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Pyrolytic Thermal Decomposition Behavior and Kinetic Parameters of *Tetraselmis chuii* Microalgae

Aloon Eko Widiono¹, a), Sukarni Sukarni², ³, b), Retno Wulandari², c), Ardianto Prasetiyo¹, d), Heru Suryanto², e), Uun Yanuhar⁴, f)

¹Master Program of Mechanical Engineering, Graduate School, State University of Malang, Semarang Street 5, Malang 65145, East Java Indonesia
²Department of Mechanical Engineering, State University of Malang, Semarang Street 5, Malang 65145, Indonesia
³Centre of Advanced Materials for Renewable Energy, State University of Malang, Semarang Street 5, Malang 65145, Indonesia
⁴Biotechnology Laboratory, Department of Water Resources Management, Faculty of Fisheries and Marine Sciences, University of Brawijaya, Malang, 65145 Indonesia

a) email: aloon.eko89@gmail.com
b) Corresponding author: sukarni.ft@um.ac.id
c) email: retno.wulandari.ft@um.ac.id
d) email: ardianto.prasetiyo.ft@gmail.com
e) email: heru.suryanto.ft@um.ac.id
f) email: doctoruun@ub.ac.id

Abstract. The pyrolysis characteristic of the *Tetraselmis chuii* microalgae has been investigated through a thermogravimetric device. This experiment was carried out on 10 °C/min heating rate with 50 ml/min continuous nitrogen flow rate and 25-900°C temperature range. The results verified that four stages degradation processes were encountered during *Tetraselmis chuii* pyrolysis. During the pyrolysis process, the active region of volatile release occurs in two different stages. Degradation of carbohydrates and proteins take place in stage 2, whereas lipids are decomposed in stage 3. Analysis of kinetics parameters includes *Ea* (activation energy), *A* (pre-exponential factor), and *n* (reaction order) yielded the respective values of 70.68 kJ/mol, 1.72/minute, 1.22 and 223.25 kJ/mol, 11.43/minute, 2.44.

INTRODUCTION

Industrial development and increasing world population have a significant effect on the increasing energy demand. The main energy sources are decreasing due to their extensive utilization [1]; therefore it must be criticized that the reserves of respective petroleum, natural gas, and coal will deplete in a period of 9, 42, and 68 next years [2]. To minimize fossil-based energy dependence, it is necessary to investigate a sustainable and cost-effective alternative energy sources [3]. One of the alternative energy offers to address this problem is biomass energy [4].

Among the abundant biomass, microalgae are aquatic organisms that are widespread in waters that are interesting to study as energy materials, because of the following some reasons: microalgae is an attractive source of biomass for industrial applications [5] and able to supply energy stocks in a short time [6]. Generally, microalgae
produce biomass for 24 hours by asexually [7] with production estimated at around 5 million kg/hectare/year [8]. So this superiority indicates that microalgae can be a promising natural resource for the feedstock of sustainable renewable and environmentally friendly energy materials [5]. Although microalgae have the potential as an alternative fuel, it has not been applied yet to the industrial power plant. Hence, in-depth study of the microalgae conversions to the energy, such as thermochemical conversion, is being critical challenges in the future.

Thermochemical conversions can be distinguished into three types, i.e., gasification, pyrolysis, and combustion. Among these modes of conversions, pyrolysis is considered an efficient process because the ratio of feedback to fuel is higher than combustion, and gasification [9]. Microalgae pyrolysis experiments have been performed previously, including Chlorella vulgaris and Dunaliella salina [8, 10, 11]. Namocloropsis oculata [12], Botryococcus braunii [13], Chlorococcum hunicola [14], Aurantiochytrium sp [15]. These seven experiments could be used as a basis for understanding the microalgae pyrolysis process. However, from the current literature study, the Tetraselmis chuii pyrolysis has not been found.

Tetraselmis chuii live in the tropics because they have eurythermal and euryhaline characters that are easily developed in Indonesian marine waters [16]. This species is generally used as live food for crustaceans, postlarvae, rotifers, and mollusks bivalves because its nutritional value is high enough to be a major role in the aquaculture food chain [16–19]. In addition, this species also has a high possibility as a biofuel because it contains carbohydrates, proteins, and high lipids [16, 19].

In the pyrolysis, biomass exposure to heat without the presence of oxygen [20] resulted in gas, tar (liquid), and charcoal (solid). In fact, the products depend on several conditions, including the heating rate, the final temperature of pyrolysis, pressure, and presence of catalyst [21]. Understanding the pyrolysis behavior and kinetic parameters can help to design the proper reactor in industrial scale [22]. For this purpose, investigation on mass loss and rate of mass loss during temperature escalation are critical tasking. The common equipment has been used to obtain these both parameters is the thermogravimetric analyzer. In accordance with both mass loss and rate of mass loss as a purpose of temperature or time, subsequently, the kinetic evaluation can be done to get the activation energy, pre-exponential factor, and reaction order.

MATERIAL AND METHOD

Materials

The sample of Tetraselmis chuii was prepared by Central of Brackish Water Aquaculture (BBPBAP), Jepara, Indonesia. The microalgae were cultivated, harvested, cleaned using distilled water, then filtered to be sediment. The washing process of this microalgae was performed at two times. The sediment product was subsequently subjected to an oven at 80°C temperature and 24 h long time. The dried samples resulted from the previous process than were ground to be powder and then sieved to 60 mesh size. Microalgae powder is then stowed in a tightly closed bottle.

Thermogravimetric test

The thermal analysis tool (Mettler Toledo TG/DSC 1) was used for examining the decomposition characteristic of microalgae that underwent the heating process using carrier gas of nitrogen to avoid oxidation. Samples weighed approximately 10 mg were placed in the crucible and put into the reactor under non-isothermal conditions, at 10 °C/min heating rate, 50 ml/min nitrogen flow rate, and 25-900°C temperature interval. The thermal behavior of the sample is monitored using a controlled computer during the rising temperature and time and resulted in the thermogravimetric (TG) curve. After obtaining the TG curve, then the derivative thermogravimetric (DTG) curve is attained by differentiating the TG curve to the temperature or time.

Kinetic parameters

Pyrolysis of microalgal biomass is generally described as a single reaction [13, 23]:

\[
\text{Microalgae Biomass} = \text{Volatile} + \text{Char}
\]

The reaction rate of biomass while heating is expressed in the following Arrhenius Equation:

\[
\frac{da}{dt} = k f(\alpha) = A \exp \left(\frac{-E_a}{RT}\right) f(\alpha)
\]  

(1)
Where $T$ is temperature in absolute conditions (K), $k$ is the rate of reaction stable depending on temperature, $A$ is a pre-exponential factor ($s^{-1}$), $f(\alpha)$ is a temperature-independent conversion function, $E_a$ is activation energy (kJ/mol), $R$ is a universal gas constant (8.314 kJ/mol K), and $t$ is time (minutes).

In pyrolysis, the material fraction ($\alpha$) remaining during the experiment is defined in the following equation:

$$\alpha = \frac{m_i - m_t}{m_i - m_\infty}$$

Where $m_i$ is the initial mass, $m_t$ is the actual mass at time $t$, $m_\infty$ is the final weight which cannot be degraded during the reaction.

For pyrolysis, experiments are carried out non-isothermally with a constant heating rate $\left(\beta = \frac{dT}{dt}\right)$. Then, the substitution Equation (1) with $\left(\frac{dT}{dt}\right)$ and then describing the $n$th reaction model so that the kinetics equation is obtained as follows:

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

In Equation (3), determining the kinetic parameters in the thermochemical conversion of biomass can be evaluated.

**RESULT AND DISCUSSION**

**Thermal Decomposition Behavior**

**FIGURE 1.** TG and DTG Curve of *Tetraselmis chuii* Pyrolysis analysis at 10°C/min

TG and DTG curve in Fig 1 states the pyrolysis *Tetraselmis chuii* microalgae decomposes in four stages: stage 1 (moisture released), stage 2 and 3 (volatile evolution), and stage 4 (char decomposition). Similar results were found in previous researchers conducted by Ky et al., [15]. Stage 1 takes place at a temperature of 25-153°C, proven in the first small basin on the DTG curve associated with the release of moisture bound in microalgae cells [10]. However, it should be noted that pyrolysis generally uses basic biomass dry material so that the release of moisture is very little or even nonexistent [24]. This was confirmed by an analysis of the TG curve that mass loss was around 3%.

Stage 2 starts at 153°C and finishes at 401°C. As much as 56% of the *Tetraselmis chuii* mass disappears at this stage, evidenced by the steep slope in the TG curve. This event is also justified by the sharp curvature of the DTG curve, where some organic components of the biomass are released to become volatile. However, it should be noted that strange phenomena occur at around temperatures of 265°C. This phenomenon is associated with decomposition carbohydrate content in microalgae. In addition, the main peak in stage 2 found in 311°C, was related to the decomposition of protein content. This result is almost the same as the results of Ky et al., [15] in microalgae *Aurantiochytrium sp*, which obtained 2 maximum peaks of DTG curve on stage 2: first at 290°C related to
carbohydrate decomposition, and second at 337°C related to protein decomposition. However, this result differs from *Chlorella vulgaris* that was studied by Agrawal, [11] in which stage 2 was taken place at higher temperatures compared to this study, i.e., in the temperature range of 200-395°C. This differentiation is highly determined by the distinction of their composition, mainly the carbohydrate of *Chlorella vulgaris* (51-58%) that was higher than that of *Tetraselmis chuii*, that was around 16.38% [6, 25, 26].

Stage 3 is characterized by the existence of small basins on the DTG curve. This stage is finished at a temperature of 529°C with a weak peak at 420°C representing lipids decomposition [11]. This revealed that lipids in microalgae are decomposed at a slower rate at high temperatures than carbohydrates and proteins with a slight mass loss of around 11%. Kim et al., [27] and Goldfarb et al., [28] also investigated the thermal characteristics of pyrolysis of *Dunaliella tertiolecta*, and they found small peaks at temperature 450°C are linked to lipid decomposition. Each type of microalgae has a different composition; generally, depending on culture conditions, therefore provide different effects on decomposition behavior [15].

In stage 4, the pyrolysis process is finished at 900°C. At this stage, the carbon material in the biomass char continuously degraded at a slow rate. Therefore, the mass loss at this stage is due to the gasification process and is justified in the relatively flat of TG curve. On the other hand, the carbon element in this region is difficult to convert into CO and CO₂ [11]. At this stage, the mass lost is 20% with a final residue is around 8%.

### Analysis of kinetic reaction

Calculation of kinetic reaction is applied at the stage of volatile release (stage 2 and stage 3), where these stages are assumed to be the active pyrolysis region as a one-step reaction of the *n*th model. In accordance with the TG-DTG curve, the pyrolysis active region parameters can be determined as follows; initial temperature (*T₀*), terminated temperature (*Tₓ*), peak temperature (*Tₚ*), maximum reaction rate during the process of pyrolysis (*Mp*), and total mass loss in the specified region. In this study, the active region parameters of pyrolysis of *Tetraselmis chuii* microalgae are presented in Table 1.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Stage 2</th>
<th>Stage 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>To</em> (°C)</td>
<td>153</td>
<td>401</td>
</tr>
<tr>
<td><em>Tx</em> (°C)</td>
<td>401</td>
<td>529</td>
</tr>
<tr>
<td><em>Tp</em> (°C)</td>
<td>311</td>
<td>420</td>
</tr>
<tr>
<td><em>Mp</em> (%/s)</td>
<td>0.097</td>
<td>0.021</td>
</tr>
<tr>
<td>Mass Loss (%)</td>
<td>56</td>
<td>11</td>
</tr>
</tbody>
</table>

In the Coats-Redfern method, evaluation of kinetic parameters based on Equation (3) was completed by using Taylor series technique [29]. Therefore, exponential integrals of Equation (3) is manipulated and resulted in the final form as follows:

$$\ln g(\alpha) = \frac{Ea}{RT} + \ln \frac{AR}{\beta E}$$  \hspace{1cm} (4)

Where if *n* = 1 then $g(\alpha) = -(\ln(1 - \alpha))/T^2$ and if *n* ≠ 1 then $g(\alpha) = (1 - (1 - \alpha)^{(1-n)}/((1 - n)T^2))$. In equation (4), a straight line is obtained from the plot between $\ln g(\alpha)$ to $(1/T)$, if *n* (reaction order) is determined precisely. Determination of *n* was chosen randomly and justified at the value of $R^2$ (correlation coefficient) closed 1. The value of *n* selected, then used to find $\ln g(\alpha)$ from *α* (degree conversion) in the region of pyrolysis. So, the plot among $\ln g(\alpha)$ to $(1/T)$ will describe the relationship of *T* on *α*. The *Ea* values (activation energy) and *A* (pre-exponential factor) are obtained from the final gradient and intercept [29].
FIGURE 2. The $R^2$-$n$ curve is obtained by the Coats-Redfern method stages 2 and 3

As in Fig 2, the $n$ value is randomly chosen in the range 0.5-4.0, after which it is applied to calculate $\ln g(\alpha)$ at a between 0.05-0.95. The plot between $\ln g(\alpha)$ and $1/T$ in each $n$ produces $R^2$. For stage 2, the highest value of $R^2$ (0.998) is found at $n$ of 1.22. While stage 3, the highest peak $R^2$ of 0.981 on the curve is related to $n$ of 2.44. The most appropriate $n$ value is then used to find the kinetic parameters in the region of pyrolysis. The latest plot of $\ln g(\alpha)$ and $1/T$ is presented in Fig 3. The pre-exponential factor and activation energy of the active pyrolysis region of microalgae pyrolysis are described in Table 2.

FIGURE 3. The final plot is obtained by the Coats-Redfern method in stages 2 and 3

TABLE 2. Kinetics parameters of active region pyrolysis of *Tetraselmis chuii* microalgae

<table>
<thead>
<tr>
<th>Stage</th>
<th>$\beta$ (°C/min)</th>
<th>Trendline equation</th>
<th>$R^2$</th>
<th>Kinetics parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$E_a$ (kJ/mol)</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>-8501.4x + 1.6669</td>
<td>0.998</td>
<td>70.68</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>-26853x + 24.033</td>
<td>0.981</td>
<td>223.25</td>
</tr>
</tbody>
</table>

Activation energy is the minimum total energy needed in the material for a chemical reaction to occur. In other words, the higher the activation energy value will require a higher temperature and a longer reaction rate for the reaction to occur [30]. In Table 2, it can be understood that the activation energies of the active pyrolysis region of
Tetraselmis chuii stages 2 and 3 are 70.68 and 223.25 kJ/mol. This value is higher than the pyrolysis of microalgae Chlorella vulgaris, where in stage 2 is 51.45 kJ/mol, and stage 3 is 64.63 kJ/mol [11]. This is understandable in every type of microalgae having varied activation energy. It can be estimated that the conditions of culture and type of microalgae resulted in differences in the percentage of carbohydrate, protein, and lipid content. So that the energy needed for the reaction takes place is varied.

CONCLUSION

Pyrolysis characteristics of microalgae Tetraselmis chuii have been analyzed in non-isothermal experiments with thermogravimetric analysis. During pyrolysis, Tetraselmis chuii is degraded in 4 stages. The active pyrolysis region occurs in the devolatilization stage (2 and 3). Stage 2 indicates carbohydrate and protein decomposition, and stage 3 reveals lipid decomposition. Calculation of kinetic parameters in the pyrolysis region using the Coats-Redfern method resulted in activation energy of 70.68 and 223.25 kJ/mol for stage 2 and stage 3, respectively.

ACKNOWLEDGMENTS

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