Pyrolysis of microalgae residues – A kinetic study

Wei-Hsin Chen
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Hau-Huu Bui a,⇑, Khanh-Quang Tran b, Wei-Hsin Chen c

a The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330, Thailand
b Department of Energy and Process Engineering, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway
c Department of Aeronautics and Astronautics, National Cheng Kung University, Tainan 701, Taiwan

highlights

- Non-isothermal pyrolysis of microalgae residues.
- First parallel-model employed for kinetic modelling of microalgae pyrolysis.
- Five pseudo-components model was applied for kinetic modelling.
- Protein and lipid were included in the model.
- The simulation was successful to reflect the kinetic of pyrolysis process.

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abstract

Pyrolysis of residues from the oil extraction process of two types of microalgae, Chlamydomonas (C. sp. JSC4) and Chlorella sorokiniana (C. Sorokiniana CY1) was studied by means of a thermogravimetric analyzer. Five pseudo-components (hemicellulose, cellulose, lignin, lipid and protein) model with \( n \neq 1 \) resulted in a slightly better fit quality and reasonable kinetic parameters. The calculated activation energy of hemicellulose, cellulose, lignin, lipid, protein was 115.12–117.12 kJ/mol, 181.67–198.30 kJ/mol, 61.74–62.75 kJ/mol, 104.93–114.14 kJ/mol and 90.75–99.31 kJ/mol, respectively, for C. sp. JSC4; and 113.12–117.12 kJ/mol, 218.73–28.79 kJ/mol, 64.77–66.39 kJ/mol, 131.97–143.63 kJ/mol and 108.03–118.13 kJ/mol, respectively, for C. Sorokiniana CY1.

1. Introduction

Microalgae-derived biofuels have been gaining more and more attention because of the capacity (Chen et al., 2015; Patil et al., 2008) to overcome the limitation of the first generation biofuels including the land use conflict and consequently increasing food prices (Patil et al., 2008). Microalgae is an aquatic biomass, therefore the production of microalgae does not compete with food crops. It can be cultivated in marine seawater, freshwater, or even wastewater (Bahadar and Bilal Khan, 2013). Microalgae is also considered as CO₂ fixer due to its ability to consume CO₂ during the growing process; thus it reduces significant emission of the greenhouse gas (Brown and Zeiler, 1993; Chen et al., 2014b; Gong et al., 2014; Zhu et al., 2014).

After extracting the lipid and other extractives from microalgae biomass, for pharmaceutical chemicals such as Omega 3 and/or for biodiesel production, the residue is normally considered as waste. The residue contains hollocellulose (celluloses and hemicelluloses), lignin, remaining lipid and protein. This residue is a valuable resource for bioenergy production via thermochemical conversion (Keibelmann et al., 2013).

Recently, several studies on microalgae pyrolysis have been reported. Shuping et al. studied the pyrolysis characteristics and kinetics of the marine microalgae Dunaliella tertiolecta and reported that the activation energy of D. tertiolecta pyrolysis was 145.713 kJ/mol using Kissinger’s method and 146.421 kJ/mol by using Flynn–Wall–Ozawa’s method (Shuping et al., 2010). Similarly, Kim et al. found that the pyrolysis activation energy of the alga Saccharina japonica was within 102.5–269.7 kJ/mol, depending on the pyrolysis conversion (Kim et al., 2012). In another work, the pyrolysis of two types of autotrophic microalgae, Spirulina Platensis and Chlorella Potothecoides, were examined by means of thermogravimetric analysis at different heating rates and the simple kinetic analysis adopting Freeman–Carroll method revealed the activation energy of 76–97 kJ/mol and 42–52 kJ/mol for S. Platensis...
and C. Potothecoides, respectively (Peng et al., 2001b). These values of activation energy are quite low for biomass pyrolysis. Liu et al. also investigated the pyrolysis of two types of microalgae Botryococcus braunii and Hapalosiphon sp. and their residues after partial oil extraction (Liu et al., 2012). The result revealed that the pyrolysis characteristic of both original microalgae and residual biomass after oil extraction was similar. Noticeably, the pyrolysis activation energy of as low as 5.5 kJ/mol was reported for the residue of Hapalosiphon sp. These significant variations in the kinetic data indicate limitations of the single reaction model assumptions.

In the open literature, there were no reports available for kinetic study on pyrolysis of microalgae or microalgae residue applying pseudo-component models, despite the fact that lignocellulosic material is the main component of the microalgae cell wall and the pyrolysis of such complex material cannot be closely described by the simple models. Therefore, the work reported in this paper was carried out to perform a kinetic analysis for the pyrolysis of microalgae residues adopting the pseudo-components model.

2. Methods

2.1. Material and experimental methods

All samples of microalgae residues used in this study were characterized and obtained from the previous work (Chen et al., 2014a; Su et al., 2007). Two species of microalgae, Chlamydomonas sp. JSC4 (C. sp. JSC4) and Chlorella sorokiniana CY1 (C. sorokiniana CY1) were collected from Southern Taiwan. The lipid oils were then extracted by the direct transesterification method (Su et al., 2007).

In the process of oil extraction, the microalgae cells separated by centrifugation (10,000 rpm) were washed twice with deionized water to remove the salt and then lyophilized. For transesterification, 0.1 g of the lyophilized cells and 8 ml of 0.5 N alcoholic KOH was mixed together then sonicated for 3 min. After that, the mixture was heated to 100 °C for 15 min for saponification and then cooled to room temperature. For esterification, the mixture was added with 8 ml of 0.7 N HCl in methanol and 14% (v/v) BF3(CH3OH) were mixed together then sonicated for 3 min. After that, the mixture was heated to 100 °C for 15 min for saponification and then cooled to room temperature. For esterification, the mixture was added with 8 ml of 0.7 N HCl in methanol and 14% (v/v) BF3(CH3OH) (Sigma, St. Louis, MO, USA) then heated also to 100 °C for 15 min. After being cooled to room temperature, the mixture was emulsified by adding 2 ml of a saturated solution of NaCl. Finally, the obtained fatty acid methyl esters were extracted by applying aliquots of n-hexane.

After the step of oil extraction, the samples were dried at 105 °C for 24 h, following by grounding and sieving to obtain the particle size less than 0.42 mm. The obtained powder was stored in sealed plastic bags and kept at room temperature.

Table 1 presents results from the characterization of the microalgae residues, which includes data from composition analysis, proximate analysis, and elemental analysis. For the composition analysis, the contents of crude protein, crude lipid and carbohydrate were determined by three different methods, being Kjeldahl method, Soxhelt method and phenol–sulfuric acid method, respectively (Peng et al., 2001a). The proximate analysis was performed adopting the US standard method ASTM E870-82. A PerkinElmer 2400 Series II CHNS Omar elemental analyzer was employed to study the elemental analysis; meanwhile the oxygen content was determined by difference. The calorific value was measured by a bomb calorimeter (IKA C5000).

A thermogravimetric analyzer (TGA), PerkinElmer Diamond TG/DTA, was employed to investigate the non-isothermal pyrolysis (or decomposition in nitrogen environment) of microalgae residues. Approx. 5 mg of the dried samples, together with the nitrogen flowrate of 100 cc min⁻¹, was used for each TG analysis. The nitrogen flow was employed as purging gas to eliminate any possible air content in the reactor and prevent the loaded samples from oxidation reaction. The TGA analyses were performed while the samples were being heated from room temperature to 1000 K, with the heating rate of 20 °C min⁻¹.

2.2. Five pseudo-components model

Although the pyrolysis process of lignocellulosic material involves various different complex reactions, it can be simplified as the global reaction scheme (Tran et al., 2014):

\[ \text{Solid biomass} \rightarrow \text{char} + \text{volatiles} \]

In general, the kinetic equation for the global reaction scheme can be expressed in the form of Eq. (1)

\[ \frac{dx}{dt} = A_e \frac{e^{-E_a/RT}}{a} f(x) \]  

(1)

In Eq. (1), \( A_e \), \( E_a \), \( T \) are the pre-exponential factor, activation energy and absolute temperature, respectively, \( R \) is the universal gas constant, 8.314 J mol⁻¹ K⁻¹. In addition, \( f(x) \) is the conversion function of the conversion degree, \( x \), and \( t \) is the reaction time. The conversion degree \( x \) is defined according Eq. (2)

\[ x = \frac{m_0 - m_t}{m_0 - m_f} \]  

(2)

where \( m_0 \), \( m_t \) and \( m_f \) is the initial mass, final mass, and the mass at time \( t \), of the sample under investigation, respectively.

Various forms of the conversion function can be found elsewhere (Gai et al., 2013; Hu et al., 2015; Vlaev et al., 2003). These model functions were developed basically on the basis of the assumption that the pyrolysis of biomass material is just a single reaction to produce volatile matters and char. However, this assumption is too ideal due to the fact that biomass material comprises of many different components and every of them exhibits distinct thermo-decomposition behavior. Recently, the parallel-reaction model has been adapted by researchers and its advance as well as accuracy has been proved (Hu et al., 2007; Tran et al., 2014). Lignocellulosic biomass materials are basically composed of hemicellulose, cellulose and lignin. The parallel-reaction model applied for these materials is therefore called three pseudo-components. For the present study, it is reasonable to assume a five pseudo-components model for the pyrolysis of microalgae residue. It is because microalgae residues are consisted of the remaining lipid and protein, and the cell wall including hemicellulose, cellulose, and lignin as presented in Table 1 where the carbohydrates are holocelluloses and the “others” mainly means lignin. With this

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Characterization of two microalgae residues.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass</td>
<td>C. sp. JSC4</td>
</tr>
<tr>
<td><strong>Composition analysis (wt%)</strong></td>
<td></td>
</tr>
<tr>
<td>Crude protein</td>
<td>12.18</td>
</tr>
<tr>
<td>Crude lipid</td>
<td>6.85</td>
</tr>
<tr>
<td>Carbohydrate</td>
<td>35.70</td>
</tr>
<tr>
<td>Others</td>
<td>42.27</td>
</tr>
<tr>
<td><strong>Proximate analysis (wt%)</strong></td>
<td></td>
</tr>
<tr>
<td>Moisture</td>
<td>75.50</td>
</tr>
<tr>
<td>Fixed carbon (FC)</td>
<td>15.60</td>
</tr>
<tr>
<td>Ash</td>
<td>3.50</td>
</tr>
<tr>
<td><strong>Elemental analysis (wt%, dry-ash-free)</strong></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>40.32</td>
</tr>
<tr>
<td>H</td>
<td>7.38</td>
</tr>
<tr>
<td>N</td>
<td>2.61</td>
</tr>
<tr>
<td>O (by difference)</td>
<td>44.50</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>C₂₇_H₅₀_O₁₁_N₅.96</td>
</tr>
<tr>
<td>HHV (MJ kg⁻¹, dry basis)</td>
<td>17.41</td>
</tr>
</tbody>
</table>
assumption, the pyrolysis can be described kinetically by Eqs. (3) and (4), in which \( c_i \) is the contribution factor of \( i \) component.

\[
\frac{dx_i}{dt} = A_i \cdot e^{-\frac{Ea}{RT}}(1 - x_i) \quad i = 1, 2, 3, 4, 5
\]  

(3)

\[
\frac{dx}{dt} = \sum_{i=1}^{5} c_i \frac{dx_i}{dt}
\]  

(4)

Two types of five pseudo-components model are simulated, depending on the assumption that the reaction order equals one \((n = 1)\) or different from one \((n \neq 1)\).

2.3. Numerical method

The kinetic simulation of the adopted model was implemented and optimized by applying the non-linear least square method. The objective function to minimize is described in Eq. (5) (Orfão et al., 1999).

\[
S = \sum_{i=1}^{n} \left[ \left( \frac{dx_i}{dt} \right)_{\text{exp}} - \left( \frac{dx_i}{dt} \right)_{\text{model}} \right]^2
\]  

(5)

where \( \left( \frac{dx}{dt} \right)_{\text{exp}} \) and \( \left( \frac{dx}{dt} \right)_{\text{model}} \) are the experiment and modelled conversion rate, \( n \) is the number of experimental points. The quality of curve fitting is evaluated by Eq. (6) (Branca and Di Blasi, 2003).

\[
\text{Fit} (\%) = \left( 1 - \frac{\sqrt{S}}{\left( \frac{dx}{dt} \right)_{\text{max}}^{\text{exp}}} \right) \times 100\%
\]  

(6)

3. Results and discussion

3.1. Thermogravimetric characterization of microalgae residues

Fig. 1 presents the mass loss in the form of raw data (TGA) curves and the mass loss rate in the derivative form (DTG) curves of the microalgae residues during the pyrolysis process in the range temperature from 300 K to 1000 K. In general, the pyrolysis process can be divided into three different stages. The first stage was taking place from the initial temperature to 473 K approximately. The mass loss of each sample within this stage was small, about 4%, mainly contributed by the intrinsic dehydration of the biomass sample. This was then followed by the second stage, which lasted to around 873 K and accounted for the main thermal decomposition (pyrolysis) of the sample. During the second stage, the main components of the sample including carbohydrates, lignin, lipid and protein underwent different decomposition mechanisms including depolymerization, decarboxylation and cracking (Peng et al., 2001a,b). Therefore, this stage is always responsible for the main mass loss of the whole process, which amounted up to approx. 67% for C. sp. JSC4 and 74% for C. sorokiniana CY1 samples. The last stage was not pronounced, accounting the small mass loss caused by light further decomposition of the residual (char) material (Rizzo et al., 2013). At 1000 K, 24% mass of C. sp. JSC4 sample remained as char, being slightly higher than that (20%) of C. sorokiniana CY1 sample.

Overall, the thermal decomposition behavior of two residue samples was quite similar to one another with regards to the shape of the TGA and DTG curves, although C. sorokiniana CY1 was somehow more reactive than C. sp. JSC4. Indeed, the DTG curves of both microalgae residues share some common features. They started skyrocketing at temperatures around 500 K and decreased rapidly from 650 K. Another common feature is the shoulders observed on the second haft of the DTG curves, which can be attributed to the presence of lipid and protein as reported in the literature (Kebelmann et al., 2013). The main differences are in the peak location (at 577 K and 582 K for C. sp. JSC4 and C. sorokiniana CY1 samples, respectively) and intensity of the curves as can see in Fig. 1.

3.2. Simulation and kinetic analysis

The assumed five pseudo-components model was simulated for C. sp. JSC4 and C. sorokiniana CY1 and graphically presented in Figs. 2 and 3, respectively. The extracted kinetic parameters from the modelling and simulation are shown in Table 2.

From Figs. 2 and 3, it is observed that among the cellulosic components, hemicellulose started decomposing first, followed...

Other studies (Chen et al., 2014a; Kebelmann et al., 2013; Phusunti, 2013). Indeed, Phusunti studied the pyrolysis of Chlorella vulgaris microalgal residue and found that lipid started decomposing after protein (Phusunti, 2013). This observation was confirmed by another investigation on pyrolysis of protein and lipid extracted from green microalgae (Kebelmann et al., 2013).

The calculated kinetic parameters of hemicellulose, cellulose and lignin, presented in Table 2, are in good agreement with the literature (Grønli et al., 2002; Hu et al., 2007; Manyà et al., 2003). The common activation energy of hemicellulose for example varies between 105–111 kJ/mol, 195–213 kJ/mol for cellulose and 35–65 kJ/mol for lignin (Grønli et al., 2002; Hu et al., 2007; Manyà et al., 2003). The activation energy of hemicellulose, cellulose and lignin are approximately 115 kJ/mol, 207 kJ/mol and 60 kJ/mol, respectively. On the other hand, according to the report of a kinetic study on pyrolysis of C. vulgaris microalga, the activation energy of lipid was 200 kJ/mol (Phusunti, 2013), which is comparable to 114.14 kJ/mol for C. sp. JSC4 and 143.64 kJ/mol for C. sorokiniana CY1 obtained from the present study. Nevertheless, it is worthwhile to note that the model assumption and modelling method of the present study is different from and more relevant that employed by the past studies on pyrolysis kinetics of microalgae biomass in the open literatures. In addition, the reaction order of every component was in the range between one and two.

On the other hand, the fit quality for both cases, being around 98%, is high, which indicates the suitability of the kinetic modelling and five pseudo-components assumption. The fit quality for the case of n = 1 is slightly better than that of n = 1 and the result from the case of n # 1 is more favourable. The contribution factors of the residues components obtained from the kinetic model are also in good agreement with the literature and the proximate analysis data (Table 1). For C. sp. JSC4, the calculated activation energy of hemicellulose, cellulose, lignin, lipid, protein was 115.12–117.12 kJ/mol, 181.67–198.30 kJ/mol, 61.74–74.27 kJ/mol, 64.77–66.39 kJ/mol, 131.97–143.64 kJ/mol and 90.75–99.31 kJ/mol, respectively. These of C. sorokiniana CY1 were 113.12–117.12 kJ/mol, 218.73–28.79 kJ/mol, 64.77–66.39 kJ/mol, 131.97–143.64 kJ/mol and 108.03–118.13 kJ/mol, respectively. Remarkably, the lipid of C. sorokiniana CY1 has higher activation energy than this of C. sp. JSC4.

### 4. Conclusion

The assumed five pseudo-components model has been proven suitable to simulate the pyrolysis of microalgal residues. The extracted kinetic data are within the reasonable range in comparison with the literatures. For both cases of n = 1 and n # 1, there was no significant difference in the obtained kinetic data. The results from the case of n # 1 are however slightly better than that of n = 1 with regards to the fit quality. Small differences between the simulations for n = 1 and n # 1 in term of pre-exponential coefficient, activation energy and contribution factor were observed.

### Table 2


<table>
<thead>
<tr>
<th>Sample</th>
<th>Pseudo-component model n = 1</th>
<th>Pseudo-component model n # 1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A (min⁻¹)</td>
<td>Ea (kJ/mol)</td>
</tr>
<tr>
<td>C. sp. JSC4</td>
<td>H 1.07E + 11</td>
<td>115.12</td>
</tr>
<tr>
<td></td>
<td>C 1.10E + 18</td>
<td>198.3</td>
</tr>
<tr>
<td></td>
<td>L 2.58E + 04</td>
<td>61.74</td>
</tr>
<tr>
<td></td>
<td>Ld 1.20E + 08</td>
<td>104.93</td>
</tr>
<tr>
<td></td>
<td>P 5.08E + 07</td>
<td>90.75</td>
</tr>
<tr>
<td>C. sorokiniana CY1</td>
<td>H 3.70E + 10</td>
<td>113.12</td>
</tr>
<tr>
<td></td>
<td>C 5.67E + 20</td>
<td>228.79</td>
</tr>
<tr>
<td></td>
<td>L 5.10E + 04</td>
<td>64.77</td>
</tr>
<tr>
<td></td>
<td>Ld 2.20E + 10</td>
<td>131.97</td>
</tr>
<tr>
<td></td>
<td>P 1.66E + 09</td>
<td>108.03</td>
</tr>
</tbody>
</table>
Acknowledgements

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References