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Anhydrous Weight Loss Prediction of Meranti Sawdust during Torrefaction using Rousset Model

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Abstract. In torrefaction, the mass loss distribution is evaluated in terms of anhydrous weight loss (AWL). Since temperature gives significant effects on AWL and the behaviour of biomass is highly associated with the AWL, therefore a suitable model for estimating the reaction kinetics is necessary for describing the thermal degradation and predicting the AWL in order to improve its process. In this study, the kinetic parameters of Meranti sawdust are estimated by applying three-parallel reaction models namely the Rousset Model for torrefaction of Meranti sawdust at temperatures of 240°C, 270°C and 300°C. All kinetic parameters are estimated according to the degradation of biomass constituents which are lignin, cellulose and hemicellulose by following the Arrhenius Law. The result shows that AWL estimation using the kinetic parameters predicted from the Rousset model is in good agreement with the experimental result as the $R^2$ value obtained is 0.99. It shows that the Rousset Model successfully described the degradation of lignin, cellulose and hemicellulose as well as the formation of char, volatile, tar and intermediate compound. Therefore it can be concluded that the Rousset Model is applicable to represent the torrefaction behaviour.

1. Introduction

Malaysia is blessed with huge amounts of biomass which comes from logging, agriculture and forestry sectors. Other than palm oil wastes, saw mill industries also produce a large amount of waste in the form of sawdust. Meranti sawdust is one of the most available sawdust because a huge amount of Meranti is used for producing furniture. One of the attractive options to utilise the available biomass is by converting it to the alternative biofuel or pellets. One of the promising techniques that can be used to convert biomass into valuable biofuel products is by using torrefaction.

Theoretically, torrefaction is a thermal treatment process of biomass in the inert environment at atmospheric pressure. It is a mild pyrolysis process where biomass is heated up to 200°C–300°C in order to improve the properties of the biomass. This process upgrades the fuel properties of biomass by reducing the moisture content, increasing heating value, improving grindability, increasing carbon content as well as changing the characteristic of biomass to become more brittle [1]. In recent years, many studies on the torrefaction process have been conducted, but little attention has been paid to the kinetic parameters study of biomass torrefaction. Most researchers are focusing more on the effects of torrefaction on the physical and chemical property changes of the biomass [1-3]. However, the fundamental knowledge of thermal behaviour and decomposition kinetics of biomass are important to
understand the process of torrefaction for further improvement. Here the kinetic study of torrefaction process is crucial in optimising the yield of the desired products. Usually, thermal degradation in torrefaction is best described by anhydrous weight loss (AWL) of the particular biomass which is highly dependent on the composition of the three main constituents of biomass, namely lignin, cellulose and hemicellulose. Typically, biomass is a build-up of 40–50 wt% cellulose, 25–35 wt% hemicellulose and 15–35 wt% lignin [3]. Among the three constituents, hemicellulose decomposes at the lowest temperature within 220°C–315°C. Meanwhile cellulose decomposes at a temperature range of 315°C–400°C, whereas lignin decomposes slowly within the range of 160°C–900°C [2].

Therefore, three-parallel reactions using the Rousset model can be employed to predict the AWL of Meranti sawdust torrefaction. The Rousset model is used to describe the decomposition of lignin, cellulose and hemicellulose [4]. However, the current Rousset model has been developed by considering the isothermal phase of torrefaction only. Usually, considerable mass loss is produced during heating process before it reaches the desired torrefaction temperature. In order to obtain an accurate result that can be used to represent the real process, both heating and isothermal phases of torrefaction are taken into account when deriving the kinetic parameters. Based on both phases, the kinetic parameters for the Rousset model were estimated and fitted against the residual mass obtained from thermogravimetric analysis (TGA). The applicability of these models to predict the residual mass and the mass yield for each constituent were also discussed.

2. Methodology

2.1. Thermogravimetric Analysis

The sample used for the torrefaction process was Meranti sawdust, a type of logging residue which was collected from a saw mill at Gambang, Pahang, Malaysia. After the collection, the samples were oven-dried at 105°C for 4 hours and were grinded and sieved. Only particles in the range of 500 µm to 1 mm were collected and used in this work. Torrefaction of Meranti sawdust was carried out using a TGA/DSC 1 Mettler Toledo analyser with nitrogen flow of 30 ml/min at three different temperatures: 240°C, 270°C and 300°C at a heating rate of 10°C/min. Prior to the analysis, 2 mg of samples were weighed and pre-heated from room temperature to 105°C at 10°C/min for 4 minutes in order to remove all moisture trapped in the samples. Later on, the samples were heated to the desired temperature. Once the desired temperature is reached, the temperature was maintained for 90 minutes. AWL is then calculated by using the mass loss data obtained from the TGA experiment.

2.2. Mathematical Model for AWL

The mathematical model for AWL is useful to describe the mass loss behaviour of Meranti sawdust during torrefaction. In this work, the Rousset Model was chosen to determine the decomposition kinetic parameters of Meranti torrefaction in order to evaluate the decomposition rate of Meranti sawdust during the process. The Rousset Model is a three–parallel steps kinetic model which demonstrates the wood degradation as three independently decomposition kinetic mechanisms [4]. Degradation of wood is related to decomposition of its constituents, which are lignin, cellulose and hemicellulose. Table 1 shows the mathematical modelling using the Rousset model. There are two sets of equations for heating phase and isothermal phase. As shown in table 1, there are 3 main reactions for each constituent. The first reaction involves the decomposition of lignin into char and volatile. Cellulose is transformed into char, volatile and tar components in the second reaction. Meanwhile hemicellulose is decomposed through two reactions in series where firstly intermediate component and volatile are produced from hemicellulose, and subsequently this intermediate component is decomposed into char and volatile. All equations are assuming to follow first order reaction where $k$ is the rate constant for each reaction (1/s) and $\beta$ = heating rate (°C/s) in the heating phase only.
Table 1. Mathematical modelling for AWL

| Reactions                                      | Heating Phase                                      | Isothermal Phase                                      |
|------------------------------------------------|---------------------------------------------------|-------------------------------------------------------|
| Lignin[\text{L}] \rightarrow \text{Char}[\text{C}] + Volatile[\text{V}1] | \[ \frac{d[L]}{dt} = \frac{1}{\beta} \left( -k_1[L] \right) \] | \[ \frac{d[L]}{dt} = -k_1[L] \] |
| Cellulose[\text{CL}] \rightarrow \text{Tar}[\text{T}]                      | \[ \frac{d[\text{CL}]}{dt} = \frac{1}{\beta} \left( \frac{1}{2} k_1[L] \right) \] | \[ \frac{d[\text{CL}]}{dt} = \frac{1}{2} k_1[L] \] |
| Cellulose[\text{CL}] \rightarrow \text{Char}[\text{C}] + Volatile[\text{V}2] | \[ \frac{d[\text{CL}]}{dt} = \frac{1}{\beta} \left( -k_1[L] \right) \] | \[ \frac{d[\text{CL}]}{dt} = -k_1[L] \] |
| Hemicellulose[\text{H}] \rightarrow \text{Intermediate}[\text{B}]           | \[ \frac{d[\text{H}]}{dt} = \frac{1}{\beta} \left( -k_{r3} + k_{c3} \right)[\text{H}] \] | \[ \frac{d[\text{H}]}{dt} = -k_{r3} + k_{c3} \text{[H]} \] |
| Hemicellulose[\text{H}] \rightarrow \text{Volatiles}[\text{V}3]          | \[ \frac{d[\text{C}2]}{dt} = \frac{1}{\beta} \left( \frac{1}{2} k_{c3}[\text{CL}] \right) \] | \[ \frac{d[\text{C}2]}{dt} = \frac{1}{2} k_{c3}[\text{CL}] \] |
| Intermediate[\text{B}] \rightarrow \text{Char}[\text{C}]                   | \[ \frac{d[\text{B}]}{dt} = \frac{1}{\beta} \left[ k_{m3}[\text{H}] - \left( k_{c3} + k_{r3} \right)[\text{B}] \right] \] | \[ \frac{d[\text{B}]}{dt} = k_{m3}[\text{H}] - \left( k_{c3} + k_{r3} \right)[\text{B}] \] |
| Intermediate[\text{B}] \rightarrow \text{Volatiles}[\text{V}4]          | \[ \frac{d[\text{C}3]}{dt} = \frac{1}{\beta} [k_{c3}[\text{B}] \right] \] | \[ \frac{d[\text{C}3]}{dt} = k_{c3}[\text{B}] \] |

### 3. Results and discussion

Figure 1a) shows the mass loss profiles obtained from TGA for Meranti torrefaction at 240°C. Thermogravimetric (TG) and differential thermogravimetric (DTG) reflect the degradation process that occurs during torrefaction of Meranti sawdust. As described by Bergman et al. [5], torrefaction can be divided into three main stages; non-reactive drying that occurs from 50°C to 150°C, reactive drying where hydrogen and carbon bonds start to break which occurs at 150°C to 200°C and destructive drying (from 200°C to 300°C) in which the chemical composition of biomass are altered and destructed. As shown in figure 1a), the removal of moisture (non-reactive and reactive drying) accounted about 8.04% and the destructive drying accounted around 9.12% of the Meranti decomposition. Based on the established thermal degradation (TDT) temperature of biomass chemical constituents and two TG curves in figure 1a), the Meranti torrefaction at 240°C can be best described by dehydration (up to 105°C) followed by hemicellulose decomposition (220°C–315°C).

![Figure 1](image_url)

Figure 1. a) Mass loss profiles from TGA and DTG, b) Residual mass of sawdust at 240 °C

Figure 1b) shows the torrefaction process of Meranti sawdust obtained from TGA. It can be divided into two main stages which are heating and isothermal stages. The first stage is the heating stage where sample is heated from drying temperature (200°C) up to the torrefaction temperature (240°C). During this phase, Meranti sawdust sample is heated up at a rate of 10°C/min for 4 minutes until it reached the desired torrefaction temperature. The second stage is the isothermal stage. At this stage, the sample is continuously heated at torrefaction temperature for 90 minutes. Both stages need to be
considered in deriving kinetic parameter because there will be weight loss at both stages which significantly contribute to the entire degradation process, especially at higher heating rate and temperature [6-7]. Therefore, two sets of equation are needed to derive the AWL of Meranti torrefaction using the Rousset model as shown in table 1. The kinetic parameters in the mathematical model in table 1 can be estimated by assuming the initial conditions based on the mass loss fraction of the biomass. The initial conditions used for all the three main constituents [8] for Meranti sawdust are used as follows: Lignin = 0.34, Cellulose = 0.42, Hemicellulose = 0.33.

In addition, the initial conditions for other components in the Rousset model are assumed to be zero. The AWL model consists of seven reactions which contribute to seven kinetic rates. As the reactions are assumed to follow the Arrhenius Law \(k = A \exp (-Ea/RT)\), both pre-exponential factor \((A)\) and activation energy \((Ea)\) need to be considered in the parameter estimation. Thus, it gives a total amount of 14 parameters that need to be estimated for the whole model. The pre-exponential factors \((A)\) and activation energies \((Ea)\) for every temperature were calculated by using Arrhenius Law and the iteration was repeated until constant values of both \(A\) and \(Ea\) were reached. The iteration was done using MATLAB (R2014a) software and ‘lsqcurvefit’ routine was selected for nonlinear optimisation due to its ability to minimise the variance between experimental and simulated data in order to find the optimal parameters that best fit the data. The kinetic parameters obtained by fitting the experimental data at temperatures of 240°C, 270°C and 300°C are shown in table 2.

| Parameters | \(A\) \((s^{-1})\) | \(Ea\) \((Jmol^{-1})\) |
|------------|-----------------|-----------------|
| \(k_L\)    | \(3.21 \times 10^4\) | 116500          |
| \(k_T\)    | \(1.57 \times 10^9\) | 179000          |
| \(k_{CC}\) | \(5.83 \times 10^{15}\) | 240500          |
| \(k_{33}\) | \(2.31 \times 10^5\) | 91400           |
| \(k_{11}\) | \(2.14 \times 10^1\) | 66.1            |
| \(k_{CI}\) | \(1.97 \times 10^4\) | 56300           |
| \(k_{34}\) | 55.70           | 52600           |

Figure 2a) shows the residual mass of Meranti sawdust torrefaction for both experimental and modelled data for 240, 270 and 300°C respectively. Here, the residual mass is obtained based on the total main constituents degradation (lignin, cellulose and hemicellulose). As shown in Figure 2a), the modelled data at all torrefaction temperatures fitted well with the experimental data. This proves the estimated kinetic parameters used in the three-parallel reactions are accurately describing the residual mass from torrefaction process. Residual mass is the amount of sample retained after the torrefaction. A small amount of residual mass indicates a huge amount of mass is loss in the form of volatiles due to the heating effect. At a high temperature (300°C), the residual mass obtained at the end of operation is about 40%, while at a low temperature (240°C) the residual mass obtained is about 70%. This indicates around 60% of mass is lost at a temperature of 300°C but only 30% mass is lost at a temperature of 240°C as char, volatiles, tar and intermediate compounds. The high amount of mass loss at high temperature is due to the destruction of biomass structure caused by extensive heating of torrefaction [9]. Figures 2b) – d) demonstrates the Meranti sawdust decomposition based on the degradation of lignin, cellulose and hemicellulose. Based on the model, lignin was degraded into char and volatiles by following a one step reaction model. As shown in Figure 2b), the composition of lignin at 240°C is decreased to 0.332115 from its initial state which is 0.34. Loss of 0.0007885 of lignin contributed to the equal formation of char and volatile. Meanwhile, cellulose was decomposed into tar, char and volatiles by two separate reactions, following the Broido-Shafizadeh model [10]. In figure 2c), cellulose is slightly decomposed during the torrefaction at 240°C. Initially, its composition is 0.42 and to the end of the process, 0.419988 of it is still retained. So, only 0.000025 of cellulose is decomposed to tar, char and volatile. From the amount, 0.0000125 is tar while the rest is divided in half between char and volatile.
Hemicellulose, corresponding to the Di Blasi-Lanzetta model was decomposed into char and volatiles with formation of intermediate compound. In contrast to lignin and cellulose, hemicellulose is totally decomposed at the end of the torrefaction. It was decomposed to five respective components in two steps. The first step is the decomposition of hemicellulose to intermediate and volatile. As shown in figure 2d), from initial composition of 0.33 at 240°C, hemicellulose was continuously decomposed into intermediate compound and volatiles until it diminished at the end of the reaction. Figure 3a) shows the composition of intermediates increased to 0.0326 at the beginning but decreased towards the end of operation. This is due to the fact that decomposition of intermediates led to formation of char and volatiles at the end of the reaction. It is also important to note that char, volatile and tar were also formed throughout the torrefaction process. Char was formed from the decomposition of lignin, cellulose and intermediate compounds while volatiles were released from the decomposition of lignin, cellulose, hemicellulose and intermediate compounds. In addition, tar was solely formed from the first reaction of cellulose decomposition. Among the volatile matter produced, the amount of char and volatile are the highest as shown in figures 3b) and c). Torrefaction temperature of 300°C recorded the highest amount of char and volatile produced which are approximately 0.8 and 0.7 respectively. At temperature of 270°C about 0.4 of char and 0.3 of volatile has been obtained while at the temperature of 240°C, only 0.3 char and 0.15 volatile is produced with small amount of tar and intermediate compounds. Furthermore, the yield of tar is not significant in the Meranti sawdust torrefaction due to the fact that around 0.02 tar is produced at all temperature. The slow decomposition rate of cellulose is found to be a contributing factor for insignificant tar production. Overall, the degradation of main components and formation of constituents show similar trends over the temperatures. However, the rate of decomposition and formation at a temperature of 300°C is higher compared to temperatures of 240°C and 270°C. This trend is supported by the fact that high decomposition rate for Meranti sawdust approximately began at a temperature of 250°C [9].

Figure 2. Residual mass and constituents of Meranti sawdust at three different temperatures
Figure 3. Production of intermediate, char, volatile and tar components from decomposition of lignin, cellulose and hemicellulose

4. Conclusions
In this study, three-parallel reactions, namely the Rousset Model was used to evaluate the kinetic of Meranti sawdust torrefaction. In contrast to other available kinetic models, this model evaluates the torrefaction of biomass with respect to the individual composition of biomass which are lignin, cellulose and hemicellulose. Based on the reactions model, the kinetic parameters for Meranti sawdust are estimated by considering both heating and isothermal period during torrefaction process. Then, the result is validated against the experimental data. The result shows that the mathematical model using the estimated kinetic parameters is accurately describing the AWL of the Meranti sawdust torrefaction between the temperatures 240°C and 300°C as it shows good agreement between experimental and modelled data, which subsequently can be used to predict the behaviour of the individual constituents. In addition, it was also found that hemicellulose is the dominant constituent in the Meranti sawdust torrefaction due to its significant decomposition rate compared to the lignin and cellulose constituents.

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