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## Prediction of higher heating values (HHVs) and energy yield during torrefaction via kinetics

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### Abstract

Torrefaction is a promising process to upgrade biomass and produce solid biofuel. The purpose of this study is to predict the higher heating values (HHVs) of biomass and energy yield during torrefaction. A two-step model and a direct method are adopted to obtain the torrefaction kinetics and the prediction of elemental composition in the present study. The experiments were performed at the temperature range of 200-230 °C in a pilot-scale reactor, which can record the mass loss dynamics during the treatment. The results point out that the prediction of solid yield and elemental composition profiles are in good agreement with the experiments. The predicted HHVs are calculated from C, H, and O based on an empirical equation. As a while, the HHVs of torrefied wood are in the range of 19.85-20.71 MJ kg<sup>-1</sup> and the energy yields are in the range of 92.3-97.4 %.

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**Keywords:** torrefaction; two-step kinetics; sustainable material; mild pyrolysis

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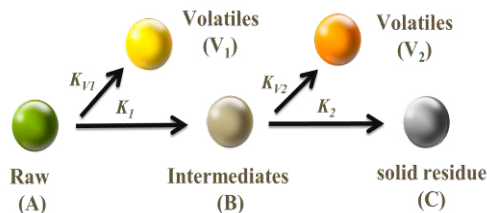
## 1. Introduction

Bioenergy is an important renewable energy and it has been extensively employed worldwide. Solid biomass can be burned directly to get heat and power. The moisture, oxygen and hydrogen contents as well as the volume of raw biomass are high, whereas its calorific value is low. Therefore, the utilization efficiency of untreated biomass is low. Torrefaction is a mild pyrolysis process in the temperature range of 200–300 °C conducted to improve the poor properties of biomass. In recent years, numerous studies concerning biomass torrefaction have been performed and the advantages of the pretreatment method have been reported [1]. In order to identify the behavior of degradation during biomass torrefaction, kinetic analysis have to be conducted. In the literature, some studies have proposed kinetic models to represent the thermal degradation of biomass during torrefaction. These models, usually applied to TGA (thermogravimetric analysis) data to simulate the intrinsic decomposition of biomass, can be sorted in two major sections: the detailed models and the pseudo-components models. The most used of the detailed models was initially proposed by Ranzi et al. [2] and further developed by Blondeau and Jeanmart [3], Gauthier et al. [4] and Anca-Couce et al. [5]. This model considers separately the decomposition of the three biopolymer components (hemicelluloses, cellulose, and lignin) in biomass and predicts the volatile matters that are produced. It is the only model based on the description of the chemical reactions occurring during the treatment. However, this model is complex and hard to extend to various species or torrefaction conditions. The pseudo-components models are the most used in the literature because of their simplicity. They aim to represent the global mass loss and can be based on a one-step reaction scheme [6], on several reactions in parallel schemes [7,8] or on several steps in series schemes [9,10]. These models, even if they are simpler, present the advantage to be easily adaptable.

In the present work, a two-step in series model is adopted to obtain the associated kinetic constants and the torrefaction kinetics from the experimental results. Poplar (*Populus nigra*), a common European wood species, was chosen for the torrefaction. The contents of hemicelluloses, cellulose, and lignin in poplar are 22.45, 49.91 and 24.61wt% respectively. The torrefaction experiments were carried out at 200, 210, 220, and 230 °C in a pilot-scale reactor, which could record the mass loss dynamics during the treatment. The detailed informations about experiments have been reported in a previous study [11]. The aim of the present study is to predict higher heating values (HHVs) and energy yields from the torrefaction kinetics. A direct method is also introduced to simulate the elemental composition during torrefaction. The obtained results will be relevant to evaluate the torrefaction performances and provide a useful insight about the mechanisms of biomass thermal degradation.

## 2. Methodology

The two-step kinetic scheme was originally applied for isothermal pyrolysis by Di Blasi and Lanzetta [12] to describe pure hemicellulose (xylan) decomposition. The kinetic scheme consists of two series-reactions, as shown in **Fig.1**. In this model, it is assumed that raw wood material A is converted to an intermediate solid B and volatiles  $V_1$ . The intermediate solid B reacts afterwards to form solid residue C and additional volatiles  $V_2$ .



**Fig. 1.** Two-step kinetic scheme

Assuming that all reactions are of first order, the solid yield equations for the solids (A, B, C) and volatiles ( $V_1$ ,  $V_2$ ) can be written as:

$$\begin{cases} \frac{dm_A(t)}{dt} = -(k_1 + k_{V1}) \times m_A(t) \\ \frac{dm_B(t)}{dt} = k_1 \times m_A(t) - (k_2 + k_{V2}) \times m_B(t) \\ \frac{dm_C(t)}{dt} = k_2 \times m_B(t) \\ \frac{dm_{V1}(t)}{dt} = k_{V1} \times m_A(t) \\ \frac{dm_{V2}(t)}{dt} = k_{V2} \times m_B(t) \end{cases} \quad (1)$$

where  $m_i$  is the mass of each pseudo-component ( $i = A, B, C, V_1, V_2$ ). The rate constants obey the Arrhenius law:  $k_i = A_i \exp(-E_i/RT)$ , in which  $A_i$  and  $E_i$  are respectively the pre-exponential factor and the activation energy of the component  $i$ ,  $R$  is the universal gas constant and  $T$  is the absolute temperature. A numerical approach (MATLAB®) was used to obtain the kinetic parameters for poplar wood. Eight parameters for the four pre-exponential factors ( $A_i$ ) and four activation energies ( $E_i$ ) were assumed to start the calculation. A minimizing function and ODE resolutions were used to obtain the optimized values for the rate constants ( $k_i$ ) and calculate the components yields (A, B and C) during heat treatment.

The calculation for the elemental composition ( $C_i, H_i, N_i, O_i$ ) of the pseudo-components  $i$  is expressed in the matrix form below:

$$\begin{bmatrix} Y_A^{(200)} & Y_B^{(200)} & Y_C^{(200)} \\ Y_A^{(210)} & Y_B^{(210)} & Y_C^{(210)} \\ Y_A^{(220)} & Y_B^{(220)} & Y_C^{(220)} \\ Y_A^{(230)} & Y_B^{(230)} & Y_C^{(230)} \end{bmatrix}_j \times \begin{bmatrix} C_A & H_A & O_A & N_A \\ C_B & H_B & O_B & N_B \\ C_C & H_C & O_C & N_C \end{bmatrix}_j = \begin{bmatrix} C_S^{(200)} & H_S^{(200)} & O_S^{(200)} & N_S^{(200)} \\ C_S^{(210)} & H_S^{(210)} & O_S^{(210)} & N_S^{(210)} \\ C_S^{(220)} & H_S^{(220)} & O_S^{(220)} & N_S^{(220)} \\ C_S^{(230)} & H_S^{(230)} & O_S^{(230)} & N_S^{(230)} \end{bmatrix}_j \quad (2)$$

where  $i = A, B, C$  and  $S$  represent the pseudo-components A, B, C and the solid after torrefaction (S), respectively;  $j$  denotes the data point;  $Y_i^{(T)}$  and  $X_i^{(T)}$  are the mass fraction and the relative elemental content of the component  $i$  at a temperature  $T$ , and  $X = C, H, N, O$ . The elemental composition of each pseudo-component and thus the treated wood at any temperature and time will be obtained after substituting the ultimate analyses of the initial untreated wood and treated wood at the end of treatment, as well as the instantaneous fraction into the matrix [13].

### 3. Results and discussion

A two-step kinetic model is established and used to predict dynamic mass loss during wood treatment. The mass loss is predicted by a curve-fitting to fit to the experimental data (as shown in Fig. 2).

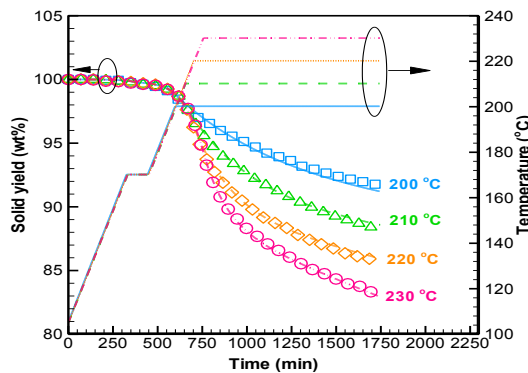


Fig. 2. Profiles of predicted (lines) and experimental (symbols) solid yield during torrefaction

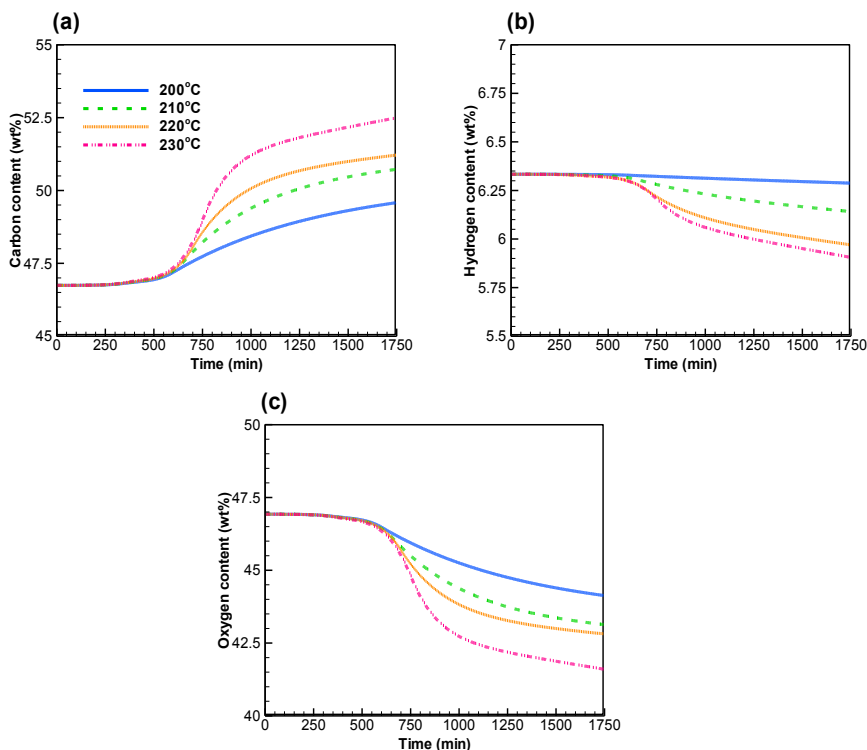
It is found that accurate fits between the simulated and experimental data are achieved in **Fig. 2**. As a result, kinetic parameters are in a reasonable range compared with the kinetic parameters for the degradation of xylan reported in the literature [12]. The pre-exponential factors and activation energies are:  $A_1=4.80 \times 10^8 \text{ s}^{-1}$ ,  $E_1=104.42 \text{ kJ mol}^{-1}$ ;  $A_{V1}=9.65 \times 10^9 \text{ s}^{-1}$ ,  $E_{V1}=125.10 \text{ kJ mol}^{-1}$ ;  $A_2=3.2 \times 10^6 \text{ s}^{-1}$ ,  $E_2=97.60 \text{ kJ mol}^{-1}$ ;  $A_{V2}=2.75 \times 10^7 \text{ s}^{-1}$ ,  $E_{V2}=111.57 \text{ kJ mol}^{-1}$ . It is found that reaction rates are higher during the degradation of the initial wood material (A) to form the intermediate (B), than those in the second step during the further decomposition of the intermediate to produce the final solid [13].

**Table 1.** Elemental analysis of raw and torrefied biomass.

Material	C (wt% <sup>a</sup> )	H (wt%)	N (wt%)	O (wt%) <sup>b</sup>
Raw (Poplar)	46.61	6.32	0.28	46.79
Wood torrefied at 200 °C	49.44	6.27	0.28	44.01
Wood torrefied at 210 °C	50.54	6.12	0.36	42.98
Wood torrefied at 220 °C	51.02	5.95	0.38	42.65
Wood torrefied at 230 °C	52.25	5.88	0.45	41.42

<sup>a</sup>: dry-ash-free; <sup>b</sup>:by difference.

According to the elemental analysis of torrefied wood (**Table 1**) and the torrefaction kinetics, the predicted elemental compositions of wood during torrefaction are obtained, as plotted in **Fig. 3**. The results point out that the C, H, and O profiles are in good agreement with expected composition changes in the wood materials after torrefaction (i.e. higher carbon, lower hydrogen and lower oxygen contents at stronger thermal intensity of treatment). When increasing the treatment temperature, the elemental compositions in treated wood tend to be changed more aggressively. At the temperature of 230 °C, the carbon content in treated poplar quickly increases and the oxygen content dramatically decreases. This result is attributed to the thermal cross-linking reactions that obviously occur at higher temperature [11,14]. Overall, the prediction of elemental composition of torrefied wood works well at any treatment temperature and time.



**Fig. 3.** Profiles of predicted (a) carbon, (b) hydrogen and (c) oxygen contents during torrefaction

The higher heating value (HHV) of torrefied wood is obtained from the predicted elemental composition by the empirical equation. The obtained HHV can be applied to evaluate the potential opportunity for solid fuel in the end of use. The HHVs of untreated and torrefied wood are calculated based on the correlation by Boie [10] presented in Eq. (3):

$$\text{HHV} = 0.3517\text{C} + 1.16249\text{H} + 0.10467\text{S} - 0.1195\text{O} + 0.0628\text{N} \quad (3)$$

where the C, H, O, and N are the mass percentages of carbon, hydrogen, oxygen, and nitrogen on a dry-ash free basis. The results are displayed in Fig. 4a. The HHV started to increase at the thermal homogenization stage, and it is owing to the removal of extractives and light volatile matters [11]. As a while, the HHVs of poplar tend to increase with increasing temperature, and they are in the range of 19.85–20.71 MJ kg<sup>-1</sup>. The increasing of HHV is mainly due to the changes of elemental composition in treated wood. Chen *et al.* [1] pointed out that carbon and hydrogen in a fuel are the major sources of heat released during the combustion. However, more hydrogen contained in a fuel is usually accompanied by a lower content of carbon. Oxygen contained in biomass is conducive to fuel burning, but it reduces the heating value of biomass. Based on the results of solid yields and HHVs, the energy yields can be determined [1], as expressed as:

$$\text{Energy yield}(\%) = \text{Solid yield}(\%) \times \frac{\text{HHV of torrefied biomass}}{\text{HHV of raw biomass}} \quad (4)$$

The results indicated that the energy yield is in the range of 92–98%, as shown in Fig. 4b. With these obtained results, it can be conducted with other informations, such as energy consumption and manufacturing cost, to optimize the biomass torrefaction process.

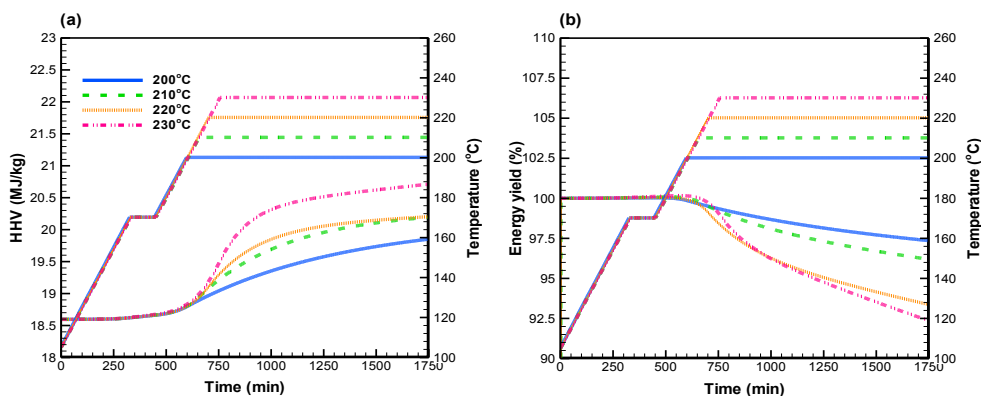


Fig. 4. Profiles of predicted (a) HHVs and (b) energy yields during torrefaction

#### 4. Conclusions

The prediction of higher heating values (HHVs) and energy yields of torrefied wood in a pilot-scale reactor have been investigated in this study. One common European wood species (poplar) and four different treatment temperatures (200, 210, 220 and 230 °C) have been employed. A two-step model was adopted to evaluate the torrefaction kinetics and a direct method was applied to predict the elemental composition. The results point out that the C, H, and O profiles are in good agreement with expected composition changes in the wood materials after torrefaction. The HHVs of treated wood are computed from the predicted elemental composition by an empirical equation. As a while, the HHVs of torrefied poplar tend to increase with increasing temperature, and they are in the

range of 19.85–20.71 MJ kg<sup>-1</sup>. Concerning the energy yield of treated wood, it is in the range of 92–98% which is close to the results of light torrefied biomass [1].

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