the beginning of torrefaction (\(t = t_0\)). At the condition of \(n = 1\), Eq. (3) reveals that the plot of \(\ln(1 - X)^{1-1}\) versus torrefaction time \((t - t_0)\) gives a straight line with the slope equal to the rate constant \(k\). If the order of reaction is not unity (i.e. \(n \neq 1\)), the plot of \((1 - X)^{1-n}\) versus torrefaction time gives a straight line with the slope equal to \((n - 1)k\). For a given material at various torrefaction temperatures, a set of data of rate constant can be obtained. The relationship between the reaction rate constant and reaction temperature is normally assumed to obey Arrhenius law, that is

\[
k = A \exp \left( -\frac{E_a}{RT} \right) \quad (4)
\]

The logarithmic form of Eq. (4) gives

\[
\ln k = \ln A - \frac{E_a}{RT} \quad (5)
\]

When a set of reaction rate constant and torrefaction temperature is obtained, the plot \(\ln k\) versus \(1/T\) gives a straight line with the slope equal to \(-E_a/R\) and the intercept equal to \(\ln A\). From the slope and intercept, the activation energy \((E_a)\) and pre-exponential factor \((A)\) in the kinetics of microalgae torrefaction are obtained.

2.3.2. Non-isothermal torrefaction

With regard to non-isothermal torrefaction, substituting Eq. (4) into Eq. (1) gives

\[
\frac{dX}{dt} = A \exp \left( -\frac{E_a}{RT} \right) (1 - X)^n \quad (6)
\]

For a constant heating rate \(\beta = dT/dt\), Eq. (6) can be rearranged to the following form

\[
\frac{dX}{dT} = \frac{1}{\beta} A \exp \left( -\frac{E_a}{RT} \right) (1 - X)^n \quad (7)
\]

The integral method based on Coats and Redfern (CR) equation (1964) was used to obtain the approximate integration of Eq. (7). The results are indicated below (Lu et al., 2013)

\[
\left\{ \begin{align*}
\ln \left[ \frac{1 - (1 - X)^{1-n}}{1 - (1 - X_0)^{1-n}} \right] &= \ln \frac{\beta}{E_a} \left[ 1 - \frac{2RT}{E_a} \right] - \frac{E_a}{RT} & \text{if } n = 1 \\
\ln \left[ \frac{1 - (1 - X)^{1-n}}{1 - (1 - X_0)^{1-n}} \right] &= \ln \frac{\beta}{E_a} \left[ 1 - \frac{2RT}{E_a} \right] - \frac{E_a}{RT} & \text{if } n \neq 1
\end{align*} \right. \quad (8)
\]

For most reactions, the value of \(2RT/E_a\) is very small. Eq. (8) can thus be approximated by

\[
\left\{ \begin{align*}
\ln \left[ \frac{1 - (1 - X)^{1-n}}{1 - (1 - X_0)^{1-n}} \right] &= \ln \frac{\beta}{E_a} - \frac{E_a}{RT} & \text{if } n = 1 \\
\ln \left[ \frac{1 - (1 - X)^{1-n}}{1 - (1 - X_0)^{1-n}} \right] &= \ln \frac{\beta}{E_a} - \frac{E_a}{RT} & \text{if } n \neq 1
\end{align*} \right. \quad (9)
\]

The plot of \(\ln[1 - (1 - X)/T^2]\) versus \(1/T\) gives a linear line for \(n = 1\), while the plot of \(\ln[1 - (1 - X)/(1 - n)/T^2]\) versus \(1/T\) is a linear line for \(n \neq 1\). Accordingly, the activation energy and pre-exponential factor of microalgae non-isothermal torrefaction can be determined from the slope and intercept of the regression line, respectively.

3. Results and discussion

3.1. Basic properties

The basic properties of S. obliquus CNW-N, such as composition, proximate, elemental, and calorific (higher heating value, HHV) analyses, are described in Table 2. Crude protein in S. obliquus

<table>
<thead>
<tr>
<th>Mode</th>
<th>Heating process</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (pyrolysis)</td>
<td>Room temperature → 105 °C (heating rate = 20 °C min⁻¹) → keep at 105 °C for 5 min → 800 °C (heating rate = 20 °C min⁻¹)</td>
</tr>
<tr>
<td>2 (isothermal torrefaction)</td>
<td>Room temperature → 105 °C (heating rate = 40 °C min⁻¹) → keep at 105 °C for 5 min → 200, 225, 250, 275, or 300 °C (heating rate = 40 °C min⁻¹) → isothermal torrefaction for 1 h → 800 °C (heating rate = 40 °C min⁻¹)</td>
</tr>
<tr>
<td>3 (non-isothermal torrefaction)</td>
<td>Room temperature → 105 °C (heating rate = 40 °C min⁻¹) → keep at 105 °C for 5 min → 235, 220, or 205 °C (heating rate = 40 °C min⁻¹) → non-isothermal torrefaction for 1 h (heating rate = 0.5, 1.0, or 1.5 °C min⁻¹) → 800 °C (heating rate = 20 °C min⁻¹)</td>
</tr>
</tbody>
</table>
CNW-N is 30.38 wt.%, which accounts for the largest content in the microalga. Carbohydrate reveals 13.41 wt.% in S. obliquus CNW-N, and crude lipid is as low as 4.66 wt.%. The moisture content is also low (=5.13 wt.%), whereas others are 22.98 wt.%. With regard to the proximate analysis, S. obliquus CNW-N contains around 70.00 wt.% of volatile matter which is much higher than fixed carbon (=5.29 wt.%), and the ash content is as high as 24.71 wt.%. From the elemental analysis, the weight percentages of C, H, N, and O in S. obliquus CNW-N are 37.37, 5.80, 6.82, and 50.02 wt.%, respectively. The nitrogen content in the microalga is much higher than that in lignocellulosic biomass (Chen et al., 2012). This could be a consequence of a high protein content in the microalgal biomass. Alternatively, in view of relatively high oxygen contained in consequence of a high protein content in the microalgal biomass. 

3.2. Pyrolytic characteristics

Fig. 1 shows the distributions of the TGA and DTG curves of S. obliquus CNW-N at a heating rate of 20 °C min⁻¹ to figure out its pyrolytic characteristics in an inert or N₂ environment where the heating temperature ranges from 25 to 800 °C. The entire pyrolytic process can be divided into four stages. The entire DTG profile of S. obliquus CNW-N is similar to that of Chlorella spp. observed by Rizzo et al. (2013) but different from raw wood or coal pyrolysis featured by the three-stage decomposition (Lu et al., 2013). In the first stage (25–200 °C), the weight loss of the biomass, resulting from dehydration or the elimination of water and light volatiles release (Zou et al., 2010), is slight. The peak developed at 105 °C is due to the drying for 5 min. The second stage (200–430 °C) is the main pyrolysis or devolatilization process. The pyrolysis reactions include depolymerization, decarboxylation, and cracking (Peng et al., 2001a,b). The peak exhibited in this stage could be due to the thermal decomposition of carbohydrate and protein (Rizzo et al., 2013), especially from the latter because protein in S. obliquus CNW-N is as high as 30.38 wt.%. The maximum decomposition rate is 0.37% min⁻¹ occurring at around 320 °C. This reveals that the thermal degradation of S. obliquus CNW-N is sensitive to the heating process in the vicinity of this temperature. In the third stage (430–530 °C), a smaller peak stemming from lipid pyrolysis is observed (Rizzo et al., 2013). The maximum decomposition rate (=0.085% min⁻¹) in the third stage is substantially lower than that in the second stage in that the lipid content of S. obliquus CNW-N is by far lower than protein and carbohydrate contents. In the fourth stage (530–800 °C), a low level of DTG curve is attributed to the continuous and slow weight loss of carbonaceous matters in the solid residue (Rizzo et al., 2013).

3.3. Isothermal torrefaction

From the TGA curves and temperature distributions shown in Fig. 2a, a higher torrefaction temperature leads to a more significant microalga weight loss in the course of torrefaction. For S. obliquus CNW-N at the torrefaction temperatures of 200 and 225 °C, the weight loss is less than 10 wt.% and the solid yield is higher than 80%, as listed in Table 3. Moreover, the maximum decomposition rates after the torrefaction at 200 and 225 °C are 0.37 and 0.35% min⁻¹, respectively, which are close to that shown in Fig. 1. Accordingly, the two torrefaction temperatures can be categorized as light torrefaction. The weight loss and solid yield of the microalga at the torrefaction temperature of 250 °C are around 16 wt.% and 76%, respectively, and the maximum decomposition rate is 0.29% min⁻¹. The decay of the maximum decomposition rate from 0.29 to 0.37% min⁻¹ reveals that the biomass affected by the torrefaction at 250 °C is mild, rendering the mild torrefaction. At the torrefaction temperatures of 275 and 300 °C, the weight loss of S. obliquus CNW-N is larger than 23 wt.% while the solid yield is smaller than 68%. In addition, the DTG curves reveal that carbohydrate and protein are consumed greatly from the torrefaction in that the maximum decomposition rates at 275 and 300 °C are abated to 0.17 and 0.10% min⁻¹, respectively. As a consequence, the two torrefaction temperatures can be classified as severe torrefaction. The above observations of TGA and DTG curves are similar to the torrefaction of lignocellulosic biomass (Chen et al., 2011b). That is, the classification of light, mild, and severe torrefaction for lignocellulosic biomass can also be applicable to microalgae torrefaction. On the other hand, Fig. 2b indicates that the torrefaction intensity at 275 °C is higher than that at 300 °C. This indicates that the heating process prior to reaching 300 °C has a crucial impact on the weight loss of S. obliquus CNW-N.

3.4. Non-isothermal torrefaction

The temperature ranges of the three non-isothermal torrefaction processes are presented in Fig. 3a and Table 3 where the mean torrefaction temperature is 250 °C. Corresponding to the heating process, the two torrefaction temperatures can be classified as light torrefaction. The weight loss and solid yield of the microalgae at the torrefaction temperature of 250 °C are around 16 wt.% and 76%, respectively, and the maximum decomposition rate is 0.29% min⁻¹. The decay of the maximum decomposition rate from 0.29 to 0.37% min⁻¹ reveals that the biomass affected by the torrefaction at 250 °C is mild, rendering the mild torrefaction. At the torrefaction temperatures of 275 and 300 °C, the weight loss of S. obliquus CNW-N is larger than 23 wt.% while the solid yield is smaller than 68%. In addition, the DTG curves reveal that carbohydrate and protein are consumed greatly from the torrefaction in that the maximum decomposition rates at 275 and 300 °C are abated to 0.17 and 0.10% min⁻¹, respectively. As a consequence, the two torrefaction temperatures can be classified as severe torrefaction. The above observations of TGA and DTG curves are similar to the torrefaction of lignocellulosic biomass (Chen et al., 2011b). That is, the classification of light, mild, and severe torrefaction for lignocellulosic biomass can also be applicable to microalgae torrefaction. On the other hand, Fig. 2b indicates that the torrefaction intensity at 275 °C is higher than that at 300 °C. This indicates that the heating process prior to reaching 300 °C has a crucial impact on the weight loss of S. obliquus CNW-N.
rates of 0 (i.e. the isothermal torrefaction at 250 °C), 0.5, 1.0, and 1.5 °C min⁻¹, the weight losses of *S. obliquus* CNW-N from the torrefaction are 16.05, 17.71, 20.51, and 23.94 wt.%, respectively (Table 3), while the solid yields are 76.45%, 75.34%, 72.56%, and 69.53%, respectively. The weight drop of *S. obliquus* at the heating rate of 1.5 °C min⁻¹ is relatively slight in the initial torrefaction period, but it becomes drastic in the final torrefaction period due to higher torrefaction temperatures. The higher weight loss at 1.5 °C min⁻¹ illustrates that the role played by the latter torrefaction period on the weight loss is more significant than that by the initial torrefaction period, even though the average torrefaction temperatures in the four cases are the same. Meanwhile, the maximum decomposition rates of *S. obliquus* CNW-N at the heating rates of 0, 0.5, 1.0, and 1.5 °C min⁻¹ are 0.29, 0.28, 0.24, and 0.20% min⁻¹, respectively. The observations of weight loss, solid yield, and the maximum decomposition rate reveal that, under the same average temperature, non-isothermal torrefaction gives more significant thermal degradation than isothermal torrefaction, while a higher heating rate leads to higher torrefaction severity. This implies, in turn, that microalgae can be torrefied by a higher heating rate in a shorter time under the same pretreatment extent.

3.5. van Krevelen diagram

The elemental analysis (C, H, N, and O) of raw *S. obliquus* CNW-N (Table 4) indicates that its atomic H/C, O/C, and N/C ratios are 1.86, 0.51, and 0.16, respectively. The chemical formula of the raw microalgae can thus be expressed as CH_{1.86}O_{0.51}N_{0.16}. In both isothermal and non-isothermal torrefaction, it is noteworthy that increasing torrefaction severity, such as increasing torrefaction temperature or heating rate, diminishes the relative contents of C, H, and N, whereas the relative content of O grows. The van Krevelen diagram of raw and torrefied *S. obliquus* CNW-N shown in Fig. 4 depicts that the H/C ratio decreases with increasing the torrefaction severity and this trend is the same as the
torrefaction of lignocellulosic biomass. On the other hand, when the severity goes up, the atomic O/C ratio increases and this behavior is opposite to the torrefaction of lignocellulosic biomass. This may be attributed to the pronounced decomposition of protein in the course of torrefaction which contains less oxygen. With regard to atomic N/C ratio, it is in the range of 0.14–0.16, implying that the weight loss in the two elements from is in a comparable level. Within the investigated ranges of torrefaction temperature (200–300 °C) and heating rate (0–1.5 °C min⁻¹), the chemical formula of S. obliquus CNW-N can be given by CH₁.18–1.86O₀.44–0.57N₀.14–0.16, as shown in Table 4.

### Table 4
Elemental analyses and the formulas of raw and torrefied S. obliquus CNW-N.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Elemental analysis (wt.%)</th>
<th>Formula CₙHₙOₙN₂ₙ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw material</td>
<td>37.37 5.80 6.82 25.30</td>
<td>CH₁.86O₀.51N₀.16</td>
</tr>
<tr>
<td>Isothermal torrefaction</td>
<td>200 39.26 5.47 7.38 23.19</td>
<td>CH₁.67O₀.44N₀.16</td>
</tr>
<tr>
<td></td>
<td>225 38.58 5.09 7.31 24.33</td>
<td>CH₁.58O₀.47N₀.16</td>
</tr>
<tr>
<td></td>
<td>250 38.42 4.92 7.20 24.76</td>
<td>CH₁.54O₀.48N₀.16</td>
</tr>
<tr>
<td></td>
<td>275 38.02 4.28 7.05 25.94</td>
<td>CH₁.35O₀.53N₀.16</td>
</tr>
<tr>
<td></td>
<td>300 36.93 3.63 6.53 28.21</td>
<td>CH₁.18O₀.57N₀.15</td>
</tr>
<tr>
<td>Non-isothermal torrefaction</td>
<td>235–265 39.29 4.80 6.90 24.31</td>
<td>CH₁.47O₀.46N₀.15</td>
</tr>
<tr>
<td></td>
<td>220–280 39.03 4.51 6.40 25.47</td>
<td>CH₁.39O₀.49N₀.14</td>
</tr>
<tr>
<td></td>
<td>205–295 38.53 4.34 6.40 26.03</td>
<td>CH₁.35O₀.51N₀.14</td>
</tr>
</tbody>
</table>

* a By difference O (%) = 100−C−H−N.

3.6. Torrefaction kinetics

In isothermal torrefaction five torrefaction temperatures are practiced, hence five reaction rate constants can be obtained from the plot of ln(1−X)⁻¹ or (1−X)⁻ⁿ versus torrefaction time, depending on the value of n (i.e. Eq. (3)). In examining the profile of the coefficient of determination (R²) from the regression line of the plot of ln k versus 1/T, the best regression line can be obtained at n = 2 in that the maximum R² develops therein. From the slope (−6918.7) and intercept (=0.016) of the regression line of the plot of ln k versus 1/T, as shown in Fig. 5, the activation
energy and the pre-exponential factor are $57.52 \text{ kJ mol}^{-1}$ and $3.03103 \text{ min}^{-1}$, respectively.

In the DTG curves of the non-isothermal torrefaction processes (Fig. 3b), two-peak distributions for temperature ranging from 200 to 300 °C can be observed. At the heating rate of 0.5 °C min$^{-1}$, two peaks partially overlap, whereas the two separated peaks are exhibited at the heating rates of 1.0 and 1.5 °C min$^{-1}$. The first peak is presumably due to the thermal decomposition of protein while the second peak could be due to the decomposition of xylan and other carbonaceous matters (Zou et al., 2010). The obtained kinetics can be used for solid fuel production from microalgae.

### Table 5

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$A$ (min$^{-1}$)</th>
<th>$R^2$</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isothermal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200–300</td>
<td>57.52</td>
<td>$3.03 \times 10^3$</td>
<td>0.9897</td>
<td>2</td>
</tr>
<tr>
<td>Non-isothermal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heating rate (°C min$^{-1}$)</td>
<td>The first torrefaction peak</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5 200–242</td>
<td>88.41</td>
<td>$4.42 \times 10^6$</td>
<td>0.9547</td>
<td>1</td>
</tr>
<tr>
<td>1.0 200–235</td>
<td>70.55</td>
<td>$1.23 \times 10^7$</td>
<td>0.9872</td>
<td>1</td>
</tr>
<tr>
<td>1.5 200–230</td>
<td>48.28</td>
<td>$6.20 \times 10^7$</td>
<td>0.9847</td>
<td>1</td>
</tr>
<tr>
<td>The second torrefaction peak</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5 242–264</td>
<td>51.70</td>
<td>$4.97 \times 10^7$</td>
<td>0.9993</td>
<td>1</td>
</tr>
<tr>
<td>1.0 235–280</td>
<td>41.16</td>
<td>63.54</td>
<td>0.9979</td>
<td>1</td>
</tr>
<tr>
<td>1.5 230–295</td>
<td>40.14</td>
<td>71.37</td>
<td>0.9958</td>
<td>1</td>
</tr>
</tbody>
</table>

### 4. Conclusion

The pyrolysis of microalgae *S. obliquus* CNW-N in a gravimetric analyzer is featured by four-stage decomposition where the thermal degradation of protein, carbohydrate, and lipid can be clearly identified. According to the torrefaction temperature, light, mild, and severe torrefaction of the microalgae can be classified. A comparison between isothermal and non-isothermal torrefaction suggests that non-isothermal torrefaction gives the more severe pretreatment than the isothermal one, and an increase in the heating rate of non-isothermal torrefaction intensifies the pretreatment severity, even though the average torrefaction temperature is equivalent. The obtained kinetics can be used for solid fuel production from microalgae through torrefaction.

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### References


