Degradation Rate of Brown Macroalgae *Sargassum* sp. Conversion to Bio-Oil via A Slow Pyrolysis

Obie Farobie*‡, Apip Amrullah**, Novi Syaftika***, Asep Bayu****, Edy Hartulistiyoso*

*Department of Mechanical and Biosystem Engineering, IPB University, 16002 Bogor, Indonesia
**Department of Mechanical Engineering, Lambung Mangkurat University, Banjarmasin, South Kalimantan, Indonesia.
***Center for Energy Resource and Chemical Industry Technology, National Research and Innovation Agency (BRIN), South Tangerang, Indonesia.
****Research Center for Biotechnology, National Research and Innovation Agency (BRIN), Cibinong, Bogor 16911, Indonesia.
(obiefarobie@apps.ac.id, apip.amrullah@ulm.ac.id, novi017@brin.go.id, asep044@brin.go.id, edyhartulistiyoso@apps.ipb.ac.id)

‡ Corresponding Author: PO Box 220, 16002 Bogor, Indonesia, Tel: +62 812 898 11381,
obiefarobie@apps.ac.id

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Abstract- *Sargassum* sp. is a brown macroalgae posing a problem to the marine biota due to eutrophication in the coastline. Therefore, the utilization of *Sargassum* sp. for bioenergy, especially bio-oil is essential. However, the degradation rate of *Sargassum* sp. conversion to bio-oil during pyrolysis has yet to be examined. Hence, the purpose of this work is to examine the degradation rate of *Sargassum* sp. conversion to bio-oil during pyrolysis. Slow pyrolysis was performed using a batch reaction vessel under varied temperatures (400–600 °C) and reaction times (10–50 min). The activation energy as well as the pre-exponential factor were determined by assuming a first-order reaction and employing the Arrhenius equation. The activation energy of 15.27 kJ mol^{-1} and pre-exponential factor of 0.477 s^{-1} were determined for the degradation of *Sargassum* sp. during pyrolysis.

Keywords Brown algae, degradation rate, pyrolysis, reaction kinetics, Sargassum

1. Introduction

It is well known that energy is one of primary needs for daily life [1]–[5]. Pyrolysis technology has been known to be an effective method to obtain high energy bio-oil, a liquid fuel that can substitute fossil oil [6], [7]. This method is basically biomass thermal decomposition at elevated temperature, in anoxic or almost anoxic condition, with or without catalysts [6], [8].

Lignocellulosic biomass such as palm kernel shell, wood chips, rice husk, coconut fiber, coconut shell, or other agricultural residue are most commonly used as feedstock to produce bio-oil using pyrolysis technique [9]–[12]. However, these biomasses are terrestrial that causes issues on fertilizers, land and fresh water-use competition with other sector like food and feed industry [13], [14].

Alternatively, macroalgae is an attractive option over terrestrial biomass since they are aquatic species who can grow in the ocean, contains high organic matter, has high growth rate and do not require land, fresh water, nor fertilizers to be cultivated [15], [16]. Macroalgae or commercially known as seaweed has been for centuries mainly for food industry. In 2019, total global production of seaweed was 35.7 million ton in which green and red macroalgae including *Sargassum* sp. share the largest contribution [17]. On the other hand, some species of macroalgae like *Sargassum* sp causes eutrophication problem [18]. Thus, its diversified utilization, not only for food industry but also energy sector will increase *Sargassum* sp.'s value and at the same time can minimize the burden of algae blooming towards the environment.

There are number of studies on *Sargassum* sp. as feedstock to obtain bio-oil via pyrolysis pathway in recent years. Milledge et al., (2015) calculated that bio-crude oil from *Sargassum* sp. was 15.6 MJ Kg^{-1}, that is quite attractive as fuel resource [19]. The effect of temperature and retention times towards product distribution from the pyrolysis of *Sargassum* sp. was investigated by Farobie et al., (2022) and found that the content the bio-oil is mostly carboxylic acids (25.07–35.01%), followed by furan derivatives, aliphatic hydrocarbons, N-aromatic compounds and other chemicals in lower amount [7]. The maximum liquid product yield obtained from *Sargassum tenerrimum* using pyrolysis was found to be 24.6% at temperature 450 ºC [20]. The use of catalyst was also examined by Cao et al. by using ZSM-5 to decrease the N-containing and organic acid compound, to improve the quality of bio-oil from *Sargassum fusiforme* [21]. Co-pyrolysis technique of *Sargassum* sp. with other type of resource was also elaborated such as with polystyrene by Kositkanawuth et al. 2017 [22]. However, kinetic studies of *Sargassum* sp. under pyrolysis process is still rarely found in the literature. Kinetic studies are essential as fundamental knowledge to predict the conversion process, the reaction mechanism, so that the design of reactor for implementation will be accurate [23]. Thus, in this study the behavior of *Sargassum* sp. under pyrolysis condition was investigated by calculating its degradation rate of *Sargassum* sp. pyrolysis including the activation energy and pre-exponential factor.

2. Materials and Methods

2.1. Feedstock provision

Sargassum sp. was received from East Lombok Beach, Nusa Tenggara Barat, Indonesia. The fresh *Sargassum* sp. was firstly rinsed with tap water to take the debris off. Subsequently, the feedstock was dried at 105 °C for 24 h. Afterward, the feedstock was ground and sieved to obtain a 0.25 mm fine sample.

2.2. Experimental

Sargassum sp. feedstock was thermally pyrolyzed using a batch reaction vessel. The feature of this reaction vessel has been presented in our earlier papers [24], [25]. Briefly, the pyrolysis reactor was made of stainless steel and equipped with an electric furnace, a thermocouple, a PID temperature controller, and a condenser. The nitrogen gas inert was used prior to the pyrolysis process to make sure that there is no air and oxygen inside the reactor. The slow pyrolysis was carried out at various temperatures (400–600 °C) and times (10–50 min). Bio-oil products were separated from solid products upon completion of pyrolysis. The bio-oil yield was determined by dividing the mass of the bio-oil product by the initial mass of *Sargassum* feedstock.

2.3. Analysis

The thermal stability of *Sargassum* sp. and its corresponding bio-char was performed using a thermogravimetric analysis (TGA 4000, Pekin Elmer). The *Sargassum* sp. feedstock, as much as 8 mg, was placed in an alumina crucible. The mass loss of samples was recorded as a function of temperature and time by heating the samples from ambient temperature to 800 °C at a contact heating rate of 10 °C min^{-1}. The nitrogen gas with a flow rate of 50 mL min^{-1} was employed to keep an inert condition.

3. Results and Discussion

3.1. Effect of Temperature and Time on Bio-oil Production

The effect of temperature and time on bio-oil production was investigated. Fig. 1 shows the changes in bio-oil yield by varying temperature and time during slow pyrolysis of *Sargassum* sp. As expected, temperature considerably affects the bio-oil yield. Bio-oil yield increased significantly as an increase in the parameter condition from 400 to 500 °C. This might be because the primary destruction of the macroalgal feedstock was enhanced. Moreover, increasing the temperature could also increase the secondary degradation of the solid residue (bio-char) [26]. However, the bio-oil yield was not increased with a further increase in the temperature to 600 ºC. This might be because bio-oil was thermally cracked into vapors at a temperature beyond 500 ºC. This result is following the previous findings reported by Choi et al. [27] and Aboulkas et al. [26], who observed that increasing temperature from 400 to 500 ºC results in an increase in bio-oil yield, but it decreased after that.

Reaction time also has a substantial impact on bio-oil production during the pyrolysis of brown algae *Sargassum* sp. As observed, the bio-oil yield obtained was very low at the initial stage of the pyrolysis process. The bio-oil yield was obtained to be only 11.05% at 400 ºC and 10 min of reaction time. It might be linked due to incomplete pyrolysis at short reaction times and low temperatures. By prolonging the reaction time from 10 to 50 min, the yield of bio-oil increased considerably from 11.05 to 28.28% at 400 ºC. At 500 ºC, the trend is almost similar to 400 ºC, of which bio-oil yield increased from 18.46 to 30.42% with prolonging reaction time from 10 to 50 min. Meanwhile, it is not the case at 600 ºC. Bio-oil yield first increased once the reaction time was extended from 10 to 30 min, but the yield was not increased after that. It might be linked to the cracking of pyrolysis vapors at higher temperatures and longer reaction times.

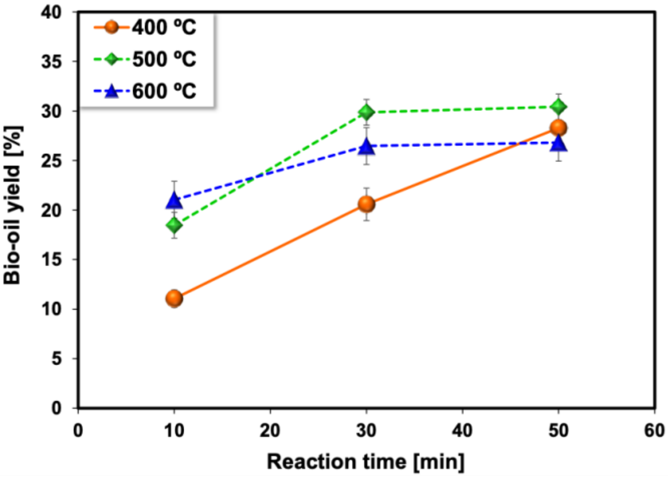

Fig. 1. Effect of temperature and time on bio-oil yield during slow pyrolysis of *Sargassum* sp.

The bio-oil yield obtained from this study was also compared with previous works using the feedstock from empty fruit bunch (EFB), coconut shell, and purun tikus, as presented in Fig. 2. As observed, the bio-oil yield reported herein is considerably lower range than that of previous works using EFB [28], coconut shell [2], and purun tikus [19]. This might be due to the difference in lignin content in the biomass. Notably, macroalgae contains lower lignin content than commonly land plants [13]. On the other hand, Klemetsrud et al. reported that lignin content in biomass generally results in high bio-oil rich in phenolic compounds [29].

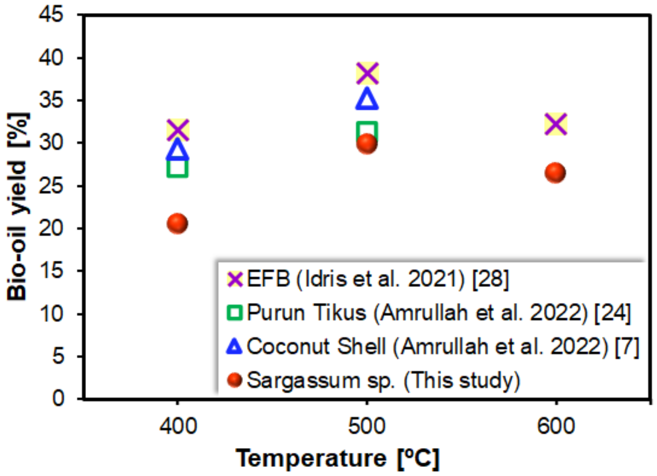

Fig. 2. Comparison of bio-oil yield from pyrolysis of *Sargassum* sp. and terrestrial plant biomass.

3.2. *Effect of Temperature and Degradation of Solid*

To evaluate the pyrolysis process temperature, the *Sargassum* sp. and its corresponding biochar was analyzed in terms of mass loss using thermogravimetric analysis. The behavior of the *Sargassum* sp. and its corresponding biochar using thermogravimetric analysis is presented in Fig. 3. For the case of *Sargassum* sp. feedstock, the mass loss was significantly observed at 278 ºC and 438 ºC. The *Sargassum* sp. lost its mass by around 15.4 and 56.4% for 278 ºC and 438 ºC, respectively. During pyrolysis, the primary mass loss under these conditions might be linked to the de-volatilization process. Kim et al. reported that the mass loss of biomass represents the degradation of macromolecules such as proteins and carbohydrates [30]. Moreover, at a higher temperature beyond 600 ºC, a substantial loss of Sargassum sp. was observed around 68.1%. This could be attributed to the decomposition of inorganic materials in macroalgae, especially metal carbohydrates [31]. It is interesting to note that half the mass of *Sargassum* sp. was decomposed beyond 398 ºC, indicating that the pyrolysis of *Sargassum* must be conducted at temperatures beyond 398 ºC. Therefore, the pyrolysis of this study was conducted at 400, 500, and 600 ºC. Meanwhile, in the case of biochar, the mass loss was not significantly observed even after 300 ºC. However, the mass loss of biochar of around 10.1% was found at 400 ºC. It could be explained because biochar's main component is polyaromatic compounds that are more challenging to decompose than carbohydrates and proteins. At a higher temperature of 600 ºC, the mass loss of biochar was found to be around 21.9%. This is because biochar can be thermally decomposed at higher temperatures to generate gaseous compounds [11].

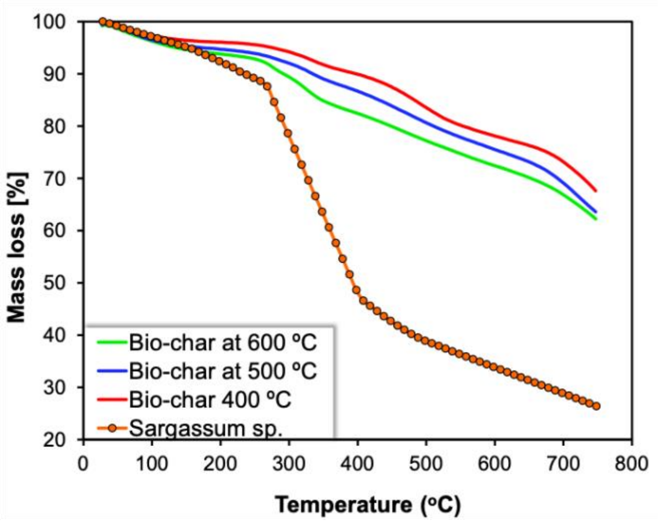

Fig. 3. Thermogravimetric analysis of *Sargassum* sp. and its corresponding bio-char.

3.3. *Determination of reaction rate parameters*

Reaction rate parameters play a substantial role in giving insights regarding the behavior of solid biomass conversion during the pyrolysis process. For the case of pyrolysis of *Sargassum* sp., the model of the solid degradation process during slow pyrolysis is depicted in Fig. 4.

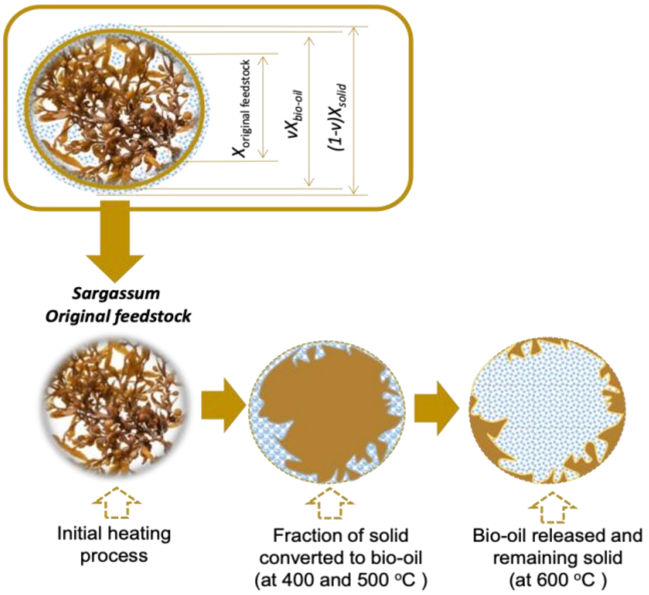

Fig. 4. Model of solid degradation process during slow pyrolysis of *Sargassum* sp.

Considering that the model of the degradation of solid process follows the first-order reaction, the fraction and reaction rate constant of solid decomposition can be determined. From the illustration of the solid degradation process as presented in Fig. 4, the mathematical model can be written as:

$$X_{sargassum} \rightarrow vX_{liquid} + (1-v)X_{solid} \qquad (1)$$

where, $X_{sargassum}$ represents the fraction of the initial feedstock of *Sargassum* sp. The symbol of v is the fraction of the solid transformed into the liquid. X_{liquid} and X_{solid} represent the fraction of liquid and remaining solid, respectively.

By assuming the first-order reaction, the differential rate equation of *Sargassum* sp. at time t can be determined following this equation:

$$\frac{d\left[X_{sargassum}\right]}{dt} = -k\left[X_{sargassum}\right] \qquad (2)$$

where, $\left[X_{sargassum}\right]$ represents the concentration of $X_{sargassum}$.

Considering the mass balance concept, the equation of balance can be expressed as follows:

$$\begin{aligned}&\left[X_{sargassum}\right] + \left[X_{liquid}\right] + \left[X_{solid}\right] = \text{constant}\\ &= \left[X_{sargassum}\right]_i + \left[X_{liquid}\right]_i + \left[X_{solid}\right]_i\\ &= \left[X_{sargassum}\right]_t\end{aligned} \qquad (3)$$

where the symbol of i and t represents the initial condition and total amount of *Sargassum* sp. during the pyrolysis. Meanwhile, the concentration of $\left[X_{sargassum}\right]$ can be expressed as:

$$\left[X_{sargassum}\right] = \frac{1-v}{v}\left[X_{liquid}\right] \qquad (4)$$

By substituting Eq. (4) with Eq. (3), the mass balance can be expressed as

$$\begin{aligned}&\left[X_{sargassum}\right] = \left[X_{sargassum}\right]_t - \left[X_{liquid}\right] - \left[X_{solid}\right]\\ &= \left[X_{sargassum}\right]_t - \left[X_{liquid}\right] - \frac{1-v}{v}\left[X_{liquid}\right]\\ &= \left[X_{sargassum}\right]_t - \left(1 + \frac{1-v}{v}\right)\left[X_{liquid}\right]\\ &= \left[X_{sargassum}\right]_t - \frac{1}{v}\left[X_{liquid}\right]\end{aligned} \qquad (5)$$

After that, by substituting Eq. (5) into Eq. (2), the rate of change can be determined as:

$$\begin{aligned}&\frac{d}{dt}\left(\left[X_{sargassum}\right]_t - \frac{1}{v}\left[X_{liquid}\right]\right) =\\ &-k\left(\left[X_{sargassum}\right]_t - \frac{1}{v}\left[X_{liquid}\right]\right)\end{aligned} \qquad (6)$$

Eq. (6) can be rewritten as:

$$\frac{d}{dt}\left(\left[X_{liquid}\right]\right) = vk\left(\left[X_{sargassum}\right]_t - \frac{1}{v}\left[X_{liquid}\right]\right) \qquad (7)$$

Meanwhile, the liquid yield can be written as:

$$Y_{liquid} = \frac{\left[X_{liquid}\right]}{\left[X_{sargassum}\right]_t} \qquad (8)$$

Hence, Eq. (7) can be determined as follows:

$$\frac{d}{dt}Y_{liquid} = vk - kY_{liquid} \qquad (9)$$

Eq. (9) can be simplified as follows:

$$\frac{dY_{liquid}}{vt - kY_{liquid}} = dt \qquad (10)$$

$$\ln\left(v - Y_{liquid}\right) = -kt + C \qquad (11)$$

$$Y_{liquid} = v - A\exp\left(-kt\right)) \qquad (12)$$

The rate constant can be determined from the Arrhenius equation as follows:

$$k = A\exp\left(\frac{E_a}{RT}\right) \qquad (13)$$

where, T represents temperature, A represents the pre-exponential factor, E_a represents the activation energy, and R represents the gas constant.

Finally, by substituting the Arrhenius equation into Eq. (12), the equation can be written as:

$$Y_{liquid} = v - \left(v - Y_{liquid,i}\right)\exp\left(-A\exp\left(\frac{E_a}{RT}\right)t\right) \qquad (14)$$

The reaction rate constant as well as the fraction of solid converted into liquid, were determined using the least-squares-error (LSE) approach. The results of the fitting curve between experimental data with the calculated value expressing the temperature versus bio-oil yield are presented in Fig. 5. As observed, the experimental data fitted well with the calculated values. Moreover, it was also confirmed by the parity plots, which resulted in the high R^2 (coefficient of determination), i.e., 0.9982, as shown in Fig. 6.

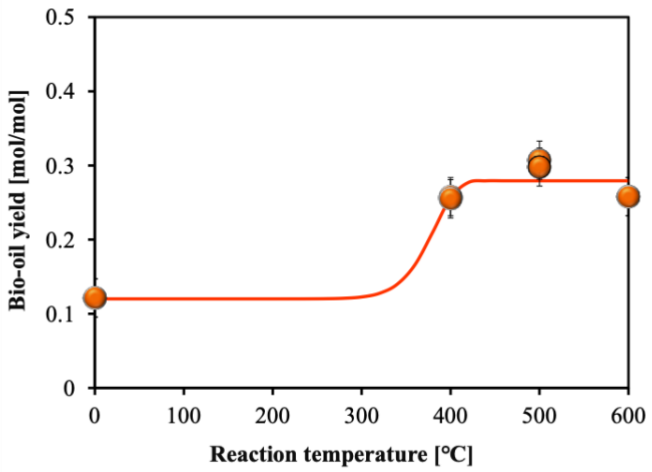

Fig. 5. Result of curve fitting for bio-oil yield at different temperatures during slow pyrolysis of *Sargassum* sp.

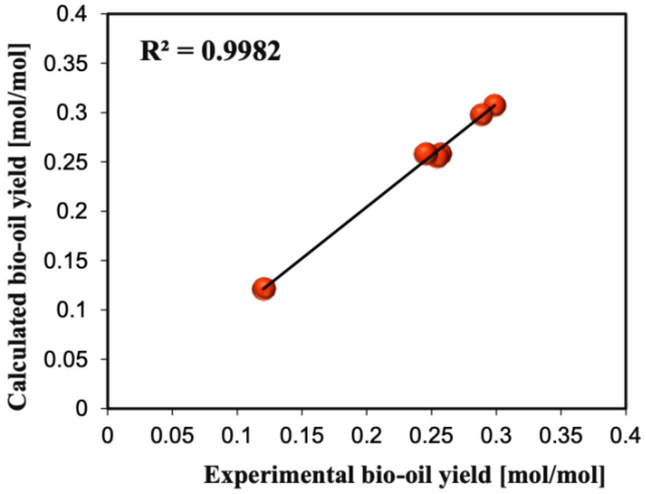

Fig. 6. Parity plots comparing experimental bio-oil yield versus calculated bio-oil yield.

The Arrhenius plot for the degradation rate of *Sargassum* sp. during pyrolysis is shown in Fig. 7. The activation energy, as well as a pre-exponential factor, were obtained from the Arrhenius plot. The pre-exponential factor for the pyrolysis of *Sargassum* sp was calculated about 0.477 s^{-1}. Moreover, the activation energy for the pyrolysis of *Sargassum* sp. was calculated around 15.27 kJ mol^{-1}. The activation energy obtained from this study was considerably lower than that from the other works using terrestrial biomass of coconut shells and almond shells. Amrullah et al. determined the activation energy to be about 153 kJ mol^{-1} for the pyrolysis of coconut shells [7]. Furthermore, Genieva et al. calculated the activation energy for the pyrolysis of almond shells to be around 125.3 kJ mol^{-1} [8]. The different activation energy values might be because of the different chemical compositions in biomass. It is noted that macroalgae is mainly composed of carbohydrates and has lower lignin content than terrestrial biomass. Therefore, the energy needed to decompose macroalgae is lower than terrestrial biomass.

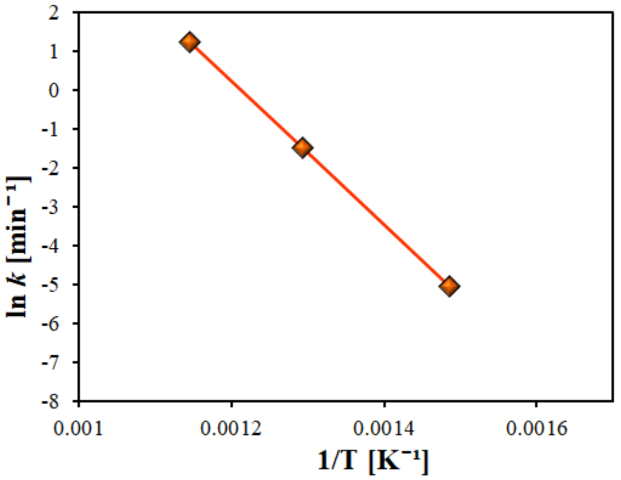

Fig. 7. Arrhenius plots for pyrolysis of *Sargassum* sp. (experimental conditions: 400–600 ºC and 10–50 min)

4. Conclusion

Degradation rate of brown macroalgae *Sargassum* sp. conversion to bio-oil via a slow pyrolysis was investigated. The effect of temperature and time on the bio-oil yield was examined. Increasing the pyrolysis temperature significantly decomposed the *Sargassum* sp. Pyrolysis decomposed the macroalgal feedstock, discharging the cell of macroalgae, and thereby enhancing the yield of bio-oil. The degradation rate of *Sargassum* sp. was assumed following a first-order reaction and obeyed the Arrhenius law. The activation energy and the pre-exponential factor were successfully calculated for the decomposition of *Sargassum* sp. as 15.27 kJ mol^{-1} and 0.477 s^{-1}, respectively.

Acknowledgments

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