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Development of kinetics model for torrefaction of empty fruit bunch from palm oil waste

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Abstract

Torrefaction is a thermal conversion method widely used for enhancing the properties of biomass. Usually this process is conducted under an inert atmosphere within a temperature range of 200°C – 300°C with residence time up to 60 minutes. During the torrefaction process, biomass is thermally decomposed thus resulted in biomass weight loss which is known as an anhydrous weight loss (AWL). As the properties of biomass are highly dependent on the AWL, therefore it is important to predict the reaction kinetics which will enable to describe the thermal degradation of the respective biomass for achieving the desired properties of torrefied biomass. In this study, the kinetic parameters of empty fruit bunch (EFB) from palm oil waste torrefied at 240°C and 270°C are predicted by applying two different kinetic models namely Di Blasi-Lanzetta Model and Rousset Model for both heating and isothermal phases. For Di Blasi-Lanzetta Model, the kinetic parameters are estimated based on the degradation of EFB into intermediate compound and char whereas kinetic parameters for Rousset Model are predicted based on the degradation of three main constituents of EFB which consists of lignin, cellulose and hemicellulose. All kinetic parameters are estimated according to Arrhenius law and fitted to the experimental result. The result shows that AWL estimation using kinetic parameters predicted from both models are in a good agreement with the experimental result and thus applicable to represent AWL of EFB torrefaction. In conclusion, Di Blasi-Lanzetta Model is more relevant to represent real torrefaction in comparison to the Rousset because of its ability to provide detailed information for the evolution of solid and volatile products during torrefaction.

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1. Introduction

Recently, there has been growing interest in utilizing biomass as a way to reduce dependency on the natural gas and coal. One of the attractive options to enhance the suitability of biomass as a potential

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biofuel is by using torrefaction process. Theoretically, torrefaction is a process referring to the thermal treatment of biomass in inert or no-oxygen 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. Therefore many studies and research on torrefaction process have been conducted in recent years but most of the research work focuses on the property changes of biomass [1-5]. However, less attention has been paid to the kinetic parameters study of biomass torrefaction. The kinetics study of torrefaction process is essential because it represents the torrefaction reaction which subsequently be used to improve process control for continuous torrefaction reactor. Therefore, it is crucial to estimate the kinetic parameters of torrefaction process in order to determine the optimum condition for the thermal degradation process in order to achieve the desired properties of torrefied product. Usually, thermal degradation in torrefaction is described by anhydrous weight loss (AWL) of the particular biomass which highly dependent on the composition of the three main constituents of biomass namely lignin, cellulose and hemicellulose. Typically, biomass is build-up of 40 – 50 wt% cellulose, 25 - 35 wt% hemicellulose and 15 – 35 wt% lignin [1]. Among the three constituents, hemicellulose decomposes at lowest temperature within 220°C – 315°C. Meanwhile cellulose decomposes at temperature range of 315°C – 400°C whereas lignin decomposes slowly within the range of 160°C – 900°C [1].

In the present work, the torrefaction of empty fruit bunch (EFB) from palm oil waste at two different temperatures (240 °C and 270 °C) were conducted using thermogravimetric analysis (TGA) to determine the residual mass. For the kinetic modelling, a two-step reaction in series using Di Blasi-Lanzetta model and three - parallel reactions using Rousset model were employed to predict the residual mass. However previous studies conducted on the torrefaction kinetic studies only considering the isothermal phase of torrefaction [2]. Therefore, in this study, both heating (non-isothermal) and isothermal phases of torrefaction are taken into account when deriving the kinetic parameters. Based on both heating and isothermal phases, the kinetic parameters for Di Blasi-Lanzetta model and Rousset model were estimated and fitted against the residual mass obtained from TGA. The applicability of these models to predict the residual mass and the mass yield were also discussed.

2. Material and Method

2.1. Material and Thermogravimetric Analysis (TGA)

The sample used for the torrefaction process was empty fruit bunch (EFB), a type of palm oil waste which was obtained from the Lepar oil palm mill located in Lepar, Pahang, Malaysia. Prior to thermogravimetric analysis (TGA), the samples were dried at open air for 4 hours and were grinded using a mechanical grinder. The ground samples were sieved and only particles smaller than 50µm were collected. Torrefaction of EFB was conducted using a TGA/DSC 1 Mettler Toledo analyser with nitrogen flow of 30ml/min at two different temperatures: 240°C and 270°C at heating rate of 10°C/min. All samples were weighed within the range of 5 mg to 10 mg and were pre-heated from 30°C up to 105°C at 10°C/min for 4 minutes in order to remove all moisture content inside the samples. Later on, the samples were heated to the desired temperature (240°C and 270°C) and were held for 90 minutes at respective temperature. The data obtained from TGA experiment were used to calculate the AWL for each sample and compared with the model prediction data from simulation work.

2.2. Kinetic Parameters Estimation

Analysis of kinetic parameters for torrefaction is important to study the changes of physical and chemical behavior of biomass that occurs during the torrefaction process. In addition, kinetic parameters such as temperature and residence time are crucial for determining the optimal process condition of torrefaction for reactor design. This work focuses on applying two different models which are Di Blasi-Lanzetta model as well as Rousset model on EFB torrefaction. Di Blasi-Lanzetta model is a two-series reaction in which the isothermal weight loss kinetics of biomass is explained by two step mechanism. The first step describes the formation of volatiles and solid intermediates whereas the second step describes the degradation of solid intermediates in forming char and volatiles. The main advantage of Di Blasi-Lanzetta model is it provides an accurate brief view of biomass degradation (for example, wood to intermediate compound and solid residue). In the Di Blasi-Lanzetta works, the kinetic of xylan decomposition was described by this two-series reaction where a good agreement between modeled and experimental AWL is obtained [2]. This is due to the fact that the time derivative of solid weight fraction as a function of temperature exhibits a double peak which is well fitted by a two consecutive step reactions with deviation of only 1.3-1.7% [5]. In contrast, Rousset model is a three-parallel step kinetic model which taken into account the decomposition of lignin, cellulose and hemicellulose in correspondence to their presence in wood. This provides detailed overview on decomposition of cellulose, hemicellulose and lignin of biomass. Therefore, the individual behavior of all constituents can be determined as they react independently during the torrefaction.

Usually torrefaction can be divided into two important stages namely heating stage (biomass is heated up to certain point) and isothermal stages (process is hold for certain time after achieving the torrefaction temperature). Figure 1 shows the phases that involve in torrefaction of EFB at 240°C. Heating phase started from 0th to 4th min while isothermal phase occurred from 4th min to the end of the torrefaction. However, many kinetic studies only considered the isothermal stages in their work because of the simplicity in deriving isothermal kinetic parameter. It is also important to note that there will be some weight loss during the heating phase which significantly contributing to the entire degradation process especially at high heating rate. Hence, the heating phase must be included when deriving the kinetic parameters in order to predict residual mass accurately. Table 1 and Table 2 show the kinetic modelling using Di Blasi-Lanzetta model and Rousset model. There are two set of equations for heating phase and isothermal phase for both models respectively. As shown in Tables 1 and 2 for both models, the main different for heating phase model equations and isothermal phase model equations is the heating rate (β) is included in the heating phase model equations.

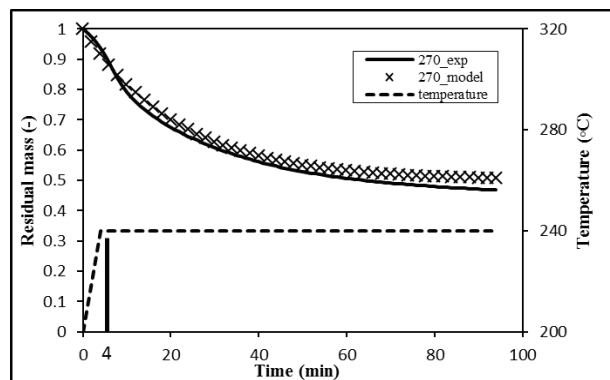


Fig. 1. Experimental and modelled result of EFB torrefaction at 10°C /min heating rate

Table 1. Kinetic modelling for Di Blasi-Lanzetta model

Reactions	Heating phase	Isothermal phase
Biomass[A] → Intermediate[B]	$\frac{d[A]}{dt} = \frac{1}{\beta} \cdot \{-(k_B + k_{v1})[A]\}$	$\frac{d[A]}{dt} = -(k_B + k_{v1})[A]$
Biomass[A] → Volatile1[V1]	$\frac{d[B]}{dt} = \frac{1}{\beta} \cdot \{k_B[A] - (k_C + k_{v2})[B]\}$	$\frac{d[B]}{dt} = k_B[A] - (k_C + k_{v2})[B]$
Intermediate[B] → Char[C]	$\frac{d[C]}{dt} = \frac{1}{\beta} \cdot \{k_C[B]\}$	$\frac{d[C]}{dt} = k_C[B]$
Intermediate[B] → Volatile2[V2]	$\frac{d[C]}{dt} = \frac{1}{\beta} \cdot \{k_C[B]\}$	$\frac{d[C]}{dt} = k_C[B]$

$\beta = \text{heating rate in } ^\circ\text{Cs}^{-1}$

Table 2. Kinetic modelling for Rousset model

Reactions	Heating phase	Isothermal phase
Lignin[L] → Char1[C1] + Volatile1[V1]	$\frac{d[L]}{dt} = \frac{1}{\beta} \cdot \{-k_L[B]\}$	$\frac{d[L]}{dt} = -k_L[B]$
Cellulose[CL] → Tar[T]	$\frac{d[C1]}{dt} = \frac{1}{\beta} \cdot \left\{ \frac{1}{2} \cdot k_L[B] \right\}$	$\frac{d[C1]}{dt} = \frac{1}{2} \cdot k_L[B]$
Cellulose[CL] → Char2[C2] + Volatile2[V2]	$\frac{d[CL]}{dt} = \frac{1}{\beta} \cdot \{-(k_T + k_{CC})[CL]\}$	$\frac{d[CL]}{dt} = -(k_T + k_{CC})[CL]$
Hemicellulose[H] → Intermediate[B]	$\frac{d[T]}{dt} = \frac{1}{\beta} \cdot \{k_T[CT]\}$	$\frac{d[T]}{dt} = k_T[CT]$
Hemicellulose[H] → Volatile3[V3]	$\frac{d[C2]}{dt} = \frac{1}{\beta} \cdot \left\{ \frac{1}{2} \cdot k_{CC}[CL] \right\}$	$\frac{d[C2]}{dt} = \frac{1}{2} \cdot k_{CC}[CL]$
Intermediate[B] → Char[C]	$\frac{d[H]}{dt} = \frac{1}{\beta} \cdot \{-(k_{v3} + k_{HB})[H]\}$	$\frac{d[H]}{dt} = -(k_{v3} + k_{HB})[H]$
Intermediate[B] → Volatile4[V4]	$\frac{d[B]}{dt} = \frac{1}{\beta} \cdot \{k_{HB}H - (k_{C3} + k_{v4})[B]\}$	$\frac{d[B]}{dt} = k_{HB}H - (k_{C3} + k_{v4})[B]$
	$\frac{d[C3]}{dt} = \frac{1}{\beta} \cdot \{k_{C3}[B]\}$	$\frac{d[C3]}{dt} = k_{C3}[B]$

$\beta = \text{heating rate in } ^\circ\text{Cs}^{-1}$

3. Results and discussions

For the kinetic parameter estimations, the initial conditions used for Di Blasi-Lanzetta model are $[A]=1; [B]=0; [C]=0$; and for the Rousset model are $[L]=0.3; [CL]=0.4; [H]=0.3$; where the other initial conditions in the Rousset model are assumed zero. The iteration was done using MATLAB (R2014a) and 'lsqcurvefit' routine was used for nonlinear optimization. The 'lsqcurvefit' routine was used to minimize the variance between experimental and simulated data in order to find the parameters that best fit the data. The calculations were done firstly using heating phase model equations from 0th to 4th minutes and secondly using isothermal phase model equations from 4th minutes onwards. Based on the calculated k values, the pre-exponential factors (A) and activation energies (Ea) for every temperature were calculated by using Arrhenius Law formula ($k = A \exp(-Ea/RT)$) where k is the rate reaction constant expressed in s^{-1} , T is the temperature in K and R is the universal gas constant which is $8.3142 \text{ J mol}^{-1}\text{K}^{-1}$. The iteration was repeated until stable values of both A and Ea were reached.

The kinetic parameters obtained by fitting the experimental data at 240°C and 270°C are shown in Tables 3 and 4 respectively.

Table 3. Kinetic parameters for Di Blasi-Lanzetta model

Parameters	$A (s^{-1})$	$Ea (Jmol^{-1})$	Parameters	$A (s^{-1})$	$Ea (Jmol^{-1})$
k_B	4.26×10^1	3.40×10^4	k_C	5.18×10^{10}	3.94×10^4
k_{V1}	5.97×10^6	8.75×10^4	k_{V2}	1.26×10^{-3}	2.56×10^4

Table 4. Kinetic parameters for Rousset model

Parameters	$A (s^{-1})$	$Ea (Jmol^{-1})$	Parameters	$A (s^{-1})$	$Ea (Jmol^{-1})$
k_{C1}	6.7×10^6	102430	k_H	10.97×10^6	91.4×10^3
k_{CL}	2.51×10^9	117900	k_B	10.09×10^2	58.3×10^3
k_T	6.66×10^9	201750	k_{C3}	10870	52.6×10^3
k_{C2}	4.26×10^1	66.1			

Figure 2 shows the experimental and modelled AWL of EFB as well as mass yield of EFB (A), intermediate compound (B) and char (C) during the torrefaction process. Figure 2(a) shows the modeled data fits the experimental data well at 240°C and 270°C. Figure 2(b) clearly shows the biomass degraded faster at higher temperature compare to lower temperature. At 270°C, EFB experienced a huge reduction of weight loss at the beginning and fully decomposed compared to 240°C. Meanwhile Figure 3(a) shows that the modelled data predicted by using Rousset model at 240°C and 270°C are in good agreement with the experimental data. In addition, Figure 3(b) shows the thermal degradation of EFB in accordance to the composition of its constituents; lignin (L), cellulose (CL), and hemicellulose (H) as well as intermediate compound (B), char (C) and tar (T) at 240°C. It shows that hemicellulose degraded faster until it was fully decomposed while lignin and cellulose decomposed slowly until the end of reaction. Therefore, it can be concluded the EFB degradation is depending on the hemicellulose. Overall decomposition of EFB can be obtained by adding the composition of lignin, cellulose and hemicellulose. It is a fact that thermal degradation of EFB itself is differ to the thermal degradation that represent by the constituents.

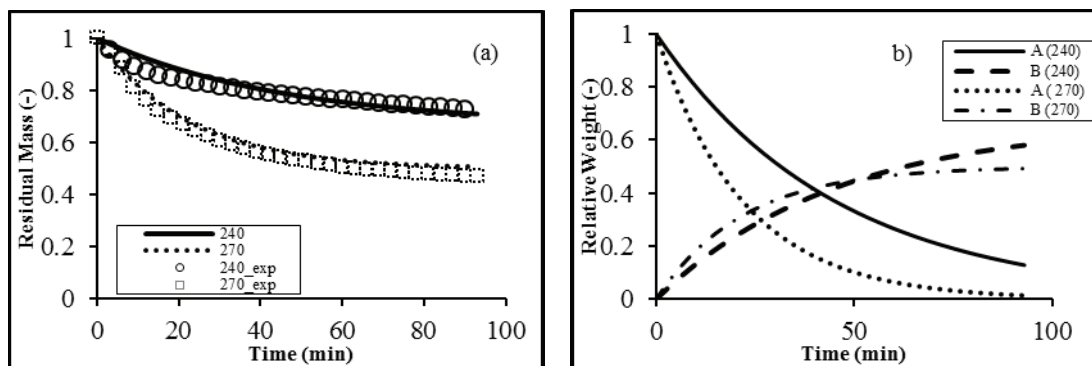


Fig. 2. (a) AWL of EFB during the torrefaction (b) Mass yield of A, B and C at all temperature with heating rate of 10 /min

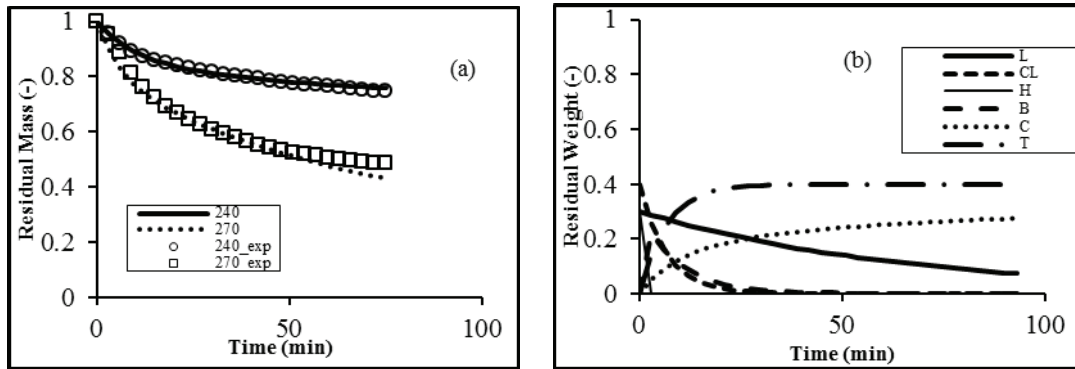


Fig. 3. (a) AWL of EFB during the torrefaction (b) Mass yield of L, CL and H at 240 °C with heating rate of 10 /min

4. Conclusion

In this study, a two-step in series reaction and a three-parallel reaction were used to evaluate the kinetic of EFB torrefaction. Kinetic parameters were estimated by considering both heating and isothermal period. The result shows that both models gave good agreement between experimental and modeled result. It can be concluded that Di Blasi-Lanzetta Model can be applied for overall EFB degradation while Rousset Model can be used to determine the most significant constituent that contribute to the EFB degradation. However, it is preferable to use less complex model in industrial application.

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Biography

Dr Suriyati Saleh obtained her PhD (biomass torrefaction and pyrolysis) from Technical University of Denmark. Currently, she is a senior lecturer at Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang.