Isothermal torrefaction of coconut fiber in a fixed bed reactor

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Abstract. Torrefaction of coconut fiber was performed in a fixed bed reactor at torrefaction temperature of 220-300°C and holding time of 20-60 mins under nitrogen atmosphere. The torrefaction reaction kinetics were determined using the Coats-Redfern method. The values of activation energy and pre-exponential factor at holding time of 20, 40 and 60 minutes are in the range of 30.25-43.61 kJ/mol and 4.03-152.69 min\(^{-1}\) respectively. The proximate analysis was performed on the raw and torrefied coconut fiber. It was identified that the moisture content and volatile matter decreased but the ash content and the fixed carbon increased when the torrefaction temperature were increased from 220-300 °C. The morphological properties of coconut fiber and torrefied coconut fiber were analyzed using Scanning electron microscope (SEM). From SEM, the degree of severity due to torrefaction process towards the surface structure of torrefied coconut fiber can be visualized and increased with increasing torrefaction temperature with merging of pores. The existence of functional group such as hydroxyl (O-H) and alkane (C-H) were identified on the surface of raw and torrefied coconut fiber by Fourier Transform Infrared spectroscopy (FTIR).

1. Introduction
Fossil fuel is a non-renewable energy resource that has become the major energy source to support the increasing demand for energy nowadays. However, fossil fuel experienced depletion and also shown negative impact on the environment via the combustion process that lead to global warming due to the emission of greenhouse gases which increase the global temperature. Therefore, the search for replacement of energy source has been initiated and biomass is a potential energy source replacement [1]. Renewable energy from biomass is a promising alternative energy source since biomass is renewable and available throughout the year. Biomass that is commonly used includes agricultural residues, woody biomass and urban wood waste. Biomass can be consumed alone or blended with coal for combustion, gasification and pyrolysis [2-6]. However, there are some limitations with utilizing raw biomass as fuel or solid fuel since biomass has high moisture content and low carbon content [1, 7,8]. Therefore, pretreatment is needed to convert biomass into a more suitable form for further processing [8].
Torrefaction is a prominent pretreatment process that reduces the moisture content of biomass with improved heating value and carbon content [9]. Torrefaction can be defined as a mild thermochemical pretreatment on biomass in an inert environment which is characterized by slow heating rate, long holding time and temperature, normally from several minutes to several hours and 200 °C-300 °C respectively [2]. Torrefaction improved the grindability, hydrophobicity, storage ability and the calorific value of biomass compared to raw biomass due to the removal of moisture content and volatile matters [10-12]. Torrefaction of several biomass such as Leucaena Leucocephala [13], empty fruit bunch [14-17], mesocarp fiber, kernel shell [18], sugarcane bagasse [19], tomato residues [20], spent coffee residue, chinese medicine residue and microalga residue [21] have been reported worldwide. In Malaysia, coconut fiber which is a seed-hair fiber obtained from the outer shell of the coconut is a good feedstock for torrefaction pretreatment process because coconut is available throughout the year. The utilization of raw coconut fiber biomass as an energy source has been reported as well as the substantial volume decreasing after physical treatment was performed on the coconut fiber [22]. It has been reported about oxidative and non-oxidative effect on microstructural changes of coconut fiber at torrefaction temperature of 285-325 °C [2]. However, it is identified that there are no reported studies on the pores changes of raw and torrefied coconut fiber under progressive torrefaction temperature of 220-300 °C under inert or completely non-oxidative environment. Therefore, this paper reports about the effect of torrefaction of coconut fiber under inert environment or nitrogen atmosphere at progressive torrefaction temperature of 220-300 °C and holding time of 20-60 mins towards improvement of porosity evolution.

2. Materials and Methods

2.1. Acquisition of coconut fiber
Coconut fiber was collected from markets and village in Padang Besar, Perlis. It was dried in the oven at 60 °C for 30 mins. It was ground using a grinder and sieved to obtain a sample with particle size < 500µm using Reitsch sieve shaker [23,24].

2.2. Torrefaction of coconut fiber
Torrefaction process of coconut fiber had been conducted in a fixed bed reactor with nitrogen flow of 150 ml/min and heating rate of 20 °C/min. The effects of two parameters such as torrefaction temperatures and holding times were investigated. The torrefaction temperature was varied in the range of 220 – 300 °C and the holding time was varied between 20-60 mins. Approximately 10 g of coconut fiber was placed into a fixed bed reactor. Then, the coconut fiber was heated up to torrefaction temperatures of 220°C, 240°C, 260°C, 280°C and 300°C at several holding times of 20, 40 and 60 mins. The physical appearance or color changes of the raw and torrefied coconut fiber were observed. The torrefied biomass was weighed. The mass yield was calculated using Equation 1. The samples were stored for further analysis [13].

\[
\text{mass yield} \% = \frac{\text{mass of torrefied coconut fiber (g)}}{\text{mass of raw coconut fiber feed into the reactor (g)}} \times 100\% \hspace{1cm} (1)
\]

Proximate analysis was performed on the raw and torrefied coconut fiber by ASTM method. Proximate analysis was used to determine the moisture content, volatile matter content, fixed carbon content and ash content in raw and torrefied coconut fiber. The analysis procedures were conducted according to American Standard Testing and Material (ASTM) ASTM E870-82 for raw coconut fiber and D-1762-84 for torrefied coconut fiber with slight modification [5]. Calculations on the kinetic parameters such as activation energy (Ea) and pre-exponential factor (Ln A) was performed on the experimental data using Coats-Redfern method [13, 25, 26].

2.3. Kinetics Analysis by Coats-Redfern method
The basic theoretical approach for thermochemical breakdown on biomass was referred [13, 25, 26]. The reaction scheme of coconut fiber torrefaction pretreatment was shown in the equation (2).

\[A \rightarrow B \rightarrow C\]  (solid sample) \rightarrow (solid residue) + (volatiles) \hspace{1cm} (2)
The basic kinetic equation is as shown in equation (3).
\[
\frac{d\alpha}{dt} = kf(\alpha)
\]  
(3)

where \( \alpha \) is the conversion or progress of reaction that occurred from 0.05 to 0.95. The value of \( \alpha \) could be calculated from equation (4).
\[
\alpha = \frac{w_0 - w_t}{w_0 - w_f}
\]  
(4)

\[ f(\alpha) = (1 - \alpha)^n \]  
(5)

where \( w_0 \) is initial sample, \( w_t \) is the sample weight at time \( t \) and \( w_f \) is final sample weight. \( f(\alpha) \) is the function of conversion of coconut fiber at progress of reaction while \( k \) is the rate constant and it was defined as Arrhenius equation.
\[
k = A \exp \left( \frac{-E_a}{RT} \right)
\]  
(6)

Equation (3) was substituted into equation (6) to produce equation (7).
\[
\frac{d\alpha}{dt} = A \exp \left( \frac{-E_a}{RT} \right) f(\alpha)
\]  
(7)

Heating rate (\( \beta \)) was introduced for dynamic non-isothermal process at increasing heating rate.
\[
\beta = \frac{dT}{dt} \text{ or } dt = \frac{dT}{\beta}
\]  
(8)

Equation (8) was substituted into equation (7).
\[
\frac{d\alpha}{d\frac{T}{\beta}} = A \exp \left( \frac{-E_a}{RT} \right) f(\alpha)
\]  
(9)

Equations (7) and (9) are two fundamental equations that could be used to generate kinetic parameters that utilize data from thermogravimetric process either at linear heating rate, \( \beta \) or at selected rate.

The Coats-Redfern method was being used to calculate the activation energy (\( E_a \)) and pre-exponential factor (\( \ln A \)) from thermochemical process. The equation is applicable when the reaction order (\( n \)) equals to 1.
\[
\ln \left[ \frac{-\ln (1 - \alpha)}{T^2} \right] = \ln \left[ \frac{AR}{\beta E_a \left( 1 - \frac{2RT}{E_a} \right)} \right] - \frac{E}{RT}
\]  
(10)

The raw and torrefied coconut fibers were analyzed for surface morphological analysis using scanning electron microscopy (SEM) and tested for functional groups using Fourier transform infrared (FTIR) spectroscopy. For SEM analysis, the analysis had been conducted using SEM (JEOL) to investigate the changes in the surface of the materials as a consequence of torrefaction process. First, the sample was placed onto SEM stub layer (layer with sticky tape). Then, the stub was put in sputter coater (Auto line cutter, JEOL: JFC-1600) for five mins for platinum coating in order to avoid being reflective during scanning process [13]. The Fourier Transform Infrared was carried out using a Perkin-Elmer
spectrophotometer, model Spectrum-65. Approximately 1 mg of sample was introduced by ATR technique and it was analyzed in the wavenumber range of 4000 – 400 cm$^{-1}$ with a resolution of 2 cm$^{-1}$ [27].

3. Results and Discussion

3.1 The effect of torrefaction on the physical features of coconut fiber

The effect of torrefaction at different torrefaction temperatures and holding times towards the physical features of coconut fibre area as shown in Figure 1. The color of coconut fiber changes from brown to black when increasing the torrefaction temperature. The color changes occurred mainly resulted from the thermochemical decomposition of hemicellulosic and partial cellulose fractions of coconut fiber during the torrefaction process. This observation is in good agreement with [1, 28].

|           | 20 min       | 40 min       | 60 min       |
|-----------|--------------|--------------|--------------|
| Raw       | ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) |
| 220 °C    | ![Image](image4.png) | ![Image](image5.png) | ![Image](image6.png) |
| 240 °C    | ![Image](image7.png) | ![Image](image8.png) | ![Image](image9.png) |
| 260 °C    | ![Image](image10.png) | ![Image](image11.png) | ![Image](image12.png) |
| 280 °C    | ![Image](image13.png) | ![Image](image14.png) | ![Image](image15.png) |
300 °C

Figure 1. Pictures of raw and torrefied coconut fiber at different torrefaction temperatures (220-300 °C) and holding times (20-60 mins).

3.2 The effect of torrefaction on the mass yield
Figure 2 shows the trend of mass yield against the torrefaction temperature of 220-300 °C at several holding times from 20-60 mins. The mass yield shows a decreasing trend for the torrefaction temperature from 220-300 °C for all holding times. These results are in good agreement with [13, 29]. During the torrefaction process, water and volatiles are removed through the partial decomposition of hemicellulose [30] and volatiles are removed via decomposition, devolatilization and depolymerization reactions [31].

Figure 2. The mass yield against torrefaction temperature of 220-330 °C at several holding times of 20-60 mins.

3.3 The kinetics parameters using the Coats-Redfern method
The values of kinetic parameters for the torrefaction of coconut fiber in a fixed bed reactor are presented in Table 1. The plot of $\ln\left[\frac{\ln(1-\alpha)}{T^2}\right]$ vs $\frac{1}{T}$ for the torrefaction of coconut fiber was performed using the Coats-Redfern method and follows the first order reaction. The values of $R^2$ which is the coefficient of determination for all equations are more than 0.9200 which indicates that there is good correlation between the dependable and non-dependable parameters [32].

Table 1. The values of kinetic parameters for the torrefaction of coconut fiber at different holding times

| Torrefaction time (min) | Equation               | $R^2$  | $E_a$ (kJ/mol) | $A$ (min$^{-1}$) |
|-------------------------|------------------------|--------|----------------|-----------------|
| 20                      | $y = -5245.9x - 3.5368$| 0.9329 | 43.61          | 152.69          |
| 40                      | $y = -4261.2x - 5.5285$| 0.9503 | 35.43          | 16.93           |
| 60                      | $y = -3637.9x - 6.8062$| 0.9219 | 30.25          | 4.03            |
From Table 1, the values of activation energy for torrefaction of coconut fiber decreased progressively from 43.61-30.25 kJ/mol with increasing torrefaction holding time from 20-60 mins. The preexponential factor, A values also decreased with the increase in time which were from 152.69 min\(^{-1}\) to 4.03 min\(^{-1}\). The lower values of \(E_a\) and \(\ln A\) indicate a higher reactivity and improved thermal properties [33].

3.4 Proximate analysis of raw and torrefied coconut fiber

Table 2 shows the proximate analysis of raw and torrefied coconut fiber at different torrefaction temperature. Generally, the moisture and volatile matter contents decreased from 3.44- 1.87% and 71.56- 38.94%, respectively with an increased in torrefaction temperature from 220-300 °C. Meanwhile, the fixed carbon and ash content increased from 24.95-55.36 % and 0.05- 3.83% respectively over increasing torrefaction temperature from 220-300 °C. This results could be due to the contribution of successive removal of physisorbed and chemisorbed water molecules and volatiles from the lignocellulosic components of coconut fiber at the expense of carbon enrichment when the torrefaction temperature was increased from 220-300 °C [9].

| Torrefaction Temperature (°C) | Volatile Matter Content (%) | Ash Content (%) | Moisture Content (%) | Fixed Carbon (%) |
|------------------------------|-----------------------------|-----------------|----------------------|-----------------|
| Raw                          | 71.56                       | 0.05            | 3.44                 | 24.95           |
| 220 °C                       | 60.91                       | 1.89            | 2.81                 | 34.39           |
| 240 °C                       | 55.92                       | 2.50            | 2.73                 | 38.85           |
| 260 °C                       | 46.92                       | 3.07            | 2.31                 | 47.70           |
| 280 °C                       | 41.93                       | 3.57            | 1.99                 | 52.51           |
| 300 °C                       | 38.94                       | 3.83            | 1.87                 | 55.36           |

3.5 SEM analysis on raw and torrefied coconut fiber

The raw and torrefied coconut fiber were analyzed by SEM to elucidate the differences in their surface morphological properties. The SEM micrographs obtained from raw and torrefied coconut fibers at different torrefaction temperature are shown in Figure 3. Figure 3(a) shows that the raw coconut fiber has compact particle structure fibrous with smooth homogeneous surface structure at 5000X magnification.

The existence of a slight deformation on the surface structure of torrefied coconut fiber at 220°C that indicates the initial onset of torrefaction process towards the surface structure of coconut fiber could be visualized in Figure 3(d). Upon increasing the torrefaction temperature to 240°C, more deformation or cracks on the surface structure of the torrefied coconut fiber (Figure 3(e-f)) which resulted from the devolatilization of hemicellulosic chemisorbed water molecules and internal volatiles from the hemicellulosic component of coconut fiber.

The degree of severity of surface deformation and cracking seemed to be increased as the torrefaction temperature was increased from 260 °C to 280 °C, as shown in Figure 3(g-i) respectively at X250 magnification. The initially smooth and homogeneous surface structure of raw coconut fiber had become deformed and formation of large pores is observed at 1000X magnification which results from recombination of adjacent pores. At higher torrefaction temperature of 300 °C, the pores recombine and emerge further as seen in Figure 3(j), which indicates that the complete degradation of the hemicellulosic portion of coconut fiber had been achieved.
3.6 FTIR Analysis on raw and torrefied coconut fiber

Figure 4 shows the FTIR spectra of raw and torrefied coconut fiber. From Figure 4, the presence of broad peak at the wavenumber of 3390-3411 cm\(^{-1}\) with O-H stretching indicates the presence of water molecules (H\(_2\)O) which could be physically adsorbed on the surface of raw and torrefied coconut fiber. The small shoulder peak at the wavenumber in the range of 2930-2938 cm\(^{-1}\) represents the existence of alkane group with C-H stretching on the raw and torrefied coconut fiber which agreed with [34]. The existence of peak at the wavenumber range of 1625-1500 cm\(^{-1}\) refers to the C=C bonds or unsaturation from alkene and benzene groups. Meanwhile, the peak at in the wavenumber range of 1450-1454 cm\(^{-1}\) is due to the presence of CH\(_{2}\) bend molecular from alkene functional group [35]. Both of peaks at the wavenumber range 1373-1318 cm\(^{-1}\) and 1035-1159 cm\(^{-1}\) show the presence of C=O stretching from COOH (carboxylic acid) group. It is also determined that all the peaks have similar characteristic which is the peak intensity decreases with increasing torrefaction temperature. The torrefaction process from temperature 220-300 °C has progressively eliminates or removed functional groups such as OH and C=O via several deoxygenation reactions such as dehydration, decarbonylation and decarboxylation.

4. Conclusion

Torrefaction of coconut fiber was performed in a fixed bed reactor at torrefaction temperature (220-300 °C) and holding times (20-60 mins). The mass yield decreased upon increasing the torrefaction temperature (220-300 °C) and holding times (20-60 mins). This was due to the thermochemical decomposition on the hemicellulosic and partial cellulosic fractions of coconut fiber. The values of activation energy decreased with increasing holding time from 43.61-30.25 kJ/mol for 20-60 mins using the Coats-Redfern method. The proximate analysis the increasing torrefaction temperature resulted in increased fixed carbon and ash content and decreased volatile matter content. From SEM analysis, the presence of emerging pores was identified in torrefied coconut fiber upon increasing the torrefaction temperature. From FTIR analysis, it is determined that the raw and torrefied coconut fiber have similar functional groups such as O-H, C-H, C=C and C=O bonds. However, the peak intensity decreased upon increasing the torrefaction temperature because the removal of the these groups occur during torrefaction process.
Figure 3. SEM micrographs for raw and torrefied coconut fiber at torrefaction temperature of 220, 240, 260, 280 and 300°C.
Figure 4. FTIR spectra for raw and torrefied coconut fibers, a) raw coconut fiber, b) torrefied coconut fiber at 220 °C, c) torrefied coconut fiber at 240 °C, d) torrefied coconut fiber at 260 °C, e) torrefied coconut fiber at 280 °C, f) torrefied coconut fiber at 300 °C.

5. References
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