Thermal degradation of Shredded Oil Palm Empty Fruit Bunches (SOPEFB) embedded with Cobalt catalyst by Thermogravimetric Analysis (TGA)

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Abstract. Thermal behavior and decomposition kinetics of shredded oil palm empty fruit bunches (SOPEFB) were investigated in this study by using thermogravimetric analysis (TGA). The SOPEFB were analyzed under conditions of temperature 30 °C to 900 °C with nitrogen gas flow at 50 ml/min. The SOPEFB were embedded with cobalt (II) nitrate solution with concentration 5%, 10%, 15% and 20%. The TG/DTG curves shows the degradation behavior of SOPEFB following with char production for each heating rate and each concentration of cobalt catalyst. Thermal degradation occurred in three phases, water drying phase, decomposition of hemicellulose and cellulose phase, and lignin decomposition phase. The kinetic equation with relevant parameters described the activation energy required for thermal degradation at the temperature regions of 200 °C to 350 °C. Activation energy (E) for different heating rate with SOPEFB embedded with different concentration of cobalt catalyst showing that the lowest E required was at SOPEFB with 20% concentration of cobalt catalyst.

1. Introduction

Palm oil production in Malaysia listed as second largest exporting country after Indonesia surpassed in 2007, and the Federal Land Development Authority, FELDA is provided 375 hectares for Palm Oil plantations besides the Malaysian Palm Oil Council, MPOC plays the roles as promoter in the vegetable oils and fat market to the international demand [8]. While the production of palm oil in Malaysia rapidly expand, the oil palm empty fruit bunches is considered as solid waste from palm oil industry gives benefits by using process of thermal degradation to converts the biomass to bio-oil.

Before the researcher discovered the specialty of OPEFB in bio-oils, OPEFB was used as organic fertilizer and burned in oil palm mills as a source of heat and energy [2]. OPEFB is considered as fibrous material and has 65% of moisture content. Based on these, the pre-treatment of OPEFB is contains almost zero sand and other contaminants (Al).

There are three components mainly consist in oil palm empty fruit bunches which are hemicellulose, cellulose, and lignin that effects the texture, physical properties and thermal and combustion reactivity. To converts biomass into bio-fuels, these three components must be decomposed properly. The idea to decomposed these components is by pyrolysis which from Thermo-
Gravimetric Analyzer, TGA and through thermal degradation process. The data from the TGA shows that the decomposition of hemicellulose occurs at temperatures 160-360 °C, while volatilization of cellulose at temperature 240 - 400 °C and decomposition of lignin are at temperature 200-700 °C [10].

To upgraded bio-oil into these conditions, the biomass is go through under catalytic fast pyrolysis and considered as most promising way [13]. To enhanced bio-oils, the catalyst used should be selected based on highly active, resistant to deactivation, readily recycled and cheap. The active metals recommended are cobalt, ferum, zinc and etc, is used in this catalytic fast pyrolysis. The purpose of this study is to investigate the thermal degradation rate and activation energy required from variation of heating rate and concentration of cobalt catalyst by analyzing the Tg/DTG curves.

2. Materials and Methods

2.1 Materials
The shredded oil palm empty fruit bunches (SOPEFB) obtained for this experiment was from Kilang Sawit FELDA Sungai Tengi. Sabak Bernam, Selangor. Sample of SOPEFB was weight 10 grams before soaked into cobalt (II) nitrate solution.

2.2 Catalyst Preparation
Cobalt catalyst solutions were prepared by mixing the Cobalt (II) nitrate powder and water into 200ml beaker with four concentrations which were 5, 10, 15, and 20% w/w. The samples were soaked for 24 hours. The SOPEFB then dried in the oven with temperature below than 60°C for 5-6 hours.

2.3 Thermogravimetric and differential thermal analyses (Tg/DTG)
Thermo-gravimetric and differential thermal analyses (Tg/DTG) were conducted by using nitrogen gas which is flow at 50ml/min and heat from 30 °C to 900 °C at four different heating rates (10, 20, 30, and 40 °C/min) adopted from Pichet Ninduangdee (2015).

2.4 Kinetic Analysis
Kinetic parameters of SOPEFB such as activation energy (E), the pre-exponential factor (A), and the reaction order (n), can be determined by using Arrhenius equation and modified Arrhenius equation.

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

Modified Arrhenius equation:

\[ k = AT^m \exp \left( \frac{-E}{RT} \right) \]

Where m is mass and at m = 0, the modified equation is become Arrhenius equation. Hence, for 1st order reaction:

\[ \frac{d\alpha}{dt} = k(1 - \alpha) \]

For nth order reaction:

\[ \frac{d\alpha}{dt} = k(1 - \alpha)^n \]

By combining modified Arrhenius equation and nth order reaction equations,
Where:

\[ A \] is the pre-exponential factor or frequency factor,
\[ E \] is activation energy,
\[ R \] is the universal gas constant,
\[ T \] is temperature at the current time,

\[ \alpha \] is the biomass decomposition rate as a time-related parameter in the dimensionless form as below:

\[ \alpha = \frac{w_o - w_\tau}{w_o - w_f} \]

Where:

\[ w_o \] is initial weight,
\[ w_\tau \] is weight at time \( \tau \),
\[ w_f \] is final weight.

At constant heating rate, \( \beta \):

\[ \beta = \frac{dT}{d\tau} \]

Then, rewritten equation is:

\[ \frac{d\alpha}{dT} = \frac{A}{\beta} T^m \exp\left(\frac{-E}{RT}\right) (1 - \alpha)^n \]

Consider as \( m = 0 \) and \( n = 1 \),

\[ \ln \left( \frac{d\alpha}{dT} \right) = \ln \left( \frac{A}{\beta} \right) - \frac{E}{RT} + \ln(1 - \alpha) \]

Consequently, the final equation can be obtained by simplified the equation above:

\[ \ln \left( \frac{d\alpha}{dT} \right) \left( 1 - \alpha \right) = \ln \left( \frac{A}{\beta} \right) - \frac{E}{RT} \]

Therefore, the activation energy, \( E \) and frequency factor, \( A \) can be deduced from the slope and intercept of \( \ln \left( (d\alpha/dT)/(1-\alpha) \right) \) vs \( 1/T \).

3. Results and Discussion

3.1 The effects of heating rate on SOPEFB

The data collected from TGA for pyrolysis of SOPEFB, and treated SOPEFB were presented in \( T_G \) and \( D_{TG} \) curves. The \( T_G \) indicating weight loss (mg) while \( D_{TG} \) indicating the derivative mass loss (mg/min) under the presence of nitrogen gas at 50 ml/min and heat from temperature 30 °C until 900 °C with four different heating rates (10, 20, 30, and 40°C/min). From the \( T_G \) curves, the shaped form was S-shaped temperature dependent weight loss. The \( D_{TG} \) curves show some peaks and represented the phases in pyrolysis of SOPEFB. Phase I which occurs at temperature below than 200°C was where the remaining water drying and evaporation light component [7]. Phase II where hemicellulose and cellulose and lignin were devolatilized at temperature 200 to 400°C. At temperature 400 to 600°C was where the remaining lignin was devolatilized and the char degradation started at temperature 600 °C and above [10].
Figure 1 shows the ignition temperature ($T_{ign}$), temperature peaks ($T_{p,1}$ and $T_{p,2}$), and burnout temperature ($T_b$). The ignition temperature ($T_{ign}$), is at the certain temperature, the weight of SOPEFB start to loss because of the degradation of hemicellulose and cellulose. The temperature peak 1 ($T_{p,1}$), is at that temperature, the mass of the weight is loss during decomposition of hemicellulose and cellulose. The temperature peak 2 ($T_{p,2}$), is at that temperature, most of the remaining lignin is decomposed before char conversion. The burnout temperature ($T_b$), is where the char production is start.

From table 1 below, the $T_{p,1}$ average for fresh SOPEFB with different heating rate was at temperature 329°C and with the average $T_{ign}$ at temperature 225°C. For SOPEFB with 5% concentration of cobalt catalyst, the average $T_p,1$ was at temperature 348°C and $T_{ign}$ was at 208°C and average Tb with temperature 530°C. SOPEFB with the 10% concentration of cobalt catalyst was recorded the average of $T_{p,1}$, $T_{ign}$ and Tb were 345°C, 201°C and 586°C respectively. There were no $T_{p,2}$ data recorded for fresh SOPEFB and SOPEFB with 5% and 10% concentration of the cobalt catalyst. SOPEFB with 15% concentration of the cobalt catalyst has average temperatures of $T_{p,1}$ at 335°C, $T_{p,2}$ at 491°C, $T_{ign}$ at 200°C and Tb at 592°C while the average temperatures for SOPEFB with 20% concentration of cobalt catalyst has $T_{p,1}$ at 335°C, $T_{p,2}$ at 485°C, $T_{ign}$ at 196°C and Tb at 604°C. The $T_{p,2}$ is present at these two concentrations.

The heating rate used in TGA is 10, 20, 30, and 40 °C/min and samples SOPEFB used were fresh SOPEFB, and 5%, 10%, 15% and 20% concentration of cobalt catalyst. From the TG curves, it was observed that the char production is decreased with heating rate increase. However, the most effective with lowest char production was at heating rate 10°C/min. It was proven that the effective heat transfer of the samples happens when it under lower heating rate.
Table 1. Thermogravimetric parameters of SOPEFB with different heating rate and concentration of cobalt nitrate.

| SOPEFB                | Heating rate (°C/min) | Temperature (°C) |
|-----------------------|-----------------------|------------------|
|                       |                       | T<sub>5,1</sub> | T<sub>5,2</sub> | T<sub>5,3</sub> | T<sub>5,4</sub> |
| Fresh                 | 10                    | 317             | -               | 153             | 533             |
|                       | 20                    | 326             | -               | 194             | 533             |
|                       | 30                    | 334             | -               | 160             | 607             |
|                       | 40                    | 338             | -               | 167             | 629             |
| 5% of cobalt catalyst | 10                    | 313             | -               | 210             | 507             |
|                       | 20                    | 354             | -               | 200             | 509             |
|                       | 30                    | 360             | -               | 203             | 504             |
|                       | 40                    | 363             | -               | 217             | 601             |
| 10% of cobalt catalyst| 10                    | 335             | -               | 186             | 562             |
|                       | 20                    | 345             | -               | 200             | 600             |
|                       | 30                    | 348             | -               | 209             | 620             |
|                       | 40                    | 353             | -               | 207             | 562             |
| 15% of cobalt catalyst| 10                    | 329             | 478             | 195             | 552             |
|                       | 20                    | 337             | 487             | 201             | 570             |
|                       | 30                    | 339             | 494             | 201             | 606             |
|                       | 40                    | 314             | 504             | 204             | 639             |
| 20% of cobalt catalyst| 10                    | 326             | 476             | 183             | 588             |
|                       | 20                    | 333             | 482             | 192             | 595             |
|                       | 30                    | 340             | 488             | 206             | 612             |
|                       | 40                    | 342             | 493             | 200             | 619             |

Figure 2, 3, 4, 5, and 6 shows the lowest char production was at 10°C/min of heating rate for sample of SOPEFB.

Figure 2. TG curves of fresh SOPEFB with different heating rate.

Figure 3. TG curves of SOPEFB with 5% concentration of cobalt catalyst with different heating rate.
From DTG curves, it was observed that the peak of the mass loss at phase II which decomposition of hemicellulose and cellulose were shifted to the right with increased heating rate which means that the highest weigh loss was at higher temperature with higher heating rate. Figure 7, 8, 9, 10, and 11 shows the patterns of the DTG curves with different heating rate.
Figure 9. DTG curves of SOPEFB with 10% concentration of cobalt catalyst with different heating rate.

Figure 10. DTG curves of SOPEFB with 15% concentration of cobalt catalyst with different heating rate.

Figure 11. DTG curves of SOPEFB with 20% concentration of cobalt catalyst with different heating rate.

3.2 The effects of different concentration of cobalt catalyst

From T_G curves which is in figure 12, 13, 14 and 15, it was observed that the char production was decreased with increased concentration of cobalt catalyst. When heating rate as constant, lowest char production was sample of SOPEFB with 20% concentration of cobalt catalyst.

If higher concentration is embedded with the samples of SOPEFB, the char production is less. However, at 15% and 20% of concentration of cobalt catalyst, at the phase I which at the water evaporation, second peak was appeared because of the coating from the cobalt catalyst like shows in DTG curves.

Figure 12. T_G curves of SOPEFB with different concentration of cobalt catalyst at heating rate 10 °C/min.

Figure 13. T_G curves of SOPEFB with different concentration of cobalt catalyst at heating rate 20 °C/min.
Figure 14. T\(_g\) curves of SOPEFB with different concentration of cobalt catalyst at heating rate 30 °C/min.

Figure 15. T\(_g\) curves of SOPEFB with different concentration of cobalt catalyst at heating rate 40 °C/min.

In D\(_{TG}\) curves, at the samples of fresh SOPEFB and SOPEFB with concentration 5% and 10% cobalt catalyst, there were no second peak at the third phase which at lignin decomposition. It was because of most of the lignin was decomposed at the second phase with hemicellulose and cellulose. It also does not have second peak at the first phase unlike SOPEFB with concentration 15% and 20% cobalt catalyst because the coating of cobalt nitrate solution was not thick. Figure 16, 17, 18, and 19 shows the D\(_{TG}\) curves of different cobalt catalyst concentration with different heating rate.

Figure 16. D\(_{TG}\) curves of SOPEFB with different concentration of cobalt catalyst at heating rate 10 °C/min.

Figure 17. D\(_{TG}\) curves of SOPEFB with different concentration of cobalt catalyst at heating rate 20 °C/min.

Figure 18. D\(_{TG}\) curves of SOPEFB with different concentration of cobalt catalyst at heating rate 30 °C/min.

Figure 19. D\(_{TG}\) curves of SOPEFB with different concentration of cobalt catalyst at heating rate 40 °C/min.
3.3 Kinetic parameters of SOPEFB
Table 2 shows the kinetic parameters of samples of SOPEFB with different concentration of cobalt catalyst for different heating rate (10, 20, 30 and 40°C). The kinetic parameters were determined for temperature regions of 200 to 350°C to give the accurate fitting of the experimental data. The accuracy of the graph proven with the correlation coefficient (r) adjacent with value 1.0.

From the table 2, shows that the activation energy (E) at heating rate 10 and 20°C/min were decreased with increased SOPEFB with concentration of cobalt catalyst. However, at heating 30 and 40°C/min the value of activation energy (E) were scattered and SOPEFB with 20% concentration cobalt catalyst was higher than 5%, 10% and 10%. This was because of the thick coated of cobalt nitrate solution required more energy to degraded the SOPEFB

Table 2. Kinetic parameters of SOPEFB.

| Heating rate, β | Samples of SOPEFB | Fitting equation | Correlation coefficient, r | Activation energy, E (J/mol) | Pre exponential factor, A (1/min) |
|----------------|-------------------|------------------|-----------------------------|-------------------------------|----------------------------------|
| 10             | Fresh             | $y = 1.0247x-2.5876$ | 0.9766                      | 160.02                        | 0.752                            |
|                | 5%                | $y = 1.7129x-3.807$  | 0.9800                      | 142.41                        | 0.222                            |
|                | 10%               | $y = 1.5498x-2.2169$ | 0.9787                      | 128.85                        | 0.147                            |
|                | 15%               | $y = 1.4322x-4.7813$ | 0.9829                      | 119.07                        | 0.103                            |
|                | 20%               | $y = 1.3692x-4.7891$ | 0.9835                      | 113.84                        | 0.0812                           |
| 20             | Fresh             | $y = 2.6093x-2.1253$ | 0.9864                      | 174.07                        | 2.388                            |
|                | 3%                | $y = 1.5207x-4.83$   | 0.9829                      | 126.43                        | 0.195                            |
|                | 10%               | $y = 1.4335x-4.7817$ | 0.9853                      | 120.80                        | 0.168                            |
|                | 15%               | $y = 1.3611x-4.9242$ | 0.9851                      | 118.35                        | 0.165                            |
|                | 20%               | $y = 1.3413x-4.9242$ | 0.9872                      | 113.78                        | 0.145                            |
| 30             | Fresh             | $y = 1.9392x-2.7277$ | 0.9856                      | 161.21                        | 1.961                            |
|                | 5%                | $y = 1.5615x-4.6681$ | 0.9863                      | 129.83                        | 0.282                            |
|                | 10%               | $y = 1.4014x-4.983$  | 0.9839                      | 116.51                        | 0.206                            |
|                | 15%               | $y = 1.4785x-4.8115$ | 0.9850                      | 122.92                        | 0.298                            |
|                | 20%               | $y = 1.9095x-3.133$  | 0.9880                      | 165.88                        | 1.282                            |
| 40             | Fresh             | $y = 2.3092x-1.5883$ | 0.9907                      | 191.99                        | 8.088                            |
|                | 3%                | $y = 1.6243x-4.4788$ | 0.9901                      | 135.94                        | 0.434                            |
|                | 10%               | $y = 1.4906x-4.7525$ | 0.9872                      | 123.93                        | 0.342                            |
|                | 15%               | $y = 1.5537x-4.4068$ | 0.9842                      | 129.34                        | 0.478                            |
|                | 20%               | $y = 2.1479x-2.707$  | 0.9948                      | 176.38                        | 2.669                            |

4. Conclusions
The data collected from TGA were used to construct T$_G$ and D$_T$G curves. From T$_G$ and D$_T$G curves, it shows that, the thermal degradation of the shredded oil palm empty fruit bunches of were divided into three phases which were phase I, phase II and phase III. At phase I, this was the temperature region where water and cobalt nitrate coating were evaporated. The average temperature region of this phase was below 200°C. Second phase was at temperature range of 200 to 400°C where the highest peak of the weight loss of shredded oil palm empty fruit bunches samples because of decomposition of hemicellulose and cellulose. The third phase was for decomposition of lignin at range temperature of 600°C and above. The peak of this phase is low rather than at phase II because the lignin also started to be decomposed at second phase besides hemicellulose and cellulose.

The effect of heating rate and different concentration was decreased in char production. The production of char was decreased with increased heating rate and increased concentration of cobalt catalyst embedded into shredded oil palm empty fruit bunches. The most effective with less char production is at 10°C/min because of the heat was effectively transferred to the samples.
Activation energy, $E$ required for degraded the shredded oil palm empty fruit bunches samples were decreased with the increased concentration of cobalt catalyst. However, at the higher heating rate, the activation energy of 20% concentration of cobalt catalyst higher than others. It can simply conclude that the energy was required more to decomposed the coating of cobalt nitrate before started to decomposed hemicellulose and cellulose. But, at lower heating rate, the heat transfer was more efficient to decomposed the coating of cobalt nitrate.

The best criteria in order to get less char production and heat transfer efficient was at lower heating rate which were at 10 or 20 °C/min and at the higher concentration which are 15% or 20% concentration of cobalt catalyst.

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