Characteristics and modeling kinetics of oil palm frond petiole pyrolysis using thermogravimetric analyzer

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Abstract. As one of the largest palm oil-producing countries globally, Indonesia produces abundant oil palm biomass; indeed, it brings large oil palm frond petiole (OPFP). OPFP is one of the oil palm biomass that can be converted into an energy source. This research focuses on analyzing thermal decomposition characteristics and pyrolysis kinetics of OPFP using thermogravimetric analysis (TGA). The results showed that the thermal decomposition of pyrolysis was divided into three steps, including the evaporation stage of moisture content, the releasing of volatile compounds and organic matter, and the final stage of lignin and tar decomposition. Both the activation energy and the pre-exponential factors were analyzed with the Coats-Redfern method in step II active pyrolysis zone are 80.56 kJ/mol and 7.21/min, respectively, as shown in the Chemical Reaction Order F1.5 model with the accuracy of a correlation coefficient of 0.99. These results provided the fundamental data useful for properly designing the reactor system for industrial purposes.

1. Introduction

Currently, both the domestic and industrial sectors of electricity are still dominated by fossil energy, in which coal is the primary fuel supply. On the other hand, the transportation sector is still heavily reliant on the use of oil fuel. The projection of renewable energy supply is undergoing rapid growth, up to 6.5% per year, including biofuel, wind, geothermal, biogas, biomass, and municipal waste. The potential for renewable energy development in Indonesia is relatively high, but it has not been optimally utilized [1]. The use of renewable energy has positive impacts since it is able to reduce CO₂ emissions and the greenhouse gas effect [2,3].

Indonesia and Malaysia are the most significant oil palm-producing countries globally, in which both Kalimantan and Sumatra are the largest producing regions for palm oil in Indonesia [4,5]. Indonesia's largest total palm oil exports in 2017 reached USD 18.7 billion [6]. Furthermore, the demand for palm oil supply increased from 8 million tonnes in 2015 to 15 million tonnes in 2018. The surge in the amount of palm oil production definitely caused a considerable increment in palm biomass waste, including oil palm shell (OPS), empty fruit bunch (EFB), and oil palm fiber (OPF) [7] as well as OPFP. The biomass waste has the great potential to be used as an energy source due to its inexhaustible renewal source. Today, along with technological developments, an oil palm tree can be utilized for many applications [8]. Fresh fruit bunches (FFB) can be converted into crude palm oil (CPO), and palm oil waste can be converted into chemical compounds, fertilizers, biomaterials, and alternative fuel sources [5]. However,
inappropriate disposal of oil palm fronds and stems trigger serious air pollution problems [9]. Therefore, utilization of oil palm waste is a critical challenge in overcoming its environmental issues and providing renewable energy reserves.

The combustion is a thermochemical conversion producing heat, in which the materials are oxidized directly without being converted into other forms of fuels [10]. In contrast, pyrolysis is a thermal conversion producing the final products in the form of char, tar, and gaseous coproducts [11]. One of the promising techniques for the analysis of thermochemical characteristics during biomass pyrolysis is thermogravimetric analysis. Nudri et al. [12] studied the pyrolysis of oil palm trunk (OPT) for producing biochar, and the results showed that thermal degradation of OPT biomass pyrolysis was divided into three decomposition steps with the first stage was between temperatures of 70 and 110 °C and the second stage, with a maximum mass loss at 360 °C, was related to lignin degradation. Sakulkit et al. [13] reported that OPT pyrolysis observed through TGA analysis occurred in 4 steps, the first stage was related to moisture evaporation, the second stage was light volatile evaporation, the third stage was the evaporation of cellulose and hemicellulose organic matter, and the fourth stage was related to lignin decomposition. However, concerning energy applications, the previous study has not reported an analysis related to the utilization of oil palm frond petiole (OPFP) waste for energy applications through the pyrolysis process to evaluate its thermal characteristics and kinetics.

Based on the presented facts, this study characterized the thermal behavior of OPFP throughout the pyrolysis process and evaluated its kinetic parameters. The analyzed kinetic parameters involve the value of the activation energy, the pre-exponential factor, and the suitable kinetic model.

2. Material and Method

2.1. Sample preparation
The OPFP material was obtained from oil palm smallholder plantations in Harapan Jaya Village, Muara Enim, South Sumatra, Indonesia. The OPFP sample was dried in an oven for 4 hours at a temperature of 110 °C. The sample was then powdered and being filtered using 40 mesh to equalize the size. After that, the OPFP sample powder was stored in an airtight bottle and maintained in a desiccator, and finally, the OPFP sample was ready to be tested.

2.2. TG experiments
The pyrolysis thermal decomposition behavior of OPFP samples was observed through the Mettler toledo TG/DSC1 thermogravimetric analyzer (TGA). An amount of 10 mg of OPFP was put into the crucible. The sample was heated at a temperature of 25 to 1000 °C in inert air gas of nitrogen. The heating rate of 20 °C/min was used, and nitrogen was flow at a rate of 100 ml/min.

2.3. Kinetics modeling
The pyrolysis kinetics of OPFP was basically determined by Arrhenius law. The basic equation of the conversion rate is written as

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

where \( \alpha \) is a mass fraction of degraded material and expressed as:

\[ \alpha = \frac{m_0 - m_i}{m_0 - m_f} \]

where, \( m_0 \) 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.

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

where \( T \) is the reaction temperature (K), \( R \) is the universal gas constant (0.008314 kJ/mol.K), \( E_a \) is the activation energy (kJ/mol), and \( A \) is the pre-exponential factor (/min). Based on equations (1) and (3), for a non-isothermal experiment \( (dT/dt = \beta) \), it is rewritten as a compound form becoming
\[
\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left( -\frac{E_a}{RT} \right) f(\alpha)
\] (4)

The integral form of the reaction model is written as \( g(\alpha) \). The analytical solution approach model is written into the following equations:

\[
g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left( -\frac{E_a}{RT} \right) dT
\] (5)

2.4. Coats-Redfern method

The Coats-Redfern method can be applied to the various selected model for predicting reaction order, activation energy, and pre-exponential factors. The basic equation for the Coats-Redfern method expressed as:

\[
\ln \left[ \frac{g(\alpha)}{T^2} \right] = \ln \frac{AR}{\beta E_a} \left( 1 - \frac{2RT}{E_a} \right) - \frac{E_a}{RT}
\] (6)

where \( R \) is the universal constant (0.008314 kJ/mol K), \( \beta \) is the heating rate and \( g(\alpha) \) is the kinetic function of the integration of \( f(\alpha) \). Plotting a graph between \( 1/T \) and \( \ln \left[ \frac{g(\alpha)}{T^2} \right] \) is able to form a straight line to get the slope and intercept values to determine the activation energy and pre-exponential factor, respectively. Most of the thermal degradation reactions mechanism of solid materials are presented in the five categories such as listed in Table 1.

| Reaction mechanism | Differential form \( f(\alpha) \) | Integral form \( g(\alpha) \) |
|--------------------|-------------------------------|-----------------------------|
| **Reaction order** |                               |                             |
| F1                 | \( 1 - \alpha \)             | \( -\ln(1 - \alpha) \)       |
| F1.5               | \( (1 - \alpha)^{3/2} \)     | \( 2(1 - \alpha)^{3/2} - 1 \) |
| **Diffusion**      |                               |                             |
| D1                 | \( \frac{1}{2}\alpha \)     | \( \alpha^2 \)              |
| D2                 | \( -\ln(1 - \alpha) \)^{-1} | \( \alpha + (1 - \alpha) \ln(1 - \alpha) \) |
| D3                 | \( 3/2[(1 - \alpha)^{1/3} - 1]^{-1} \) | \( (1 - \frac{2}{3}\alpha) - (1 - \alpha)^{2/3} \) |
| **Nucleation and growth** |                   |                             |
| N1.5               | \( 3(1 - \alpha)[-\ln(1 - \alpha)]^{2/3} \) | \( [-\ln(1 - \alpha)]^{2/3} \) |
| N2                 | \( 2(1 - \alpha)[-\ln(1 - \alpha)]^{1/2} \) | \( [-\ln(1 - \alpha)]^{1/2} \) |
| **Phase of interfacial reaction** |           |                             |
| S1                 | \( 2(1 - \alpha)^{1/2} \)    | \( 1 - (1 - \alpha)^{1/2} \) |
| S2                 | \( 2(1 - \alpha)^{2/3} \)    | \( 1 - (1 - \alpha)^{1/3} \) |
| **Power law**      |                               |                             |
| P                  | \( 1 \)                       | \( \alpha \)                 |

3. Result and Discussion

3.1. OPFP pyrolysis characteristics

The thermal behavior of the OPFP sample was observed through TGA and DTG profiles, as shown in Figure 1. These graphs show that there are three steps of OPFP pyrolysis decomposition.
The first stage occurs at 30–150.2 °C temperatures range, where the sample undergoes a mass loss of up to 8.5% due to evaporation of the moisture content. The second stage occurs at 150.2–650.5 °C temperatures range, with a mass loss of about 74.4%, related to the evaporation of both volatile compounds and volatile organic materials, including cellulose and hemicellulose [14,15]. The third stage occurs above 650.5 °C, with mass loss of almost 85.4%. The thermal degradation of OPFP at this stage is relatively sloping due to the decomposition of lignin and the remaining char. The temperature characteristics of the OPFP pyrolysis are shown in Table 2.

**Table 2. OPFP pyrolysis temperature characteristics**

| Steps | T_i (°C) | T_max (°C) | T_f (°C) | Mass loss (%) | M_max (%/s) |
|-------|----------|------------|----------|---------------|-------------|
| I     | 25       | 74.243     | 150.205  | -8.451        | -0.04526    |
| II    | 150.205  | 359.334    | 650.553  | -74.474       | -0.19526    |
| III   | 650.553  | 711.659    | 993.28   | -85.485       | -0.00931    |

3.2. Kinetic analysis of OPFP biomass pyrolysis

Table 3 shows the OPFP kinetics parameters calculated using the Coats-Redfern method proposed by Naqvi et al. [16]. The values of activation energy, R^2, and Log A are estimated at intervals of α from 0.05 to 0.95. The R^2 (correlation coefficient) value close to 1 is considered to have good accuracy.

The Chemical Reaction Order F1.5 model shows the highest R^2 value of 0.99, in which the activation energy of OPFP pyrolysis is 80.56 kJ/mol and Log A 7.21/min. This activation energy value is comparable to the microalgae *Spirulina platensis* and *Cassava stalk*, 84.61 and 91.19 kJ/mol, respectively [17,18], and it is higher than that of *water hyacinth* and palm date biomass, which are 60.74 and 22 - 43.6 kJ/mol, respectively [19,20], but it is lower than *Cornsilk*, *T.chuii*, and *N.cculata* which are 207.37; 101.05, and 251 kJ/mol, respectively [21–23]. The Chemical Reaction Order F1.5 model shows a homogeneous kinetics model, and the thermal conversion value directly proportional to the reaction rate [24].
Table 3. The kinetic parameters of OPFP biomass pyrolysis

| Models Name | Stage II |            |            |
|-------------|----------|------------|------------|
|             | Ea (kJ/mol) | R²       | Log A (1/min) |
| F1          | 42.77     | 0.903     | 2.87       |
| F1.5        | 80.56     | 0.990     | 7.21       |
| D1          | 64.62     | 0.796     | 4.34       |
| D2          | 72.79     | 0.838     | 4.89       |
| D3          | 76.37     | 0.856     | 4.61       |
| N1.5        | 25.05     | 0.873     | 1.20       |
| N2          | 16.20     | 0.829     | 0.29       |
| S1          | 34.00     | 0.822     | 1.62       |
| S2          | 36.70     | 0.852     | 1.74       |
| P           | 27.12     | 0.726     | 1.16       |

4. Conclusion
OPFP is abundant in oil palm biomass, and it can be used as an alternative fuel for energy generation. The characteristics of OPFP pyrolysis show that it is divided into three steps of decomposition, including the stage of the evaporation of moisture, followed by thermal degradation of cellulose and the hemicellulose stage, and the final stage indicating the decomposition of lignin and remaining char. The activation energy value refers to the F1.5 Chemical Reaction Order model is 80.56 kJ/mol, with the accuracy of the model of $R^2$ is 0.99 and Log A 7.21/min. Based on this thermal characterization, OPFP is profoundly feasible as an environmentally friendly future renewable energy alternative.

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