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Anhydrous weight loss kinetics model development for torrefied green waste

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Abstract. One of the compositions of municipal solid waste (MSW) is green waste (GW) that collected from landscaping, garden, yard and trimming waste. GW has potential in becoming a biomass feedstock, but poses some drawbacks such as high moisture content, low heating value, high O/C and H/C ratios. Implementation of torrefaction as pre-treatment will improve the GW properties. During torrefaction, biomass is decomposed and leads to anhydrous weight loss (AWL). The estimation model for AWL is significant to study thermal degradation of GW. The aim of this work is to study two steps reaction in series for AWL prediction. GW were torrefied under inert condition at 240-300°C, 10°C/min heating rate and 30 minutes holding time using thermogravimetric analysis (TGA). Two steps reaction series model named Di Blasi and Lanzetta with extended non-isothermal phase is used in developing the AWL model. From initial guess, the parameters of activation energy and kinetic constant are adjusted to fit the calculated AWL to experimental AWL data by applying nonlinear optimization 'lsqcurvefit' routine in Matlab. The estimated kinetic parameters been used for AWL model and later being compared to experimental data from TGA. Good agreement obtained between experimental and model data indicating good kinetic parameters estimation

1. Introduction

Department of Statistics states that Malaysia is having a massive population increment by 1.5% annual growth rate from 2015 to 31.7 million in 2016. As developing countries that currently facing fast accelerating population increment and experiences a rapid industrial growth as well as urbanization, Malaysia also received an adverse effect towards an environment due to increasing amount of municipal solid waste (MSW) generation [1-2]. In present time, Malaysia is generating over 23 000 tonnes of solid waste daily and the amount of MSW generation was expected to reach over 30 000 tonnes per day in 2020 [3]. One of the main organic waste compositions in MSW is green waste (GW) that includes garden, trimming and yard waste which represents as lignocellulosic component. Currently, landfilling has become one of the common methods for GW disposal, however open burning at dump site is the most preferable technique due to its low management cost even though it poses a lot of severe impact toward an environment due to inadequate waste treatment facilities and handling [4]. Prior to this problem, many researches have been done regarding on waste management focusing on Waste-to-Energy (WtE) technologies as GW has a potential as fuel feedstock that can be utilized for energy generation [5,6]. Also known as green technologies, WtE is a process of energy recovery through various process including torrefaction, anaerobic digestion, combustion, gasification, pyrolysis, which

transform the waste materials into fuel, heat or electricity [7]. Despites of its potential in energy recovery, GW is having some drawbacks such as relatively high moisture content and high O/C ratio, low calorific value and bulk density as well as high tar production during the process that possibly will reduce the efficiency of WtE process, and it might lead to storage and transportation difficulties [8]. Thus, GW must be subjected to pre-treatment in order to improve its properties as a fuel feedstock before undergoing any WtE process [8,9]. One of the pre-treatment processes that is suitable and has an ability to improve the GW properties is torrefaction [8,10]. Torrefaction involves the combination of two processes which is combustion and partial pyrolysis.

Torrefaction is a thermochemical treatment process that operate at temperature between 200°C to 300°C with residence time between 15 to 60 minutes under inert condition was found to be beneficial for biomass energy properties improvement [11]. Recent research has verified torrefaction process gives a significant impact in improving the properties of biomass which include moisture content reduction, increment of heating value and energy density, decrease the atomic O/C and H/C ratios and improve the grindability of biomass [11-12]. During torrefaction, mass loss is expected which was a result from the decomposition of biomass, volatile release and moisture loss [13-14]. The thermal degradation during torrefaction leads to an anhydrous weight loss (AWL) of a biomass that represent the physical-chemical transformation of the sample during the process [15]. AWL is described as the loss of mass fraction during torrefaction. The mass fraction loss here explains the amount of biomass that has been decomposed by the release of moisture, gas and volatiles throughout the torrefaction process. Hence, it is important to have a model to estimate the AWL in order to study the optimum condition for torrefaction process in achieving the desired properties of torrefied GW.

The most common technique to investigate the thermal degradation and mass loss of biomass during torrefaction process is by using thermogravimetry analysis (TGA). The kinetic evaluation of TGA data can be used in development of simple model which known as one equation global model that may able to describe the reaction accurately at low reaction temperature with only considering the isothermal stage [16-17]. In one step global model, it is only considered direct decomposition of biomass into char and neglecting the intermediate volatile. Next, kinetic model was introduced by Di Blasi and Lanzetta regarding on intrinsic kinetics of isothermal degradation at 200 to 340°C temperature range in inert atmosphere. Di Blasi and Lanzetta developed two-step models by taking volatile and solid compounds into account which include the intermediate volatiles. This model explains that the first step occurs due to degradation of fraction in hemicellulose while the second step involving the degradation of cellulose, lignin and part of hemicellulose [18]. Meanwhile, Repellin et al. have studied the torrefaction of beech and spruce chips of a continuous pilot-scale reactor by applying three different model including simple model (one step global model), Di Blasi and Lanzetta model and Rousset model [15]. As a result, these three models were successfully applied to beech and spruce chips and good correlation between calculated and experimental AWL was obtained [15].

Consequently, the decomposition of a biomass leads to AWL, hence the development of model to estimate the AWL is necessary to study the degradation of biomass during the torrefaction process. Therefore, the objective of this work is to study two steps reaction in series models that can be used to predict the AWL. Thus, the torrefaction of GW using thermogravimetric analysis (TGA) has been done at different temperature (240°C, 270°C and 300°C) in order to obtain the residual mass. In this work Di Blasi and Lanzetta model has been selected in developing the AWL model for green waste (GW) as the model describe more detailed for biomass decomposition. However, the original model of Di Blasi and Lanzetta only consider the isothermal phase and in this work, it has been extended by including the non-isothermal (heating) phase. The model needs to be extended by include non-isothermal phase due to the extractives and reactive hemicellulose fraction start to degrade this phase which also involve countable mass loss of sample. The kinetic parameters have been estimated from residual mass data obtained from TGA for both isothermal and non-isothermal phases. The AWL of GW from predicted model will be compared to the experimental data from TGA for validation purposes.

2. Materials and Methods

2.1. Materials and Thermogravimetric Analysis (TGA)

Yard and trimming waste which are considered as green waste (GW) were collected from orchard and residence nearby Gambang, Pahang, Malaysia. The GW samples being subjected to pre-drying process at temperature of 105°C overnight. Then, dried samples were grinded and sieved to 0.5-1.0 mm particle size. To evaluate the biomass mass loss during torrefaction, TGA/DSC 1 Mettler Toledo analyser was used based on 30 ml/min nitrogen flow for inert condition. GW samples weight was varied from 5 mg to 10 mg and tested at three different torrefaction temperatures of 240 °C, 270 °C and 300 °C with heating rate 10 °C/min. Samples was heated up to desired temperature (240°C, 270°C and 300°C) and were held for 30 minutes. TGA was run three times for each sample. AWL of each samples was calculated based on the data obtained from TGA experiment and was used to compared with modelled data from simulation work.

2.2. Modelling of AWL

Modelling of torrefaction process can be done through AWL model development. Di Blasi and Lanzetta has developed two stages degradation of hemicellulose (xylans) for weight loss prediction. At the beginning, this two stages model predicts one stage of degradation and later continue over the whole process. A two stages in series model as shown in equation (1) is used to study the kinetics parameter estimation. As shown in equation (1), the biomass first degrades into solid intermediate compound (B) through rate constant and volatiles (k_B and k_{V1}).

Table 1. Di Blasi and Lanzetta kinetic model [18].

Two reaction stages	Reaction mechanism
Biomass (A) → Intermediate compound (B) Biomass (A) → Volatiles 1 (V1) Intermediate compound → Char (C) Intermediate compound → Volatiles 2 (V2)	(1)

The torrefaction process sequential step is the conversion of intermediates into char (C) and another volatiles (V2) through k_C and k_{V2}. Total AWL is denoted as the total of A, B and C as shown in equation (2). The torrefaction process was assumed to be in first order reaction as the differential equations as shown in equations (4) – (6) for the decomposition of biomass under isothermal phase reaction. The rate constant is denoted as k (s^{-1}) which determined from equation (3) which known as Arrhenius equation.

$$AWL = [A] + [B] + [C] \qquad (2)$$

$$lnk = \ln(A) - \frac{Ea}{RT} \qquad (3)$$

$$\frac{d[A]}{dt} = -(k_B + k_{V1})[A] \qquad (4)$$

$$\frac{d[B]}{dt} = k_B[A] - (k_C - k_{V2})[B] \qquad (5)$$

$$\frac{d[C]}{dt} = k_C[B] \qquad (6)$$

Meanwhile, M/M_0 can be determined through TGA experiment by using equation (7). m_0 is initial mass of the sample, m_{ash} is mass of ash in the sample am m_{TGA} is the mass measured by TGA in a function of time.

$$\left(\frac{M}{M_0}\right)_{exp} = \frac{m_{TGA} - m_{ash}}{m_0 - m_{ash}} \tag{7}$$

Many kinetic studies have been done in previous study only considering isothermal stage, however there is weight loss apparently at heating stage which is significant that contribute towards the whole process of degradation especially when using high heating rate [19-20]. The existing isothermal equation do not consider the heating rate of torrefaction process. In this work, the torrefaction using TGA is conducted at three different temperature and the time taken in achieving desired temperature from heating phase to isothermal phase is different which is 4, 7 and 10 minutes for 240°C, 270°C and 300°C respectively. Equations (8) – (10) show the kinetic reaction equation for heating phase which has been included together with the original Di Blasi and Lanzetta model. Based on the modified equations, the main different for non-isothermal model equations and isothermal phase model equations is the heating rate β (s^{-1}) is included in the heating phase model equations.

$$\frac{d[A]}{dt} = \left(\frac{dt}{dT}\right) \times \{-(k_B + k_{V1})[A]\} = \frac{1}{\beta}\{-(k_B + k_{V1})[A]\} \tag{8}$$

$$\frac{d[B]}{dt} = \frac{1}{\beta} \times \{k_B[A] - (k_C + k_{V2})[B]\} \tag{9}$$

$$\frac{d[C]}{dt} = \frac{1}{\beta} \times \{k_C[B]\} \tag{10}$$

The unknown parameters that are needed in order to solve the AWL model is based on equation 1, which is the rate constant (k) for volatile 1 (k_{V1}), intermediate compound B (k_B), volatile 2 (k_{V2}) and char (k_C). Figure 1 shows the overall workflow in estimating the kinetic parameter for GW torrefaction using 'lsqcurvefit' solver in MATLAB in order to minimize the root mean square error between experimental and calculated data. It begins with the first iteration by assuming only biomass A with no intermediate compound B and char C. The activation energy (Ea) and pre-exponential factor (A) are calculated by Arrhenius equation and subsequently the calculated values were used in order to determine the mass fractions of A, B and C for isothermal and non-isothermal phases. The isothermal phase began from 4th minutes onwards where the torrefaction temperature is maintained at 240°C for 30 minutes until the end of the reaction. Both isothermal phase reaction from equations (4) – (6) and the non-isothermal phase from equations (8) – (10) were integrated for kinetic parameter derivation by using the new calculated A, B and C. From the second iteration onwards the new calculated (Ea) and (A) is used to provide the initial guess for the optimization. The procedure was repeated until the values of [A], [B] and [C] are converged.
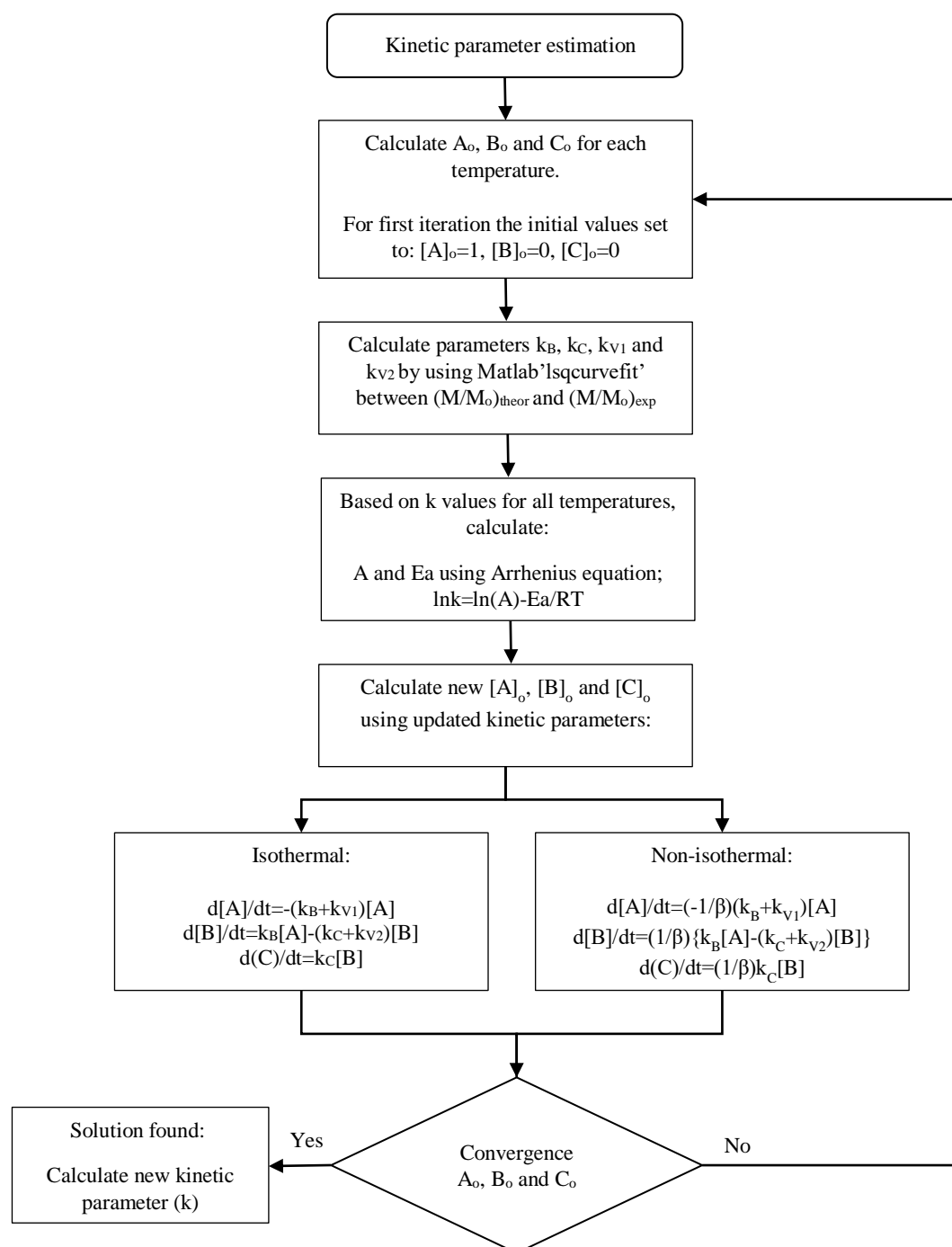
```
┌─────────────────────────────────┐
│    Kinetic parameter estimation  │
└─────────────────────────────────┘
                 │
                 ▼
┌─────────────────────────────────────────┐
│  Calculate A_o, B_o and C_o for each      │
│             temperature.                  │
│                                           │
│  For first iteration the initial values set│
│   to: [A]_o=1, [B]_o=0, [C]_o=0           │
└─────────────────────────────────────────┘
                 │
                 ▼
┌─────────────────────────────────────────┐
│  Calculate parameters k_B, k_C, k_V1 and  │
│  k_V2 by using Matlab'lsqcurvefit'        │
│  between (M/M_o)_theor and (M/M_o)_exp    │
└─────────────────────────────────────────┘
                 │
                 ▼
┌─────────────────────────────────────────┐
│  Based on k values for all temperatures,  │
│             calculate:                    │
│                                           │
│  A and Ea using Arrhenius equation;       │
│           lnk=ln(A)-Ea/RT                 │
└─────────────────────────────────────────┘
                 │
                 ▼
┌─────────────────────────────────────────┐
│  Calculate new [A]_o, [B]_o and [C]_o     │
│  using updated kinetic parameters:        │
└─────────────────────────────────────────┘
```

Isothermal:

$$d[A]/dt = -(k_B + k_{V1})[A]$$
$$d[B]/dt = k_B[A] - (k_C + k_{V2})[B]$$
$$d(C)/dt = k_C[B]$$

Non-isothermal:

$$d[A]/dt = (-1/\beta)(k_B + k_{V1})[A]$$
$$d[B]/dt = (1/\beta)\{k_B[A] - (k_C + k_{V2})[B]\}$$
$$d(C)/dt = (1/\beta)k_C[B]$$

Convergence A_o, B_o and C_o — Yes → Solution found: Calculate new kinetic parameter (k)

No →

Figure 1. Overall workflow for kinetic parameters estimation of GW torrefaction in Matlab.

3. Results and Discussion

3.1. Estimation of Kinetic Parameters

For estimation of kinetic parameters, the data from TGA test at temperatures of 240°C, 270°C and 300°C were used. The data taken is starting from temperature of 200°C since the thermal degradation of biomass roughly started at 200°C and biomass shows an immediate loss of mass. This indicates that some of the constituent in a biomass start to break down and decomposed. Table 2 shows the kinetic parameters from parameter estimation implemented in MATLAB (R2014a) software. The iteration for kinetic parameters estimation was done using the nonlinear optimization which employing 'lsqcurvefit'

routine in MATLAB. For model validation, the model was verified by comparing both experimental data and predicted data of AWL for the whole reaction at different torrefaction temperature.

Table 2. Kinetic parameters for reaction model for green waste at 240°C, 270°C and 300°C

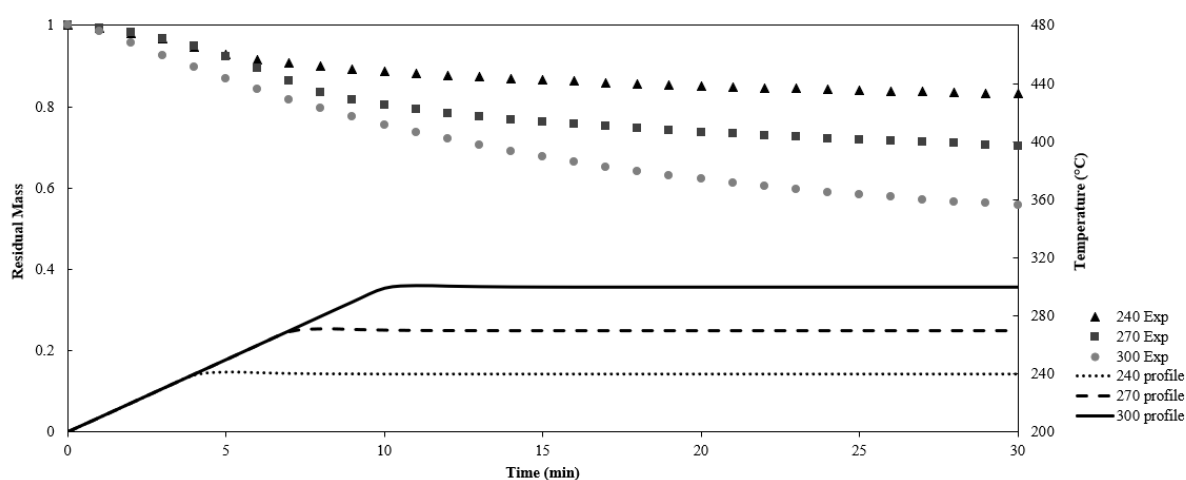| Parameters	A (s⁻¹)	Ea (Jmol⁻¹)
k_B	1.22×10^{-2}	5.27×10^{3}
k_C	3.11×10^{-8}	-3.94×10^{4}
k_{V1}	5.77×10^{-1}	8.74×10^{5}
k_{V2}	7.56×10^{-2}	3.06×10^{4}

Figure 2. Residual mass of torrefied green waste (GW) at different temperature based on TGA with heating rate 10°C/min.

Based on Figure 2, torrefaction process can be divided into two stages which is heating stage where biomass is heated up at certain temperature and continue with isothermal stage where the process was maintained at desired torrefaction temperature until the end of operational time. Thus, it is significant to develop a model in order to evaluate the AWL of GW torrefaction for both non-isothermal and isothermal phases. Shang et al. suggested to consider the weight loss during non-isothermal (heating) phase in deriving the kinetics parameters [16]. Figure 2 shows the reaction stage involve in torrefaction experiment and modelled from GW at different temperature. Based on temperature of 240°C, the heating phase occurred at the first 4 minutes and the process was held for 30 minutes at isothermal stage.

According to figure 2, the residual mass reduction of biomass is referring to AWL profiles. The AWL curve can be divided into two stages. The first stage is related to rapid increment in AWL while the second stage corresponds to slow increment of AWL. Rapid increment of AWL can be identified at first 4 minutes of reaction which indicates most of a weight loss occurred at this stage. The weight loss and decomposition as shown in figure 2 also explain the degradation rate of green waste. As shown in figure 2, AWL shows slightly increment over 4 minutes of reaction at 240°C and remain slightly constant after 25 minutes. Meanwhile, figure 3 shows the residual mass for all torrefaction temperature of 240°C, 270°C and 300°C for GW. The degradation rate of GW is higher at high torrefaction temperature. 44.25% of weight loss is detected after 30 minutes for temperature of 300°C compared to only 16.82% weight loss for temperature of 240°C. This is due to the degradation of hemicellulose and cellulose contents that contribute to evaporation of water and volatile release [18].

For model verification, figure 3 (a), (b) and (c) show the comparison of predicted residual mass and TGA experimental for both isothermal and non-isothermal phases starting at 200°C to desired torrefaction temperature. Based on figure 3 (a), (b) and (c), extended Di Blasi and Lanzetta model is

able to describe the reaction of GW precisely and both experimental results and modelled data shows a good agreement at torrefaction temperature of 240°C, 270°C and 300°C. Meanwhile, figure 3 (d), (e) and (f) explains the mass yields for reaction of A (GW), B (Intermediate compound) and C (Char) for GW at different torrefaction temperature. It can be seen that the conversion of A into intermediate compound B is starting from the beginning and fully decomposed into B within 5 minutes. The intermediate compound (B) initially increase due to the decomposition of A but shows a dramatic decrease until the end of time which indicates rapid conversion of intermediate compound (B) into char (C). The mass yield of (C) is increased steadily as most of the component (B) has been decomposed and converted into char. The mass yield of char (C) produced from intermediate compound (B) at high temperature is much lower compared to low torrefaction temperature. Only 0.46 of mass yield for (C) produce at 300°C compared to 0.83 of mass yield for C at temperature of 240°C. This is due to the more moisture and volatile release at high temperature which also related to the degradation of GW. Figure 4 shows that a good model fit has been obtained based on the comparison of residual mass value obtained by experimental and by modelling for GW. The predicted R^2 value from the analysis of variance (ANOVA) test according to this model is 0.9998. Thus, it can be said that the kinetic parameters for GW is best fit to represent the residual mass.
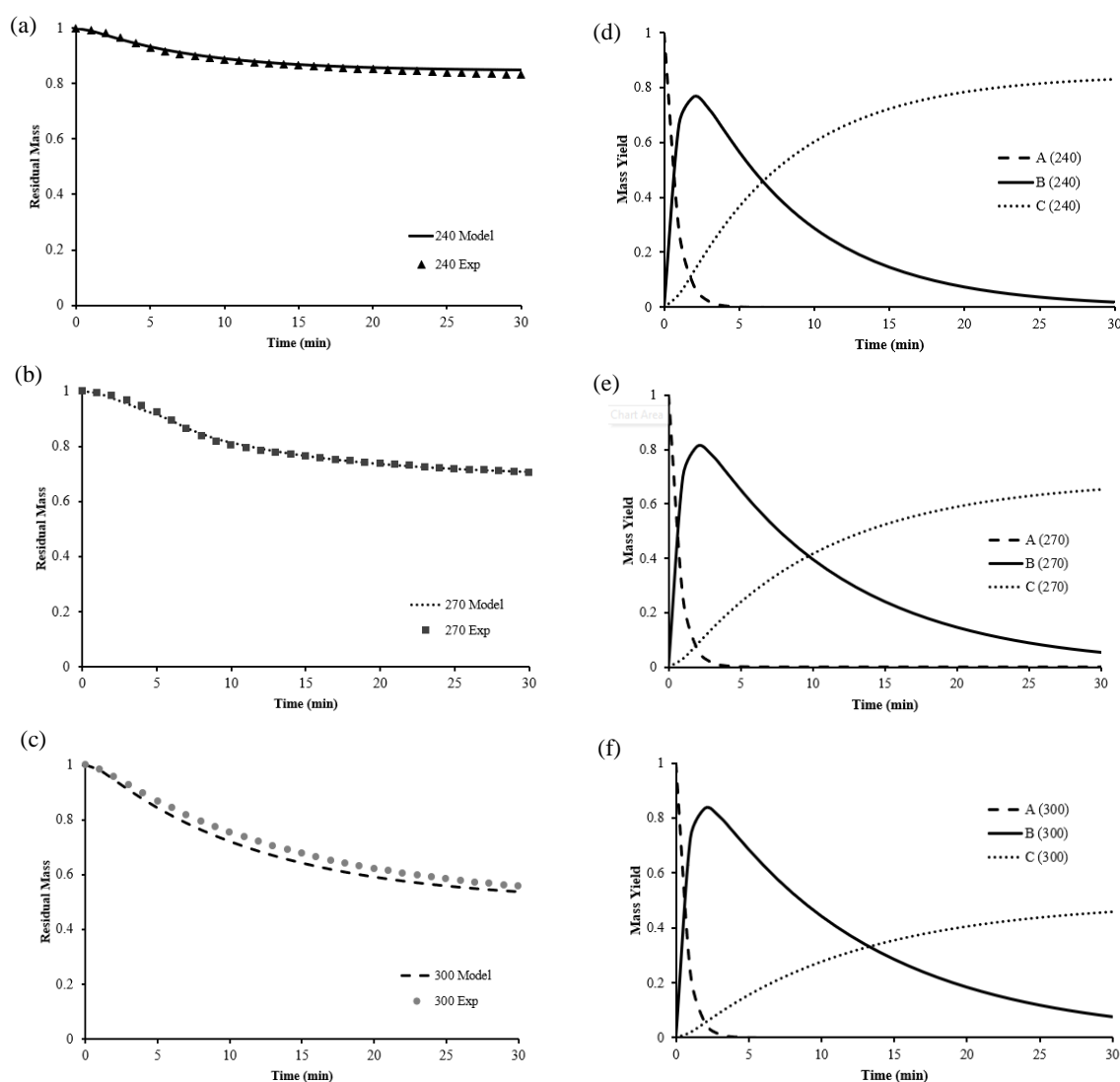

Figure 3. AWL modelling and experimental of GW (a) 240°C; (b) 270°C; (c) 300°C and, mass yield of constituent A, B and C at (d) 240°C; (e) 270°C; (f)300°C of GW torrefaction with heating rate 10°C/min.
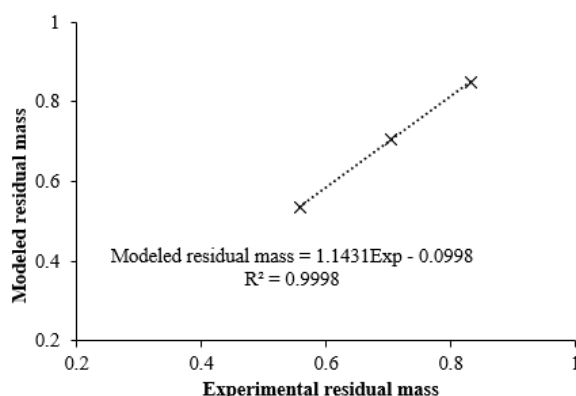
Figure. 4. Correlation between experimental and modelled residual mass of GW.

4. Conclusion

In this study, torrefaction of green waste (GW) were carried out using TGA. Green waste sample has been heated up to desired torrefaction temperatures (240°C, 270°C and 300°C) with heating rate of 10°C/min and 30 minutes holding time. Mass loss data by torrefaction time was determined from TGA and AWL of GW sample was evaluated. Two steps reaction model in series which is known as Di Blasi and Lanzetta model has been used to study the AWL of GW. In this study the original model which only considering the isothermal phase has been extended by taking into account the non-isothermal phase. The kinetic parameter estimations are able to obtain a good residual mass prediction of torrefaction process at all temperature. Based on residual mass results, the rate of degradation at temperature of 300°C is higher compared to the lower torrefaction temperature 240°C. This is due to constituent in GW such as hemicellulose and cellulose which contribute to mass loss in terms of moisture and volatiles during torrefaction process. Overall, the developed model can be concluded as a reliable model in predicting AWL of GW. Good correlation has been obtained between experimental and calculated residual mass of GW with $R^2 = 0.9998$.

Acknowledgement

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