Thermogravimetric and kinetic analyses of the *Skeletonema costatum* microalgae combustion using the fitting method

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Abstract. This work was intended to understand the potential of *Skeletonema costatum* (*S. costatum*) microalgae being the solid biofuel feedstock by studying its combustion behavior under a thermogravimetric analyzer (TGA). The following parameters were used during the experiment: about 5 mg of weighed sample was put into a ceramic crucible; the atmospheric air of 100 ml/min was flowed to the chamber to ensure sufficient combustion air; heating was escalated with a rate of 10 °C/min, and combustion was performed at a temperature range from 30 °C to 1200 °C. The results showed that the combustion process of *S. costatum* microalgae could be divided into four stages of decomposition, including the evaporation stage of moisture content from a temperature of 31.68 °C to 150.93 °C, the devolatilization stage from a 150.93 °C to 505.053 °C, the stage of char combustion from a 505.053 °C to 1018.15 °C and the final stage of ash decomposition from 1018.15 °C to 1200 °C. The kinetic parameters were calculated in the 1st, 2nd, and 3rd stages based on the fitting model of the Coats-Redfern method by selecting reaction mechanisms. The activation energy values for 1st, 2nd, and 3rd stages were 71.18; 39.49, and 56.92 kJ /mol, respectively, and correlation coefficients (R²) of 0.959; 0.988, and 0.978, respectively in the Chemical Reaction Order models.

1. Introduction

Microalgae are photosynthetic organisms living and growing rapidly in aquatic environments [1], with simple unicellular and multicellular shapes, sizes, and structures [2]. There are more than 50,000 species of microalgae worldwide [3], but only about 30,000 species are currently being analyzed and studied. Microalgae, with its potential, is a promising choice as a raw material for renewable fuels, but it still requires comprehensive exploration and understanding [4].

Various types of thermal conversion of solid renewable fuels can be obtained from microalgae, as well as the thermal pyrolysis process [5,6], combustion [7–9], converting to be biofuel [10], biodiesel [11], bioethanol [12], and biohydrogen [13]. The research on the potential of *S. costatum* microalgae into biodiesel has been presented in the paper of Gao et al. [14]. Kalhor et al., [15], reporting the fatty acid profile of *S. costatum* microalgae as an initial step for biodiesel production, showed the existence of both palmitic acid and stearic acid in algal oil, where both contents were associated with a high cetane number of biodiesel produced. A higher biodiesel cetane number would yield more ignition delay in the
diesel engine combustion chamber. However, in so far as the literature studied, the thermal conversion of *S. costatum* microalgae through the combustion process has not been found.

The thermogravimetric approach is a valuable method for studying the thermal behavior of microalgae combustion and its components [16]. The technique provides thermal degradation information of mass based on time and temperature. This knowledge then becomes the basis for determining the kinetics of the volatilization of biomass during a thermochemical reaction and being critical parameters for proper designing and modeling a combustion reactor system [17,18]. The combustion product is heavily reliant on the type of raw material, the heating rate, and the temperature setting used; therefore, a specific kinetics model is needed for a suitable conversion technique.

This research was on purpose to analyze the thermal behavior of *S. costatum* microalgae to understand its potential as raw material for solid biofuel by the route of a direct combustion process. The combustion kinetics parameters were analyzed as well, involve the value of activation energies and pre-exponential factors. The various kinetic models proposed by Naqvi et al. [19] are being used on the basis of the fitting technique of the Coats-Redfern.

2. Material and Method

2.1. Sample preparation

*S. costatum* have been cultured in the pond of the Center for Development of Brackish Water Aquaculture (BBPBAP) of Jepara, Indonesia. Microalgae in the pond were deposited with 150 ppm NaOH and resulted in 3:1 (mass ratio) of freshwater to microalgae. The precipitate was then filtered to remove the moisture content before being dried under the sun for 6 hours. To ensure an even drying, the microalgae precipitation was then re-dried in an oven at 400 °C for 3 hours. The microalgae were then mashed and filtered to uniform the size.

2.2. TG experiments

The combustion profile of the algal biomass was analyzed using thermogravimetric analysis by Mettler Toledo TG/DSC1. A sample mass of 5 mg was put into a crucible. The heating rate used was 10 °C/min, and 100 ml/min of an atmospheric air was flowed in the combustion chamber during the experiment that performed at range of 30 °C to 1200 °C. The mass loss presented as TGA graph and mass loss rate presented as differential thermogravimetric (DTG) graph related to both time and temperature were recorded continuously to determine the effect of thermal to the mass degradation and rate.

2.3. Kinetic analysis

The kinetic analysis of microalgae *S. costatum* combustion was easily defined by Arrhenius law, providing a numerical measure of the reaction rate. The conversion rate is basically expressed as the following equation:

\[
\frac{d\alpha}{dt} = k(T)f(\alpha)
\]  

(1)

where,

\[
\alpha = \frac{m_o-m_i}{m_o-m_f}
\]  

(2)

where, \(m_o\) is the initial mass, \(m_i\), and \(m_f\) are the mass at a certain time and the final mass of each end of the stage, respectively. The rate constant is a parameter that depends on temperature, which is representing the frequency of successful collisions, expressed as:

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

(3)

where the respective \(T\), \(R\), \(E_a\), and \(A\) are sign of the absolute reaction temperature (K), the universal gas constant (0.008314 kJ/mol.K), the activation energy (kJ/mol), and the pre-exponential factor (1/min). The equations (1) and (3) are rewritten as a compound form becomes:
\[
\frac{da}{dt} = \frac{A}{\beta} \exp \left(-\frac{E_a}{RT}\right) f(\alpha)
\]
where \(\beta\) is the heating rate \((\beta = dT/dt)\). The reaction model \(f(\alpha)\) then was integrated and its integral form is written as \(g(\alpha)\). The analytical solution approach model is written into the following equations

\[
g(\alpha) = \int_0^\alpha \frac{da}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp \left(-\frac{E_a}{RT}\right) dT
\]

### 2.4. The Coats-Redfern method

The Coats-Redfern selected model can be used in predicting reaction order, activation energy, and pre-exponential factors based on the variation of the selected \(g(\alpha)\). The fundamental equation for the Coats-Redfern method expressed as:

\[
\ln \left[\frac{g(\alpha)}{T^2}\right] = \ln \frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a}\right) - \frac{E_a}{RT}
\]

Plotting between \(1/T\) and \(\ln [g(\alpha)/T^2]\) is resulted in a straight line, from which the slope and intercept values are found and in turn both are used for determining the activation energies and pre-exponential factors, respectively. Most of the thermal degradation reactions of solid materials categorized in five models are listed in Table 1.

### Table 1. Model of reaction applied for kinetic parameters calculation

| Reaction model              | Symbol | Differential form \(f(\alpha)\) | Integral form \(g(\alpha)\) |
|-----------------------------|--------|---------------------------------|-----------------------------|
| **Chemical Reaction Order 1** | F1     | \(1 - \alpha\)                  | \(-\ln(1 - \alpha)\)        |
| **Chemical Reaction Order 1.5** | F1.5   | \((1 - \alpha)^{3/2}\)          | \(2(1 - \alpha)^{3/2} - 1\) |
| **Diffusion**               |        |                                 |                             |
| Parabolic law               | D1     | \(1/2\alpha\)                   | \(\alpha^2\)               |
| Valensi equation            | D2     | \(-[\ln(1 - \alpha)]^{-1}\)    | \(\alpha + (1 - \alpha) \ln (1 - \alpha)\) |
| Ginstling-Broushtein equation | D3     | \(3/2[(1 - \alpha)^{1/3} - 1]^{-1}\) | \((1 - 2/3 \alpha - (1 - \alpha)^{2/3})\) |

### 3. Result and Discussion

#### 3.1. Combustion characteristics of S. costatum

Figure 1 shows a graph of the combustion of microalgae \(S. costatum\) included TG and DTG, from room temperature up to 1200 °C. Based on Figure 1, the combustion characteristics of the \(S. costatum\) microalgae were divided into four decomposition stages. The first stage, from the temperature of 30 °C to 150.93 °C, indicates the process of releasing the moisture content of \(S. costatum\), which is indicated on the DTG graph as a very deep basin with a short temperature range and time, having a peak of mass loss rate at 49.13 °C and the mass is lost by 12.785%. Furthermore, the second stage, which occurred from 150.93 °C to 505.053 °C, characterized by the presence of the large size of the basin on the DTG curve at a longer time and temperature range, is associated to the devolatilization and combustion stage of volatile matter and char, as the similar profile was also reported by Chen et al., [20]. The third stage, which taken place from 505.053 °C to 1018.15 °C, indicated by the TG graph having a gentle decline, is related to the burning of remaining fixed carbon and organic components. The fourth stage, from the termination of the third stage to 1201 °C, is related to the small loss of mass from the decomposition of the ash as the residual matter. The classification of the combustion characteristics of \(S. costatum\) is detailed in Table 2.
Figure 1. TG and DTG curves of S. costatum combustion at 10 °C/min

Table 2. Classification of temperature characteristics of S. costatum microalgae combustion

| Stage | Temperature characteristics |  |  |  |  |
|-------|----------------------------|---|---|---|---|
|       | T_i (°C)                  | T_max (°C) | T_f (°C) | Mass loss (%) | M_max (%/s) |
| I     | 31.68                      | 49.133     | 150.933   | -12.785       | -0.05054    |
| II    | 150.933                    | 313.438    | 505.053   | -39.438       | -0.03529    |
| III   | 505.053                    | 800.979    | 1018.15   | -53.865       | -0.00911    |
| IV    | 1018.15                    | 1031.8     | 1201.69   | -53.508       | -0.00164    |

3.2. Kinetic analysis of combustion

Kinetic analysis was carried out at each stage of decomposition, including the first stage of releasing moisture content, the second stage related to the main devolatilization, and the third stage related to the burning of fixed carbon and organic components. The importance of knowing the value of the kinetics parameters at each stage is for estimating the amount of energy required for each stage and for determining the proper design and shape of the combustion reactor. Based on the reaction mechanisms on f(α) and g(α) selected in alpha (α) 0.05-0.95, then the evaluation of the kinetic parameters of S. costatum microalgae combustion with the Coats-Redfern method reaction mechanisms is shown in Table 3.

Table 3. The kinetic parameters of the S. costatum combustion at various selected models

| Model name | Stage I | Stage II | Stage III |
|------------|---------|----------|-----------|
|            | Ea (kJ/mol) | Log A (1/min) | R² | Ea (kJ/mol) | Log A (1/min) | R² | Ea (kJ/mol) | Log A (1/min) | R² |
| F1         | 37.21    | 0.793    | 5.21 | 39.49    | 0.978    | 2.40 | 56.92    | 0.988    | 1.52 |
| F1.5       | 71.18    | 0.959    | 11.65 | 71.87    | 0.976    | 6.35 | 102.62   | 0.929    | 4.96 |
| D1         | 52.49    | 0.651    | 7.18  | 61.36    | 0.903    | 3.94 | 91.01    | 0.942    | 2.90 |
| D2         | 59.62    | 0.701    | 8.15  | 68.62    | 0.933    | 4.44 | 101.57   | 0.965    | 3.29 |
| D3         | 62.78    | 0.723    | 8.06  | 71.75    | 0.945    | 4.12 | 106.08   | 0.973    | 2.93 |

In the Chemical Reaction Order 1.5 (F1.5) model, Stage I shows the highest activation energy value of 71.18 kJ/mol with R² 0.959, then it is followed by stage III at 56.92 kJ/mol with R² 0.988, and the
lowest one is stage II of which value of activation energy is 39.49 kJ/mol with R² 0.978. The mechanism model with linear regression of R² close to 0.99 is considered as a suitable model. The Chemical Reaction Order (F1 and F1.5) model shows a simple model used in homogeneous kinetics, as the reaction rate is directly proportional to the conversion value [21].

4. Conclusion
This study has investigated the combustion characteristics of 5 mg pulverized biomass of S. costatum at a thermogravimetric analyzer with a 10 °C/min of heating ramp. Four prominent stages were noticeable throughout the sample combustion process, among which three peaks were strongly recognized. The first stage (I) was correlated to the release of moisture content, and it was followed by the devolatilization stage (II) of the char and volatile matter. The third stage (III) was related to the burning of remaining fixed carbon and organic components, and the last stage (IV) was the decomposition of the ash as the residual matter. The activation energies were analyzed using the Coats-Redfern model in stages I, II, and III, respectively, those are 71.18; 39.49, and 56.92 kJ/mol in Chemical Reaction Orders (F1 and F1.5) models.

Acknowledgments
The authors would like to acknowledge the Universitas Negeri Malang for supporting this research.

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