



## Volatile State Mathematical Models for Predicting Components in Biomass Pyrolysis Products

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### Highlights:

- New equation models were developed to predict pyrolysis product compositions.
- The models introduce biomass type numbers and pseudo activation energy.
- The component pseudo activation energy is temperature dependent.
- 45 components in the biomass pyrolysis products were well predicted using the models.

**Abstract.** Volatile state mathematical models for quantifying the chemical components in volatile biomass pyrolysis products were developed. The component mass yield  $Y_i$  rate depends linearly on its pseudo kinetic constant and the remaining mass yield. The mass fraction rate of each component was modeled from the derivation of its mass yield rate equation. A new mathematical model equation was successfully developed. The involved variables are: biomass number, temperature, heating rate, pre-exponential factor, and pseudo activation energy related to each component. The component mass fraction  $y_i$  and the mass yield were predicted using this model within a temperature range. Available experimental pyrolysis data for beechwood and rice husk biomass were used to confirm the developed model. The volatile products were separated into bio-pyrolysis gas (BPG) and a bio-pyrolysis oil (BPO). Five components in the BPG and forty in the BPO were quantified. The pseudo activation energy for each pseudo chemical reaction for a specific component was modeled as a polynomial

function of temperature. The component mass fraction and yield are quantifiable using this developed mathematical model equation within a temperature range. The predicted component mass fractions and yields agreed excellently with the available experimental data.

**Keywords:** *biomass pyrolysis; bio-pyrolysis gaseous; bio-pyrolysis oils; volatile state component models.*

## 1 Introduction

As organic matter, biomass has been used as a renewable energy source for a long time. Biomass is converted thermally through pyrolysis without the presence of oxygen. This produces volatile and non-volatile products. Different types of biomass have different compositions of these three components. These chemical components in the biomass affect the types of chemicals released and their composition in its pyrolysis products (Sharma, *et al.* [1]).

Biomass type is usually identified by a Van Krevelen diagram. This diagram is formed by the element ratios from ultimate analysis data. These element ratios are the ratio between hydrogen (H) and carbon (C) and the ratio between oxygen (O) and carbon. Bindar [2] modified the Van Krevelen method using ultimate and proximate analysis data into a unique correlation to classify the biomass type. The Van Krevelen element ratios are lumped into one parameter to become the biomass type number, known as  $N_{CT}$ .  $N_{CT}$  uniquely identifies the biomass type.

Many different chemical components are released in biomass pyrolysis, which are very difficult to identify. One approach to simplifying identification is by grouping the chemical components to macro-chemical families, as employed by Garcia-Perez, *et al.* [3]. The chemical components are identified mostly using a GC-MS analytical instrument. The groups are water, monolignols, sugars, light polar compounds, extractive-derived compounds, heavy polar and non-polar compounds, insoluble MeOH-toluene, and volatile organic compounds.

Identified chemical components from the pyrolysis of inkberry biomass have been reported by Safdari, *et al.* [4], with 60 chemical components in the BPO product. The major compounds in the BPO product were phenols, naphthalene, fluorene, anthracene, phenanthrene, fluoranthene, and pyrene. Some minor compounds were pyridazine, benzyl alcohol, 1,2-benzenediol, auinoline, 1,2,3-benzenetriol, acenaphthylene, and chrysene. The mass fraction of each major component in the BPO product was less than 10%. The mass fraction of the minor components was below 1%. Gases contained in the BPG product were CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub> and other light gases.

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The pyrolysis reaction mechanism is extremely complex. A single-step global pyrolysis mechanism considers the biomass to be pyrolyzed through one global chemical reaction to produce the volatile products by observing the mass loss of the solid reactant during the pyrolysis time. The rate of the biomass mass loss fraction is linearly correlated to a single kinetic constant parameter. The one-step global model is considered to be very simple and does not yet cover the real pyrolysis mechanism.

There are many more pyrolysis models that have been developed, as can be found in references such as [5] and [6]. All these models were built based on the measurement of biomass mass loss during the pyrolysis time at a specific temperature and a certain heating rate. This approach may be classified as a solid state approach. A kinetic model of the biomass pyrolysis reaction with a solid state approach is generally constructed from thermogravimetry data generated by a TGA instrument [7].

Improvement of the pyrolysis model is definitely required. Thurner, *et al.* [8] developed a pyrolysis model using three primary reactions that compete with each other to produce light gas, tar, and char products. The kinetic model is formed by three kinetic constant parameters. The rate of the biomass mass loss fraction is constructed from the summation of these three kinetic constants. The rate of mass yield for each product is related to each related kinetic constant.

A pyrolysis kinetic model is constructible from the reaction mechanism for predicting the behavior of biomass in various conditions. The pyrolysis under different conditions may be described by varying reaction mechanisms. The effects of biomass type and heating rate should be involved in formulating a predictive model.

Being able to identify and predict the chemical components and their compositions in biomass pyrolysis volatile products as BPG and BPO for every pyrolysis condition is very much needed at the present time. The available pyrolysis models such as [5] and [6] have no capability to serve the aforementioned purpose.

The objective of the present work was to develop mathematical models to be used for predicting the chemical component compositions of BPG and BPO products for every condition of biomass pyrolysis. A promising method to predict the compositions of BPO and BPG as volatile products was formulated and developed in this work. Since the objectives were to identify the chemical components in BPO and BPG products and to predict their compositions, the developed method can be classified as a volatile state approach.

The developed mathematical models are used to predict the mass fraction and yield of each chemical component that is released during the pyrolysis process in the BPG and BPO products. The involvement of the type of biomass is quantified by the biomass type number,  $N_{CT}$ . The volatile matter yield,  $Y_{VM}$ , and the volatile yield,  $Y_{VY}$ , can be predicted for each biomass type. New mathematical models for predicting the volatile yield of each component in the pyrolysis volatile product were successfully developed and solved for different biomass types, heating rates, and pyrolysis temperatures. Moreover, a pseudo activation energy parameter for a pseudo chemical reaction related to each chemical component product in BPO or BPG was introduced and successfully correlated to temperature by using the available experimental data from the literature.

This prediction method applies a set of model equations to predict the compositions and yields of chemical components within BPG and BPO products. In our full work, there were five gas components in the BPG product and forty chemical components in the BPO product whose mass fractions during the pyrolysis process were successfully quantified. However, only some of them are reported in this paper. This prediction method of the mass yield and mass fraction of each chemical component in the volatile product is very useful for quantitatively identifying the pyrolysis process for the production of renewable fuels and chemicals from different types of biomass.

## **2 Methodology**

### **2.1 Parallel Multiple Pyrolysis Pseudo Reaction Approach**

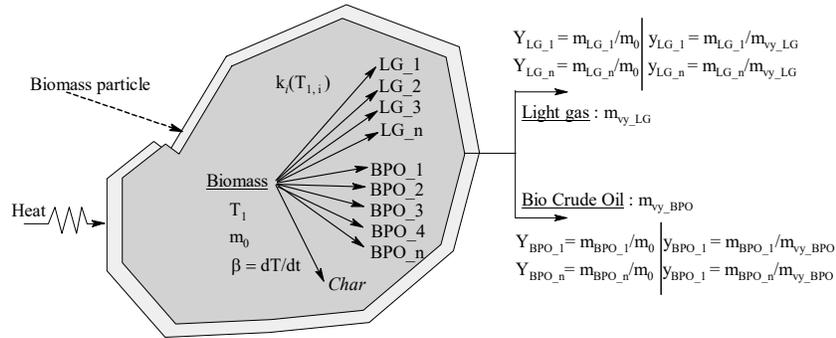
A parallel multiple pseudo reaction kinetic approach of biomass pyrolysis reactions for modeling purposes was developed and used to predict product compositions. Each pseudo reaction is considered a first-order reaction with the absence of a secondary reaction. Biomass decomposes thermally into volatile chemical components and a remaining solid material as the biochar product. With a parallel multiple pseudo reaction approach, all single pseudo reactions compete with each other.

Each chemical component type in the BPG and BPO products is of course identified from measurement. Yield  $Y_i$  and mass fraction  $y_i$  should be able to be predicted. The component yield  $Y_i$  represents the ratio between the mass amount of the produced component to the initial weight of the biomass. The component mass fraction  $y_i$  indicates the component mass fraction in the BPO or BPG product.

Figure 1 conceptually describes the parallel multiple pseudo reaction kinetic approach. At a specific temperature and heating rate, the biomass is pyrolyzed

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into released chemical components that form BPG and BPO products. Each produced chemical component related to its single-step chemical production reaction is attached to its own pseudo kinetic constant  $k_i$ .



**Figure 1** Parallel multiple pseudo reaction kinetics approach.

### 2.2 Component Yield and Mass Fraction Equation Models

The empirical mathematical correlations for  $Y_{VM}$ , Eq. (1), and  $Y_{VY}$ , Eq. (2) as functions of the biomass type number  $N_{CT}$  and temperature are available from Bindar [2]. Mathematical models for predicting the chemical component compositions of pyrolysis products are developable. The rate of the total yield of the volatile product during pyrolysis modeled by Eq. (3) is equal to the summation of all chemical component's yield rates expressed in Eq. (4).

$$\%Y_{VM} = 100 \cdot Y_{VM} = 100 \cdot e^{f_2(N_{CT})} \quad (1)$$

The conditions of the pyrolysis process may differ from the conditions in the proximate analysis measurement. The proximate analysis measurement is standardized at a temperature of 1173 K as  $T_s$ , the atmospheric pressure as  $P_a$ , and the moderate heating rate as  $\beta_s$ . The actual pyrolysis conditions may occur outside the standard condition above. The total volatile yield  $Y_{VY}$  correlation was proposed by Bindar [2] as an exponential function of pyrolysis temperature  $T$  and  $N_{CT}$  in the following equation:

$$Y_{VY}(N_{CT}, T) = e^{f_3\left(\frac{T}{T_s}\right)} \cdot e^{f_2(N_{CT})} \quad (2)$$

The exponential function of  $f_3(T/T_s)$  in Eq. (2) above actually defines the value of  $V_E$  introduced by Mill [9] and constructed by Bindar [2]. The pyrolysis modeling equation for a component yield rate with this approach is formulated as shown in Eq. (3). The component yield rate becomes a function of  $Y_{VY}$ . There are

$N_{\text{BPG}}$  components in BPG and  $N_{\text{BPO}}$  in BPO. Then the total volatile yield rate is modeled by Eq. (4).

$$\frac{d(Y_{\text{VY}})}{dt} = k(T) (1 - Y_{\text{VY}}) \quad (3)$$

$$\frac{dY_{\text{VY}}}{dt} = \sum_i^{N_{\text{BPG}}} k_i (1 - Y_{\text{VY}}) + \sum_i^{N_{\text{BPO}}} k_i (1 - Y_{\text{VY}}) \quad (4)$$

Referring to the principle of mass balance, the volatile yield  $Y_{\text{VY}}$  represents the sum of the BPG and BPO yields. The remaining yield is the biochar yield  $Y_{\text{biochar}}$ . The total volatile yield is evaluated from Eq. (5) and Eq. (6). The mass fractions of components in the BPG and BPO products are identified as  $y_{i,\text{BPG}}$  and  $y_{i,\text{BPO}}$  respectively. These mass fractions are correlated to the total volatile yield as indicated by Eqs. (7) to (12).

$$Y_{\text{VY}} = 1 - Y_{\text{Biochar}} \quad (5) \quad Y_{\text{BPG}} = \sum_i^{N_{\text{BPG}}} Y_{i,\text{BPG}} \quad (10)$$

$$Y_{\text{VY}} = Y_{\text{BPG}} + Y_{\text{BPO}} \quad (6) \quad \sum_i^{N_{\text{BPG}}} y_{i,\text{BPG}} = 1 \quad (11)$$

$$Y_i = y_i Y_{\text{VY}} \quad (7) \quad Y_{i,\text{BPO}} = y_{i,\text{BPO}} Y_{\text{BPO}} \quad (12)$$

$$\sum_i^{N_{\text{BPG}} + N_{\text{BPO}}} y_i = 1 \quad (8) \quad Y_{\text{BPO}} = \sum_i^{N_{\text{BPO}}} Y_{i,\text{BPO}} \quad (13)$$

$$Y_{i,\text{BPG}} = y_{i,\text{BPG}} Y_{\text{BPG}} \quad (9) \quad \sum_i^{N_{\text{BPO}}} y_{i,\text{BPO}} = 1 \quad (14)$$

The functions of  $f_2$  and  $f_5$  in Eq. (1) and Eq. (2) were obtained from Bindar [2]. These functions are written as follows:

$$f_2(N_{\text{CT}}) = 0.031 - 0.029 \ln(N_{\text{CT}}) - 0.038(\ln N_{\text{CT}})^2 \quad (15)$$

$$f_5\left(\frac{T}{T_s}\right) = 440.19 \left(\frac{T}{T_s}\right)^5 - 1,390.34 \left(\frac{T}{T_s}\right)^4 + 1,746.25 \left(\frac{T}{T_s}\right)^3 - 1,091.93 \left(\frac{T}{T_s}\right)^2 + 341.44 \left(\frac{T}{T_s}\right) - 43.18 \quad (16)$$

By substituting Eq. (2), Eq. (15), and Eq. (16) into Eq. (3), with the heating rate  $dT/dt$  as  $\beta$ , a model equation for a component mass fraction in the volatile product from the biomass pyrolysis is obtained. The obtained model equation is as follows:

$$\frac{dy_i}{dT} + y_i \left[ \frac{d\left[f_5\left(\frac{T}{T_s}\right)\right]}{dT} \right] = \left[ \frac{A_i}{\beta} \cdot e^{(-E_{\text{ai}}/RT)} \right] \frac{(1-Y_{\text{VY}})}{Y_{\text{VY}}} \quad (17)$$

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This model equation is solvable. The model equation is generalized by Eq. (18), which is considered a first-order linear differential equation.

$$\frac{dy}{dx} + py = Q \quad (18)$$

The parameters p and Q are defined as follows:

$$p = \frac{d\left[\frac{f_5(T)}{T_s}\right]}{dT}, \quad Q = \left( \frac{1}{e^{f_5(T)/T_s} e^{f_2(N_{CT})}} - 1 \right) \left[ \frac{A_i}{\beta} \cdot e^{(-E_{ai}/RT)} \right]$$

The exact solution for Eq. (18) is formulated by Eq. (19). This model equation is a new mathematical model equation for every pyrolysis process. The solution of this model equation predicts each component mass fraction in the volatile product. This model equation is obtained from the volatile state approach concept presented above.

$$y_i = \frac{A_i}{\beta} \frac{1}{e^{f_5(T)/T_s}} \int_{T_0}^T \left\{ \frac{1}{e^{f_2(N_{CT})}} \left( e^{(-E_{ai}/RT)} \right) - \left( e^{(-E_{ai}/RT)} \right) e^{f_5(T)/T_s} \right\} dT \quad (19)$$

Eq. (19) is solved with initial temperature  $T_0 = 25 \text{ }^\circ\text{C}$  to get  $y_i = 0$ .  $T_0$  is the initial temperature and  $T$  is the instantaneous reaction temperature. This indicates that at  $T_0$  the pyrolysis process has not yet started.

### 2.3 Solution Methods

The model equation in Eq. (19) is solved numerically by Simpson's method to provide an adequate approximation of the exact integral rule. Pyrolysis measurement data are required for the above solution. These data are: proximate analysis data, ultimate analysis data, identified chemical components, and the component compositions of the pyrolysis products. The chemical components and compositions are mostly identified and quantified at every pyrolysis temperature and a fixed heating rate.

In the present work, the available experimental data from Branca, *et al.* [10] were used. The BPO product was classified into the following component groups: major carbohydrates, minor carbohydrates, furans, guaicol, phenols, and syringols. Eqs. (15), (16), and (19) are directly involved in the solution. The values of  $A_i$  and  $E_{a,i}$  as pseudo kinetic constants for a single-step pyrolysis reaction that produces a component  $i$  in the volatile product result from the solution of the model equation above. The model equation, Eq. (19), is solved numerically. The constants from the numerical solution of Eq. (19) are then used to predict the mass fraction and yield of the identified components for any biomass at a certain heating rate.

There are two constant parameters in Eq. (19) to be determined by fitting Eq. (19) at the same time for every component to the available experimental data. In this approach, a single value of A for all components is employed. The pre-exponential constant  $A_i$  is considered to have the same values for all components. The value is noted as A. The activation energy  $E_a$  is considered by Perlmutter-Hayman [11] as temperature dependent. Then the pre-exponential factor itself is independent of temperature. Likewise, Silva, *et al.* [12] reviewed the reaction rate transition theory with the conclusion that the pre-exponential factor A is widely used as a constant, while  $E_a$  can be a function of temperature.

The value of A is obtained by fitting a single global pyrolysis reaction kinetic model. Here, the single global pyrolysis reaction kinetic model by Kissinger-Akahira-Sunose (KAS) [13] was used and transformed into a volatile state kinetic model resulting from the following equation:

$$\frac{\beta}{T^2} = \frac{AR}{(-\ln(1-Y_{VY})) E_a} \left[ 1 - \frac{2RT}{E_a} \right] \cdot e^{\frac{-E_a}{R.T}} \quad (20)$$

Using the experimental data for total volatile yield for every temperature, the value of A is obtainable from the equation model above. Since  $RT/E_a$  is much smaller than one, using Eq. (2) for  $Y_{VY}$ , Eq. (20) is modified into an exact equation solution as follows:

$$\frac{\beta}{T^2} = \frac{AR}{\left( -\ln \left\{ 1 - \exp \left( f_5 \left( \frac{T}{T_g} \right) \right) \cdot \exp \left( f_2(N_{CT}) \right) \right\} \right) E_a} \cdot e^{\frac{-E_a}{R.T}} \quad (21)$$

Then, the value of A is calculable directly from Eq. (21) above.

The experimental data for biomass pyrolysis were produced mostly in terms of the initial mass,  $m_{p,0}$ ; the mass at time t,  $m_{p,t}$ ; temperature T at time t; and the mass at the final time,  $m_{p,f}$ . Most of the previously developed kinetic models used conversion level  $\alpha$  as the ratio between  $(m_{p,0} - m_{p,t})$  to  $(m_{p,0} - m_{p,f})$  [13]. The final mass  $m_{p,f}$  can still undergo pyrolysis for further temperatures, so in this model development, the volatile yield  $Y_{VY}$  as the ratio  $(m_{p,0} - m_{p,t})$  to  $m_{p,0}$  was introduced to replace  $\alpha$ .

For a known heating rate  $\beta$  in the biomass pyrolysis process, the volatile yield is calculated for every temperature. Eq.(21) above is used to generate the plot for  $\log(\beta/T^2)$  against  $1/T$ . This plot produces the values of A and  $E_a$ .

The obtained global value of A is used as a fixed value of  $A_i$  for all released components in Eq. (19). The procedure starts with a known A and a guessed  $E_{a,i}$  at a certain temperature for each component. The calculated mass fraction for

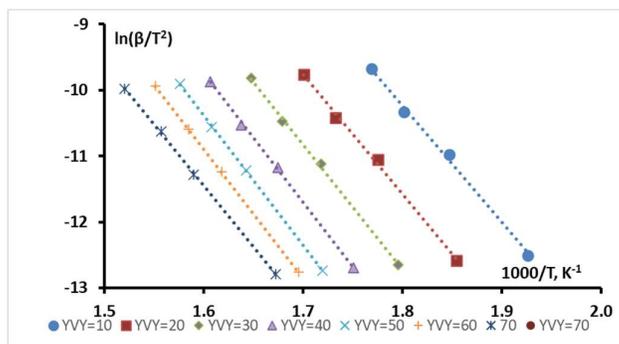
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each component is fitted to its measured value. This procedure is repeated until the difference between the calculated and the measured values approaches a very small value. The procedure is completed for all temperatures and then continues to the next component. The prediction is then continued to another type of biomass, quantified by its unique  $N_{CT}$  value with Eq. (19).

### 3 Result and Discussion

#### 3.1 Pre-Exponential Global Constant

The pre-exponential global constant  $A$  is determined from Eq. (21) above using the experimental data from Branca, *et al.* [10] for beechwood biomass with an  $N_{CT}$  of 8.6 using the solution method presented in Section 3 above. The resulted plot for obtaining the constant  $A$  is shown in Figure 2. The obtained  $A$  is averaged to obtain the value of  $1.08 \times 10^{13}$  minute<sup>-1</sup>.

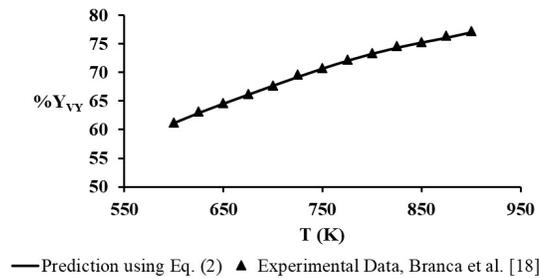


**Figure 2** Plot of the modified kinetic Kissinger-Akahira-Sunose (KAS) model using volatile yield with variables heating rate  $\beta$  and temperature  $T$ , Eq. (21), at volatile yields  $Y_{VY}$  from 10 to 70% for the beech wood biomass pyrolysis data from Branca, *et al.* [10].

The obtained pre-exponential global constant above was compared to the values reported by others in terms of its order of magnitude. Serbanescu [14] conducted a kinetics analysis of two pyrolysis reaction kinetics methods used by other researchers. The pre-exponential factor values reported by Serbanescu [14] were in the range of  $10^5$ - $10^{24}$  min<sup>-1</sup> based on the use of conversion variable  $\alpha$ . Jong, *et al.* [15] reported pre-exponential factor values for pyrolysis of miscanthus giganteus and wood pellets in the range of  $10^{11}$ - $10^{16}$  minutes<sup>-1</sup>. The pre-exponential constant value in this study fell within the values of other studies.

### 3.2 Predicted Volatile Yield ( $Y_{VY}$ )

The volatile yield  $Y_{VY}$  from experimental data such as from Branca, *et al.* [10] can easily be evaluated as the ratio of the measured mass loss to the initial mass of the biomass that undergoes pyrolysis. The biochar mass yield  $Y_{Biochar}$  is then calculated from Eq. (5). The correlation for the  $Y_{VY}$  predicted by Eq. (2) was plotted for the beechwood biomass pyrolysis process with  $N_{CT}$  at 8.6 against temperature and compared to the measured values from Branca, *et al.* [10]. The plot is shown in Figure. 3. The validity of the predicted volatile yields by comparing them to measured yields was considerably excellent by using the  $f_5$  function in Eq. (16) above.

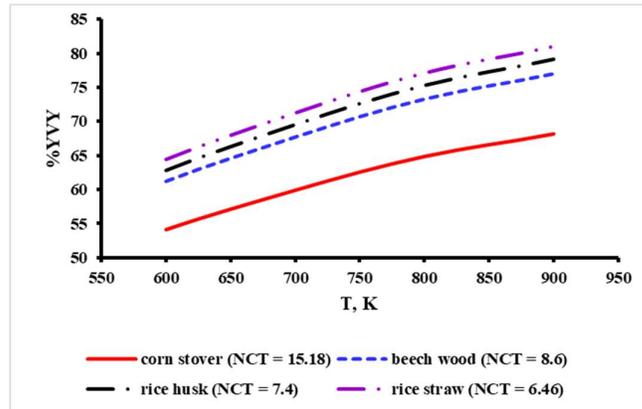


**Figure 3** Comparison of volatile yield predictions to experimental data [10] for the beech wood biomass pyrolysis process.

The effect of biomass type with a unique value of  $N_{CT}$  on  $Y_{VY}$  is well quantified using Eq. (2). The effect for different  $N_{CT}$  values is presented in Figure 4. This figure with three curves presents the predicted volatile yields for  $N_{CT}$  values 6.46, 7.4, 8.6 and 15.18. It was expected, as shown by Figure 4, that larger  $N_{CT}$  values would produce less volatility. The predicted volatile yields agreed with this expectation. These prediction results show the strength of the present model equations in covering the effect of biomass type with  $N_{CT}$  value in the predicted total and component yields from biomass pyrolysis.

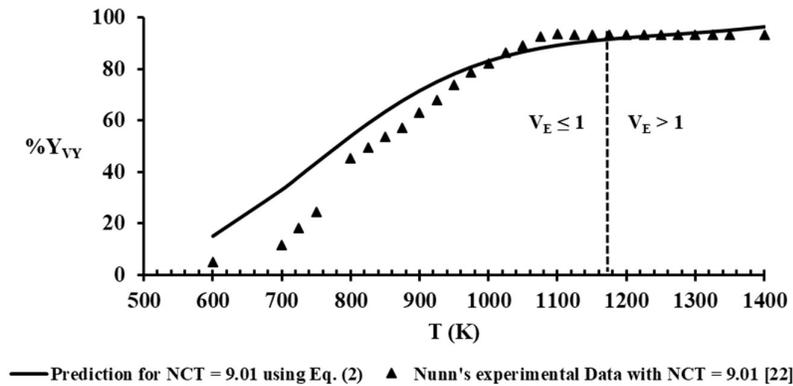
The effect of biomass type on volatile yield is predictable using Eq. (2). In this case, four types of biomass were included for prediction, where each biomass had its own  $N_{CT}$  value. The pyrolysis can be conducted below the standard temperature of 1173 K or above it. The yield for the process above  $T_s$  is expected to be larger than volatile matter  $Y_{VM}$ . The volatile enhancement can be larger than 1 for the case of a pyrolysis temperature above 1173 K (see Figure 5).

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**Figure 4** Effects of  $N_{CT}$  on predicted volatile yield at a heating rate of 40 Km-1 with  $N_{CT}$  values of 6.46, 7.4, 8.6 and 15.18.

For the case of a pyrolysis temperature exceeding the proximate analysis temperature  $T_s$ , the  $V_E$  values can be larger than 1. The experimental data for the volatile yield at a temperature above  $T_s$  are provided by Nunn, *et al.* [16] for biomass with an  $N_{CT}$  of 9.01. The comparison between the predicted  $Y_{VY}$  and the measured one for Nunn biomass is shown in Figure 5. The predicted  $Y_{VY}$  agrees with the expectation. This result indicates the strength of the present model equations in predicting the pyrolysis behaviors, even at temperature above the proximate analysis temperature.



**Figure 5** Comparison between  $Y_{VY}$  prediction and measurement for Nunn biomass pyrolysis for a wide temperature range, exceeding the proximate analysis temperature.

### 3.3 Predicted Mass Fraction $y_i$ and Mass Yield $Y_i$

The experimental data [10] were used to obtain the values of  $A$  and  $E_{ai}$  for the measured components in the volatile product of biomass pyrolysis. The required mass fractions of components  $y_i$  were calculated from the above data. There were 43 components in the volatile product that were measured quantitatively. The components in the BPG product included carbon monoxide CO, carbon dioxide CO<sub>2</sub>, and methane CH<sub>4</sub>. The other 40 components were the components that form the BPO product. Some of the BPO components were: water H<sub>2</sub>O, hydroxyacetaldehyde C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>, levoglucosan C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>, 1-hydroxy-2-butanone C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>, formic acid CH<sub>2</sub>O<sub>2</sub>, 5-methyl-2-furaldehyde C<sub>6</sub>H<sub>6</sub>O<sub>2</sub>, 2-furaldehyde C<sub>5</sub>H<sub>4</sub>O<sub>2</sub>, guaiacol C<sub>7</sub>H<sub>8</sub>O<sub>2</sub>, Vanillin C<sub>8</sub>H<sub>8</sub>O<sub>3</sub>, phenol C<sub>6</sub>H<sub>5</sub>OH, 3,4-dimethylphenol C<sub>8</sub>H<sub>10</sub>O, syringol C<sub>8</sub>H<sub>10</sub>O<sub>2</sub>, and syringaldehyde C<sub>9</sub>H<sub>10</sub>O<sub>4</sub>. The mass fractions for all 43 components were calculated using Eq. (7) for every temperature from the experimental data of Branca, *et al.* [10] and used to obtain the pseudo energy activations of these 43 components.

The experimental data from Branca, *et al.* [10] above did not cover light gas components such as hydrogen (H<sub>2</sub>), ethane (C<sub>2</sub>H<sub>6</sub>), and ethene (C<sub>2</sub>H<sub>4</sub>). Fortunately, Blasi, *et al.* [17] measured the yields of some components in the BPG product, including H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>2</sub>H<sub>4</sub>. Using these Blasi data for rice husk biomass with an  $N_{CT}$  value of 7.4,  $A$ , and  $E_{ai}$  for components H<sub>2</sub> and combined C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub> were obtained also from the solution of this model equation, Eq. (19).

The solution of the model equation in Eq. (19) starts from the obtained value for the pseudo-pre-exponential factor  $A$  in Section 4.1. The pseudo activation energy  $E_{ai}$  for each component is determined using the numerical procedure described in Section 3. The  $E_{ai}$  is adjusted to fit the predicted  $y_i$  value to its measured value for each temperature. The activation energy for each component is then modeled as a polynomial function of the temperature.

The fitted result on  $E_{ai}$  is sensitive to temperature in Eq. (19). Each temperature with the known mass fraction of the component has its own activation energy. Therefore, the activation energy  $E_{ai}$  is well presented by the quadratic polynomial function of temperature for each chemical component in the product. The result for the temperature function of  $E_{ai}$  for each related component is shown in Table 1. The temperature dependence of energy activation was shown to be very strong within the temperature range of 300 K to 350 K [18]. The activation energy from the hydrolysis of sucrose to glucose and fructose was fitted as a quadratic polynomial function of temperature [19].

## Volatile State Mathematical Models for Predicting Components in Biomass Pyrolysis Products

Table 1 shows the results for the pseudo activation energy  $E_{ai}$  of each pseudo-single-stage pyrolysis reaction producing a component in the volatile product from the pyrolysis of beechwood biomass. Only some components are presented here due to space limitations. The  $E_{ai}$  of each component in the BPG and BPO products is constructed to be temperature-dependent. The values of  $E_{ai}$  for related components in Table 1 range from 150 kJ/mol to 290 kJ/mol. In addition, Table 2 presents the values of  $A$  and  $E_{ai}$  for  $H_2$  and combined  $C_2H_6$  and  $C_2H_4$  from the pyrolysis of rice husk. The  $A$  value for rice husk pyrolysis in Table 2 is  $4.48 \times 10^{13}$   $\text{minute}^{-1}$ . The values of  $E_{ai}$  in Table 2 lie between 200 to 310 kJ/mol. The temperature-dependence of  $E_{ai}$  for each component forms a polynomial function. This can be related to the evolution of the pyrolysis process with temperature. At each temperature, the biomass as a reactant changes the chemical structure. Moreover, with this polynomial function of the pseudo activation energy, better accuracy in the prediction is achieved.

Zaman, *et al.* [20] report a multiple pathway pyrolysis reaction that is characterized by a non-linear correlation between  $\ln k$  and  $1/T$ . This leads to the activation energy being dependent on the temperature. An approach for the Arrhenius activation energy to be a temperature-dependent is also supported by Runstraat, *et al.* [7], Ward, *et al.* [21], Yoshioka, *et al.* [22], and Blais, *et al.* [23].

A different approach, with three different independent parallel reactions occurring in the pyrolysis process of biomass with the assumption of three pseudo reactions to produce components, was employed by Branca, *et al.* [24]. Three sets of kinetic parameters were quantified. Each set was formed by an activation energy  $E_a$ , a pre-exponential factor  $A$ , and a stoichiometric coefficient  $\nu$ . The values were reported at 1977 to  $1.78 \times 10^{19}$   $\text{minute}^{-1}$  for  $A$ , and 46 to 236 kJ/mol for  $E_a$ .

Assigning different values  $E_a$  and  $A$  to released components in the volatile product was also done by Nunn, *et al.* [16]. Each component had its own pseudo kinetic equation model. The experimental data were used to estimate the values of  $E_{ai}$  and  $A$ . Among the components were  $CO$ ,  $CH_4$ ,  $CO_2$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_6$ ,  $HCHO$ ,  $CH_3CHO$ , and  $H_2O$ . The values of their  $E_{ai}$  for these components resulting from sweet gum hardwood pyrolysis ranged from 11.5 to 42.8 kJ/mol. The  $A$  values for the above components were between  $4.55 \times 10^4$  and  $9.51 \times 10^{12}$   $\text{minute}^{-1}$ .

Aboyade, *et al.* [25] experimentally obtained three activation energy values for sugar cane bagasse pyrolysis by assuming the biomass as a mix of three pseudo components, representing hemicellulose, cellulose, and lignin. Three values of  $E_{ai}$  were quantified. The pseudo activation energy for the hemicellulose component from cane bagasse biomass was quantified at a value of 200 kJ/mol.

For the same hemicellulose component from corn cobs biomass,  $E_a$  was obtained at a value of 85 kJ/mol. It is interesting to note that different values of  $E_a$  for the same component but different biomass sources were exhibited. In another work, Carrier, *et al.* [26] reported their experimental work on eucalyptus grandis to have three different values of the pseudo energy activation, where each of them was dedicated to each component as holocellulose,  $\alpha$ -cellulose, or lignin with a value of 173, 208 and 197 kJ/mol respectively. They also concluded that the energy activation for the lignin fraction to be mass conversion dependent. This infers that the energy activation is temperature dependent.

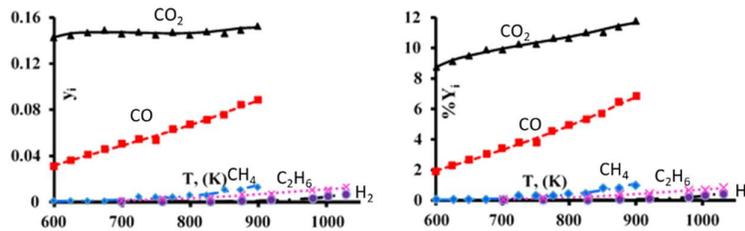
The model equation, Eq. (19), with the obtained pseudo kinetic parameters  $A$  and  $E_{ai}$  for all components, some of which are listed in Tables 1 and 2, for biomass with a unique  $N_{CT}$  value, is a new model equation for predicting the mass fractions of components in the volatile product from biomass pyrolysis and is ready to be used directly. The predicted mass fractions  $y_i$  and mass yield  $Y_i$  for gaseous and liquid components in the volatile product of biomass pyrolysis are shown in Figures 6 to 8. The predictions are excellent based on comparison with the pyrolysis experimental data for beechwood and rice husk biomass.

**Table 1** Pseudo activation energy for several components in the volatile product from beech wood biomass pyrolysis with a  $N_{CT}$  value of 8.6.

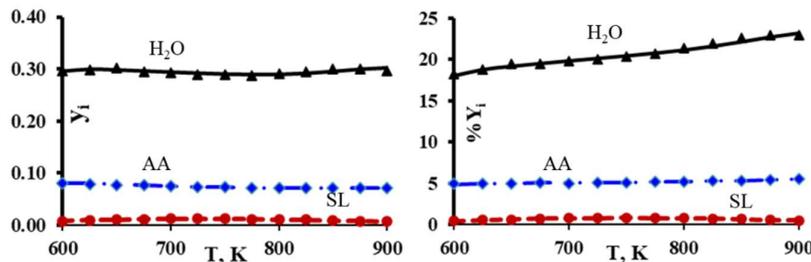
Pyrolysis product	$A = 1.08 \times 10^{13} \text{ minute}^{-1}$ $E_{ai}(\text{J/mol}) = \phi \cdot T^2 + \chi \cdot T + \delta$
<b>Bio-pyrolysis gas, BPG</b>	
Carbon monoxide, CO	$\phi = 0.003, \chi = 235.41, \delta = 18247.06$
Methane, CH <sub>4</sub>	$\phi = -0.063, \chi = 314.54, \delta = 13645.24$
Carbon monoxide, CO <sub>2</sub>	$\phi = 0.0037, \chi = 245.40, \delta = 4694.33$
Hydrogen (H <sub>2</sub> )	$\phi = 0.227, \chi = 704.31, \delta = -136094.06$
Ethane + ethene (C <sub>2</sub> H <sub>6</sub> + C <sub>2</sub> H <sub>4</sub> )	$\phi = -0.054, \chi = 162.61, \delta = 76572.87$
<b>Water and acetate acid</b>	
Water, H <sub>2</sub> O	$\phi = -0.0028, \chi = 249.97, \delta = 764.99$
Acetate acid, CH <sub>3</sub> COOH	$\phi = -0.0017, \chi = 262.37, \delta = -719.46$
<b>Bio-pyrolysis oil, BPO</b>	
Hydroxyacetaldehyde, C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	$\phi = 0.028, \chi = 211.58, \delta = 27292.18$
Levogluconan, C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	$\phi = 0.046, \chi = 190.09, \delta = 40261.19$
1-hydroxy-2-butanone, C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	$\phi = 0.058, \chi = 204.24, \delta = 28165.24$
Formic acid, CH <sub>2</sub> O <sub>2</sub>	$\phi = 0.043, \chi = 209.86, \delta = 26575.73$
5-methyl-2-furaldehyde, C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	$\phi = 0.037, \chi = 245.23, \delta = 16428.74$
2-furaldehyde, C <sub>3</sub> H <sub>4</sub> O <sub>2</sub>	$\phi = 0.035, \chi = 231.57, \delta = 17806.55$
Guaiacol, C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	$\phi = 0.207, \chi = -18.73, \delta = 111706.68$
Vanillin, C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	$\phi = 0.167, \chi = 21.09, \delta = 110122.58$
Phenol, C <sub>6</sub> H <sub>5</sub> OH	$\phi = -0.019, \chi = 316.08, \delta = -6883.25$
3,4-dimethylphenol (DMP), C <sub>8</sub> H <sub>10</sub> O	$\phi = 0.016, \chi = 270.74, \delta = 28214.02$
Syringol, C <sub>8</sub> H <sub>10</sub> O <sub>2</sub>	$\phi = 0.154, \chi = 49.06, \delta = 82978.27$
Syringaldehyde, C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	$\phi = 0.188, \chi = -16.38, \delta = 120397.99$

## Volatile State Mathematical Models for Predicting Components in Biomass Pyrolysis Products

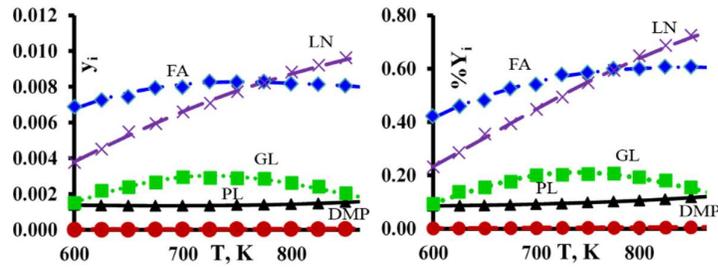
The predicted yields of acetate acid in the volatile product for different biomasses at different pyrolysis temperature are shown in Figure 9 using the model equation in Eq. (19) with the  $N_{CT}$  function in Eq. (15), the volatile enhancement model equation in Eq. (16) and the pseudo kinetic parameters above. The other two biomasses added here are rice straw from Sonabe & Worasuwanarak [27] with  $N_{CT}$  at 6.46, and corn stover from Scott, *et al.* [28] with  $N_{CT}$  at 15.18. The effect of these biomass types on the yield of acetate acid in the volatile product clearly exists, as shown in Figure 9. The equation model in Eq. (19) successfully predicts the yield and mass fraction of all components for any type of biomass.



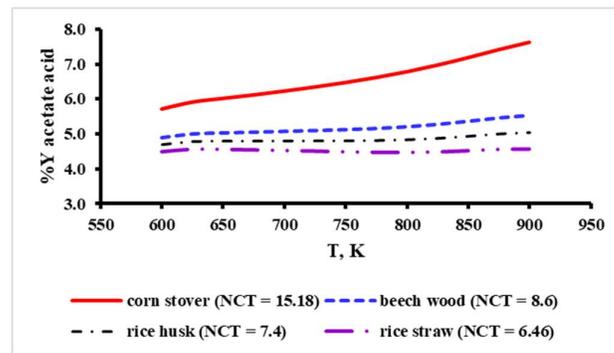
**Figure 6** Comparison of predicted mass fraction  $y_i$  and yield  $\%Y_i$  of light gas components in the volatile product as CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub> using Eq. (19) to pyrolysis experimental data for beech wood with  $N_{CT} = 8.6$  and rice husk with  $N_{CT} = 7.4$ . Symbols are experimental data from the literature and lines are predicted values from the present models.



**Figure 7** Comparison of predicted mass fraction  $y_i$  and yield  $\%Y_i$  of liquid components in the volatile product as H<sub>2</sub>O, acetate acid (AA) and syringol (SL) using Eq. (19) to pyrolysis experimental data for beech wood with  $N_{CT} = 9.6$ . Symbols are experimental data from the literature and lines are predicted values from the present models.



**Figure 8** Comparison of predicted mass fractions  $y_i$  and yield  $\%Y_i$  of liquid components in the volatile product as phenol (PL), 3,4 dimethylphenol (DMP), formic acid (FA), guaiacol (GL) and levoglucosan (LN) using Eq. (19) to pyrolysis experimental data for beech wood with  $N_{CT} = 8.6$ . Symbols are experimental data from the literature and lines are predicted values from the present models



**Figure 9** Predicted mass yield of acetate acid for certain biomasses at a heating rate of 40 K/minute and various pyrolysis temperatures in the volatile product for corn stover, beech wood, rice husk and straw biomass.

#### 4 Conclusion

The quantitative prediction of chemical components in biomass pyrolysis products using newly developed volatile state pyrolysis mathematical model equations was successfully verified with experimental data from the literature for 5 components of bio-pyrolysis gas and 12 components of bio-pyrolysis oil products. The pseudo activation energy for each chemical component was introduced and identified to be a quadratic temperature dependent function. The predicted mass fraction and yield of chemical components fit excellently to the experimental data with this pseudo activation energy. The developed volatile state pyrolysis model equations are a set of mathematical tools for quantifying

## Volatile State Mathematical Models for Predicting Components in Biomass Pyrolysis Products

chemical components in biomass pyrolysis products. In future studies, a comprehensive database of the pyrolysis performance of all types of biomass should be pursued by using the combination of experimental data and the present volatile state mathematical model equations.

### Nomenclature

$Y_i$	=	Yield component	$m_{p,0}$	=	Initial mass of biomass
$y_i$	=	Mass fraction component	$m_{p,t}$	=	Biomass mass at time $t$
$k_i$	=	Kinetic constant	$m_{p,f}$	=	Final biomass mass
$Y_{VM}$	=	Yield volatile matter	$\alpha$	=	Conversion
$N_{CT}$	=	Number of coal type	$V_E$	=	Volatile enhancement
$A_i$	=	Pre-exponential factor	$Y_{VY}$	=	Yield volatile release
$R$	=	Ideal gas constant	$P_s$	=	Atmospheric pressure
$f_5(T/T_s)$	=	Polynomial function of the ratio temperatures	$T_s$	=	Temperature standard
$f_2(N_{CT})$	=	Polynomial function of $N_{CT}$	$\beta_s$	=	Heating rate
$N_{BCO}$	=	Number of BCO components	$T$	=	Pyrolysis temperature
$N_{BPG}$	=	Number of BPG components	$E_{a_i}$	=	Energy activation component

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