Kinetic Parameters of Non-Isothermal Thermogravimetric Non-Catalytic and Catalytic Pyrolysis of Empty Fruit Bunch with Alumina by Kissinger and Ozawa Methods

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Abstract. The non-isothermal thermogravimetric non-catalytic and catalytic empty fruit bunch (EFB) pyrolysis with alumina were performed at different heating rates of 10, 15, 20, 25, 30 and 40 K/min under nitrogen atmosphere at a flow rate of 100 ml/min under dynamic conditions from 301 K to 1273 K. The activation energy were calculated based on Kissinger and Ozawa methods. Both reactions followed first order reactions. By Kissinger method, the activation energy and Ln A values for non-catalytic and catalytic EFB pyrolysis with alumina were 188.69 kJ/mol and 201.67 kJ/mol respectively. By Ozawa method, the activation energy values for non-catalytic and catalytic EFB pyrolysis with alumina were 189.13 kJ/mol and 201.44 kJ/mol respectively. The presence of catalyst increased the activation energy values for EFB pyrolysis as calculated by Kissinger and Ozawa methods.

1. Introduction
The In 2014, Malaysia had produced 19.67 million tonnes of crude palm oil. The crude palm oil processing industry created huge amount of biomass waste such as empty fruit bunch (EFB) and palm shell which required good waste management system. Due to the rapid reduction of fossil fuel, therefore developed countries pursued biomass as optional method of power generation [1]. Biomass was viewed as a potential source of renewable energy [2]. Therefore, empty fruit bunch (EFB) was targeted to replace non-renewable energy since the amount of EFB was abundant and easy to be collected. One of the promising methods for EFB utilization is via pyrolysis. Pyrolysis is a thermochemical processing of biomass under inert environment at moderate temperature of 400-700 °C to produce bio-oil, bio-char and bio-gas [3]. Thermogravimetric pyrolysis is a route to investigate the mass loss of biomass and produce information regarding the profiling of thermochemical breakdown of biomass [4;5]. The values of Ea and Ln A can be calculated from thermogravimetric data using several methods. These values are significant since the empirical information about the reaction can be elucidated. The information can be utilized in the design of reactor suitable with such reactions. Dynamic thermogravimetric pyrolysis of several biomass such as miscanthus [6], poplar wood [7], wheat straw lignin [8], rice straw [9], chestnut shells, cherry stones and grape seeds [10] and a mixture of plants tems such as cotton, wheat, rich and corn [11] had been reported. The kinetics studies were investigated by several methods such as Coats-Redfern, Kissinger and Ozawa methods. Thermogravimetric catalytic pyrolysis of biomass is an
interesting process that can be manipulated in order to modify the biomass pyrolysis process at fundamental level in the presence of catalyst added [12; 13].

The pyrolysis of EFB in reactors is a common process whereby the process parameters were optimized towards maximizing bio-oil [14]. Fast pyrolysis of empty fruit bunches [15]. Bio oils from pyrolysis of oil palm empty fruit bunches [16]. Optimum conditions for maximizing pyrolysis liquids of oil palm empty fruit bunch. A more recent interests were towards addition of various types of catalyst during EFB pyrolysis in order to improve the bio-oil properties towards reduction of oxygen content and maximization of hydrocarbon compounds. Most of the catalytic pyrolysis studies on EFB pyrolysis reported using different types of reactors such as fixed-bed [17;18], tube furnace [19] and semi-batch reactor [20].The catalytic pyrolysis of empty fruit bunch is a complex reaction involving lignocellulosic decomposition assisted by catalysts. The dynamic non-isothermal catalytic pyrolysis of EFB in thermogravimetric analyser and in the presence of alumina catalyst with its relevant kinetics parameters has not been reported yet. Therefore, this paper is aimed to report the kinetics of thermogravimetric catalytic pyrolysis of EFB with alumina by Kissinger and Ozawa methods.

2. Materials and methods

2.1. EFB pretreatment
EFB was obtained from North Star Palm Oil Mills, located in Kuala Ketil, Kedah, Malaysia. The biomass was rinsed with tap water to remove impurities and chopped manually. It was dried in the oven for 24 h at 343 K. The dried sample was shredded using shredding machine and sieved using the Retsch sieve shaker. The sieved EFB with particle size of 250–500 µm was selected for the pyrolysis process.

2.2. Catalyst preparation
Approximately 10 g of alumina (Al₂O₃) catalyst support, grade 135 (Sigma- Aldrich, Germany) was calcined in a furnace at 923 K for 5 h at a ramp rate of 3 K/min under static atmosphere and the catalyst was placed in a desiccators prior to application.

2.3. EFB pyrolysis at linear heating rates
The non-catalytic and catalytic pyrolysis of EFB were conducted using Mettler Toledo thermal analyser TGA/DSC 1 equipped with Star® software. In non-catalytic pyrolysis condition, approximately 10.00 mg of sample were placed in a 70 µl alumina crucible.

2.4. Catalytic EFB pyrolysis at linear heating rates
In catalytic condition, approximately 1.00 mg of alumina catalyst was weighed and placed inside the crucible containing 10.00 mg EFB to produce 9.09 wt% catalyst addition to biomass. The nitrogen gas was used as the carrier gas at a flow rate of 100 ml/min under dynamic conditions from 301 K towards final pyrolysis temperature of 1273 K at different rates of 10, 15, 20, 25, 30 and 40 K/min. Each heating rate produced data Excel spreadsheet and the data were calculated using Excel software with Ozawa and Kissinger methods.

2.5. Kinetic analysis using Kissinger and Ozawa method
Eq. (1) is the Kissinger equation whereas Eq. (2) is the Ozawa equation. Both Eq. (1) and (2) provided the formula for calculating the apparent activation energy (E) and the constant of ideal gas law, R. g(α) was the integral form of the kinetics mechanism function in Eq. (2) [21].

\[
\ln \left( \frac{\beta}{T^2p} \right) = -\frac{E}{RT} + \ln \left( \frac{AR}{E} \right) \quad (1)
\]

\[
\ln (\beta) = \ln \frac{AE}{Rg(\alpha)} - 5.331 - 1.052 \frac{E}{RT} \quad (2)
\]
3. Results and Discussions

3.1. TG and DTG Analysis

The TG curves for both non-catalytic and catalytic EFB pyrolysis with alumina, obtained at different heating rates of 10, 15, 20, 25, 30, 40 K/min, are plotted separately in Figures 1(a) and 1(b). The curves showed the thermal degradation of EFB that shifted towards the right as the heating rate was increased. The shift in the TGA curves at higher heating rates was due to different heat transfer and kinetic rates delaying the sample decomposition [22].

![Figure 1. TG curves for (a) EFB pyrolysis and (b) catalytic EFB pyrolysis with Al.](image)

The DTG curves for both EFB pyrolysis and catalytic EFB pyrolysis are shown in Figures 2(a) and 2(b). DTG indicates the corresponding rate of weight loss. The DTG peaks differed in their position and height, because the heating rate acted as a significant factor on lignocellulosic thermal decomposition [21].

![Figure 2. DTG curves for (a) EFB pyrolysis and (b) catalytic EFB pyrolysis with Al.](image)

3.2. Kinetics analysis based on Kissinger and Ozawa method

Kissinger and Ozawa methods were respectively differential and integral thermal analysis methods which were used to determine activation energy of degradation at different heating rates [8].

3.2.1 Kissinger method. The graph of ln (β/T²) against 1/T for non-catalytic EFB pyrolysis and catalytic EFB pyrolysis with alumina are plotted in Figure 3 and Figure 4 respectively.
3.2.2 Ozawa method.
The graph of \( \ln \beta \) against \( 1/T \) for non-catalytic EFB pyrolysis and catalytic EFB pyrolysis with alumina are plotted in Figure 5 and Figure 6 respectively.

Figure 3. Linearization curves of Kissinger method for non-catalytic EFB pyrolysis.

Figure 4. Linearization curves of Kissinger method for catalytic EFB pyrolysis with alumina.

Figure 5. Linearization curves of Ozawa method for non-catalytic EFB pyrolysis.

Figure 6. Linearization curve of Ozawa method for catalytic EFB pyrolysis with Al.
From Table 1, by Kissinger method, non-catalytic and catalytic EFB pyrolysis with alumina have good \( R^2 \) values which were 0.9561 and 0.9637 respectively. And by Ozawa method, both non-catalytic EFB pyrolysis and catalytic EFB pyrolysis with alumina have good \( R^2 \) values which are 0.9602 and 0.9670 respectively. The high values of coefficient of determination, \( R^2 \) indicated that there were strong correlation between the dependable and non-dependable parameters.

The kinetic parameters between non-catalytic and catalytic EFB pyrolysis with alumina between both Kissinger and Ozawa methods are also shown in Table 1. By both Kissinger and Ozawa methods, the activation energy values for non-catalytic EFB pyrolysis are 188.69 and 189.13 kJ/mol respectively which are much lower compared to activation energy values in catalytic EFB pyrolysis with alumina which are 201.67 and 201.44 kJ/mol respectively. The presence of alumina at about 9.09 wt% has increased activation energy values for EFB pyrolysis by 12.98 and 12.31 kJ/mol as calculated by Kissinger and Ozawa methods respectively. Therefore, the catalytic EFB pyrolysis has followed different pathway for reaction to proceed of which its mechanism is difficult to define. This could be due to the phase of alumina catalyst used which is suspected in the \( \alpha \)-phase. The x-ray diffraction (XRD) analysis is in progress and will reveal the crystalline phase of alumina catalyst. It is of our interest to investigate the values of apparent activation energy by the isoconversional model-free methods such as Flynn-Wall-Ozawa method in our subsequent analysis.

| Method   | Reaction                          | Equation               | \( R^2 \) | \( E_a \) (kJ/mol) | Ln A |
|----------|-----------------------------------|------------------------|-----------|-------------------|------|
| Kissinger| Non-catalytic EFB pyrolysis       | \( y = -22.70 \times 10^3 x + 26.81 \) | 0.9561    | 188.69            |      |
|          | Catalytic EFB pyrolysis with alumina | \( y = -24.26 x + 29.32 \) | 0.9637    | 201.67            | 39.42|
| Ozawa    | Non-catalytic EFB pyrolysis       | \( y = -25.93 \times 10^3 x + 41.66 \) | 0.9602    | 189.13            | 39.96|
|          | Catalytic EFB pyrolysis with alumina | \( y = -25.49 x + 44.17 \) | 0.9670    | 201.44            | 39.41|

4. Conclusion
Non-isothermal thermogravimetric non-catalytic and catalytic EFB pyrolysis with alumina were conducted at different heating rates. The values of activation energy and Ln A from non-catalytic and catalytic EFB pyrolysis with alumina catalyst were calculated by using Kissinger and Ozawa methods. By using Kissinger method, the \( E_a \) values calculated for non-catalytic is lower than catalytic EFB pyrolysis with alumina which are 188.69 kJ mol\(^{-1}\) and 201.67 kJ/mol\(^{-1}\) respectively. The results show the same pattern with Ozawa methods. The activation energy values calculated for non-catalytic is lower than catalytic EFB pyrolysis with Al which are 189.13 kJ mol\(^{-1}\) and 201.44 kJ mol\(^{-1}\) respectively.

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