Kinetics Analysis on Catalytic Pyrolysis of Empty Fruit Bunch (EFB) with Copper Oxide Doped Aluminium Oxide (CuO/Al₂O₃) Catalyst

A R Mohamed¹, A M Zin², S N A Ahmad Termizi¹, K S A Sohaimi¹, N I I N Izhar¹

¹Department of Chemical Engineering Technology, Faculty of Engineering Technology, Universiti Malaysia Perlis, Padang Besar, Perlis
²Department of Applied Sciences, Universiti Teknologi MARA, Penang Branch, 13500 Permatang Pauh, Pulau Pinang, Malaysia

Email: alina@unimap.edu.my

Abstract. This study focuses on dynamic non-catalytic and catalytic pyrolysis of empty fruit bunch (EFB) with copper oxide doped aluminium oxide (CuO/Al₂O₃) at linear ramp rates of 10, 15, 20, 25, 30 and 40 °Cmin⁻¹ at pyrolysis temperature of 28-1000 °C in a thermogravimetric analyzer (TGA). The thermogravimetric profiles for the thermochemical breakdown of EFB under non-catalytic and catalytic pyrolysis with CuO/Al₂O₃ comprise of three different levels. The kinetics analysis for the reactions were evaluated using the Kissinger and Ozawa methods. The values of activation energy (Ea) for non-catalytic EFB pyrolysis were 167.95 and 177.68 kJmol⁻¹ based on Kissinger and Ozawa methods respectively. For catalytic pyrolysis with approximately 9.09 wt% CuO/Al₂O₃ catalyst, the values of Ea reduced to 127.72 and 137.42 kJmol⁻¹ by Kissinger and Ozawa methods respectively. These values indicate that the presence of 9.09 wt% CuO/Al₂O₃ catalyst has successfully reduced Ea value for the EFB pyrolysis reaction.

1. Introduction

The crude palm oil (CPO) processing and production has contributed largely to the Malaysian economy. It was estimated that for the processing of every tonne of fresh fruit bunch, about 0.20-0.30 tonne of empty fruit bunch (EFB) was co-generated [1]. During the extraction process, other biomass wastes such as palm fibre and palm kernel shell were generated also [2]. EFB is an agricultural by-product or solid waste biomass rich in cellulose, hemicellulose and lignin. Any biomass can be transformed into biomass energy such as such as torrefied biomass and bio-oil via thermochemical processing such as torrefaction and pyrolysis [3-9]. The addition of catalyst during biomass pyrolysis is expected to improve the process either by increasing the yield of bio-oil or decreasing the amount of oxygenated compounds in the bio-oil [10]. Biomass pyrolysis can also be performed in a thermogravimetric analyzer (TGA). TGA is an analytical device to measure accurately the thermochemical profile of a material when it is subjected to a change in temperature.

¹ To whom any correspondence should be addressed
Dynamic non-isothermal catalytic pyrolysis of biomass can be conducted in a TGA in order to evaluate the effect of the catalyst in the biomass thermochemical process. Apart from that, the thermogravimetric and derivative thermogravimetric (DTG) data can be used to calculate the values of kinetics parameters namely activation energy (Ea) and pre-exponential factor (Ln A) [11, 12].

Usually, based-metal oxide is preferred in TG biomass pyrolysis because it is expected to be active in reducing the devolatilization temperature of biomass [13]. The addition of copper aluminium oxide (Cu/Al₂O₃) catalyst at 30 wt% catalyst loading in paper pyrolysis under dynamic non-isothermal condition in a TGA has promoted a much lower devolatilization temperature [13]. Cu/Al₂O₃ was also reported in catalytic pyrolysis of tomato waste that produced higher yield of 26.68% at 5 wt% catalyst loading [14]. It can be seen that the addition of Cu/Al₂O₃ in biomass pyrolysis is beneficial. This can also be proven by evaluating the kinetics parameters (Ea and Ln A) of the reaction. The kinetics parameters can be determined by several model-fitting methods such as Coats-Redfern [9, 15] and model-free methods such as Kissinger and Ozawa [12]. The kinetics parameters can be calculated by the model fitting method. However, the committee of International Confederation for Thermal Analysis and Calorimetry (ICTAC) would strongly recommended the performance of thermogravimetric pyrolysis process at several or multiple ramp rates [16]. Therefore, this paper reports about the dynamic non-isothermal non-catalytic and catalytic EFB pyrolysis with CuO/Al₂O₃ in TGA at several ramp rates and evaluation on the kinetic parameters (Ea and Ln A) using both Kissinger and Ozawa methods.

2. Materials and Methods

2.1 Biomass Pretreatment
EFB was collected from North Star Palm Oil Mills which was located in the northern region of peninsular Malaysia which was Kuala Ketil, Kedah, Malaysia. Firstly, EFB was washed with tap water to remove any orange fungus and unwanted materials. Then, EFB was manually shredded into bulky pieces, followed by drying in an oven at 80 °C K for 24 hours. The dried EFB was shredded again using a shredding machine and sieved to particle size of 250-500 μm. This particular particle size was chosen for the subsequent process which were non-catalytic and catalytic pyrolysis [10].

2.2 Catalyst Preparation
CuO/Al₂O₃ was synthesized by wet impregnation technique. Approximately, 10 g of aluminium oxide underwent calcination in a furnace at 650 °C for 5 hours. Meanwhile, 10 ml of deionized water was measured using a measuring cylinder and transferred into a 100 ml beaker. A certain mass of copper nitrate salt (Cu(NO₃)₂·3H₂O) was measured that refers to the atomic ratio of Cu:Al of 5:100 and it was dissolved in deionized water. After that, about 60% of the copper nitrate solution was added dropwise into the beaker that contained precalcined aluminium oxide. The mixture was dried for about 5 hours under ambient temperature. Next, the rest of the solution was added into aluminium oxide. Drying was performed again at 120 °C for 2 hours. Finally, the catalyst underwent calcination at 600 °C for 5 hours in a furnace.

2.3 Non-Catalytic and Catalytic Pyrolysis of EFB with CuO/Al₂O₃
The process of non-catalytic pyrolysis or pyrolysis in the absence of catalyst with the catalytic pyrolysis of EFB in the presence of catalyst were carried out in a TGA. Under non-catalytic pyrolysis or pyrolysis in the absence of catalyst, about 10 mg of EFB sample was used and located in a 70 μl aluminium oxide crucible. In catalytic condition or pyrolysis in the presence of catalyst, about 1.00-1.10 mg of CuO/Al₂O₃ sample was weighed and located into the 70 μl aluminium oxide crucible to yield the ration of catalyst to biomass of approximately 9.09 wt%. During both non-catalytic and catalytic pyrolysis, nitrogen gas was purged into the system at a flow rate of 100 ml/min under dynamic conditions from 28 °C to 1000 °C at multiple ramp rates of 10, 15, 20, 25, 30 and 40 °C/min. The thermogravimetric data was transferred into the Excel data spreadsheet and the calculation for kinetics parameters such as Ea and Ln A using the Kissinger and Ozawa method were performed [12].
2.4 Kinetics Analysis by Kissinger and Ozawa methods

Reaction of EFB non-catalytic and catalytic pyrolysis can be represented as Equation 1:

\[ A(\text{solid}) \rightarrow B(\text{solid}) + C(\text{volatile}) \]  

(1)

The basic kinetic equation is shown in Equation 2:

\[ \frac{da}{dt} = kf(\alpha) \]  

(2)

where \( \alpha \) is the conversion or the progress of reaction, the value of \( \alpha \) can be defined using Equation 3:

\[ \alpha = \frac{(w_0-w_t)}{(w_0-w_f)} \]  

(3)

where \( w_0 \) is the initial sample weight, \( w_t \) is the sample weight at time \( t \) and \( w_f \) is the final sample weight. Reaction rate constant, \( k \) is given by the Arrhenius equation as seen in Equation 4:

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

(4)

where \( A \) is pre-exponential factor, \( E_a \) is activation energy (\( \text{kJ mol}^{-1} \)), \( T \) is absolute temperature (\( K \)), \( R \) is a gas constant (\( 8.314 \times 10^{-3} \text{kJ mol}^{-1}K^{-1} \)). When Equation 2 and 4 are combined, a new equation is obtained as follows as shown in Equation 5:

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

(5)

\( \beta \) or ramp rate was a new parameter that was introduced when the EFB pyrolysis reaction was performed under dynamic non-isothermal condition.

\[ \beta = \frac{dT}{dt} \text{ or } dt = \frac{dT}{\beta} \]  

(6)

Insertion of Equation 6 into Equation 5 produces Equation 7 as follow:

\[ \frac{da}{dt^2} = A \exp\left(-\frac{E_a}{RT}\right)f(\alpha) \]

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

(7)

Equation 5 and 7 are the basic equations that could be used to generate kinetic parameters that utilized the thermogravimetric data obtained either at linear ramp rates, \( \beta \) or at selected ramp rate. The temperature-time relation was computed from the following expression:

\[ T = T_0 + \frac{\beta}{T} \]  

(8)

The combination of Equation 2 and 8 produced Kissinger and Ozawa equations:

The Kissinger equation is:

\[ \ln\left(\frac{\beta}{T^2}\right) = -\frac{E_a}{RTp} + \ln\left(\frac{AR}{Ea}\right) \]  

(9)

The Ozawa equation is:

\[ \ln(\beta) = \ln\left(\frac{AE}{RG(a)}\right) - 5.331 - 1.052 \frac{E_a}{RT} \]  

where \( g(a) \) is integral form of the kinetic mechanism function.

3. Results and Discussion

3.1 TG Analysis

Figure 1(a) and (b) show TG profiles for both non-catalytic and catalytic EFB pyrolysis with CuO/Al2O3 at multiple ramp rates of 10-40 °Cmin⁻¹. It is obvious that, the process of non-catalytic and catalytic pyrolysis of EFB with CuO/Al2O3 comprise of three different levels. The first level is the removal of physisorbed water that happened in the temperature range from 28 to 200 °C [5]. The second level is identified as the progressive degradation of hemicellulosic and lignocellulosic components of EFB that happened in the temperature region of 200-400 °C. The third level is the slow mass loss at temperature in the range of 400-800 °C that was contributed by the devolatilization of lignin component [5].
3.2 Derivative Thermogravimetric (DTG) Analysis

The DTG profiles for both non-catalytic or pyrolysis in the absence of catalyst and catalytic pyrolysis or pyrolysis in the presence of catalyst with CuO/Al₂O₃ are illustrated in Figure 2 (a) and (b). It can be observed that when the ramp rate is increased from 10 - 40 °Cmin⁻¹, the thermal decomposition rate increased over 160 – 400 °C for non-catalytic pyrolysis or pyrolysis of EFB in the absence of catalyst and 150 – 693 °C for catalytic EFB pyrolysis or pyrolysis in the presence of CuO/Al₂O₃ catalyst. The DTG profiles being moved towards a region of a higher temperature zone and the maximum loss of the mass also shifted towards higher values for catalytic EFB pyrolysis with CuO/Al₂O₃ in comparison to non-catalytic EFB pyrolysis [5, 12].

3.3 Kinetics analysis on Non-Catalytic and Catalytic EFB Pyrolysis with CuO/Al₂O₃ based on Kissinger and Ozawa methods.

Figure 3 (a) and (b) shows the plot of $\ln(\frac{\beta}{T^2})$ against $1/T$ for non-catalytic pyrolysis or pyrolysis in the absence of catalyst and catalytic pyrolysis or pyrolysis in the presence of catalyst with CuO/Al₂O₃ that follows the Kissinger method. Meanwhile, Figure 4 (a) and (b) shows the plot of $\ln \beta$ against $1/T$ for
both non-catalytic and catalytic EFB pyrolysis with CuO/Al₂O₃ that follows the Ozawa method. Table 1 shows the kinetic parameters for non-catalytic and catalytic EFB pyrolysis with CuO/Al₂O₃ based on the Kissinger and Ozawa methods. From Table 1, by both Kissinger and Ozawa methods, the values of R² for both non-catalytic and catalytic EFB pyrolysis with CuO/Al₂O₃ are more than 0.92 which indicate that the correlation of determination between dependable and non-dependable parameters are good. It was found that the values of Ea for non-catalytic pyrolysis of EFB were 167.95 and 177.68 kJmol⁻¹ by Kissinger and Ozawa methods respectively. The values of Ea have reduced to 127.72 and 137.42 kJ mol⁻¹ by Kissinger and Ozawa methods respectively. This indicates that the presence of 9.09 wt% CuO/Al₂O₃ catalyst has successfully reduced the values of Ea by approximately 40 kJmol⁻¹. These results are in good agreement with Yang et al. [17] that reported the Ea values of catalytic pyrolysis of biomass feedstock had reduced in the presence of Ni-based catalysts.

Figure 3(a) and (b): Linearization plots for non-catalytic and catalytic EFB pyrolysis with CuO/Al₂O₃ based on the Kissinger methods.

Figure 4(a) and (b): Linearization plots for non-catalytic and catalytic EFB pyrolysis with CuO/Al₂O₃ based on the Ozawa method.
Table 1 The kinetic parameters (Ea and ln A) from the non-catalytic and catalytic reaction of EFB pyrolysis using Kissinger and Ozawa methods.

| Method | Reaction | Equation | R²  | Ea (kJ mol⁻¹) | ln A |
|--------|----------|----------|-----|---------------|------|
| Kissinger | EFB | y = -21.252x + 24.454 | 0.9409 | 167.95 | 19.87 |
|         | EFB + CuO/Al₂O₃ | y = -16.161x + 16.228 | 0.9222 | 127.72 | 11.92 |
| Ozawa   | EFB | y = -22.483x + 39.299 | 0.9468 | 177.68 | 19.98 |
|         | EFB + CuO/Al₂O₃ | y = -17.389x + 31.069 | 0.9319 | 137.42 | 20.24 |

4. Conclusion
In this study, non-catalytic and catalytic EFB pyrolysis with CuO/Al₂O₃ were conducted at several ramp rates of 10–40 °Cmin⁻¹ and pyrolysis temperature of 28-1000 °C in TGA. The kinetics analysis for the reactions were evaluated using the Kissinger and Ozawa methods. The values of R² for the linearization curves for both Kissinger and Ozawa methods were more than 0.922 which indicated that the correlation of determination between the dependable and non-dependable parameters were good. The values of Ea for non-catalytic EFB pyrolysis were 167.95 and 177.68 kJmol⁻¹ based on Kissinger and Ozawa methods respectively. For catalytic pyrolysis with approximately 9.09 wt% CuO/Al₂O₃ catalyst, the values of Ea reduced to 127.72 and 137.42 kJmol⁻¹ by Kissinger and Ozawa methods respectively. These values indicate that the presence of 9.09 wt% CuO/Al₂O₃ catalyst has successfully reduced the value of Ea by approximately 40 kJmol⁻¹ for the EFB pyrolysis reaction.

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