

1 **Highlights:**

2 • Torrefaction temperature and holding time significantly influence the combustion
3 reactivity and kinetics of woody biomass.

4 • The effect of torrefaction pressure is insignificant.

5 • Mass fraction and activation energy of hemicellulose are reduced by wet torrefaction.

6 • Activation energy of cellulose is increased by wet torrefaction.

7

8

1 **Abstract**

2 This work continues our assessment of wet torrefaction for energy applications, looking at effects
3 of the process parameters (temperature, holding time and pressure) on the reactivity and intrinsic
4 kinetics of wood under air combustion conditions. Woody materials, Norway spruce and birch,
5 were wet torrefied in various conditions (temperature: 175, 200, 225°C; holding time: 10, 30, 60
6 min; and pressure: 15.54, 70, 160 bar). The reactivity of the treated and untreated woods was
7 thermogravimetrically examined under a synthetic air environment (21% O₂ and 79% N₂ in
8 volume). A four-pseudo-component model with different reaction orders was adopted for kinetic
9 modelling and extracting the kinetic parameters. The results showed that when increasing either
10 torrefaction temperature or holding time, the torrefied woods behaved more char-like than the
11 raw fuels. However, pressure did not show significant effect on the reactivity. Relatively longer
12 char combustion stages and higher conversion rates (up to $0.5 \times 10^{-3} \text{ s}^{-1}$) were observed for the
13 woods after torrefaction. The activation energy was decreased for hemicellulose and char, but
14 increased for cellulose after torrefaction, whereas the trend for lignin is not clear. In addition, the
15 hemicellulose mass fraction decreased after torrefaction (from 0.15 to 0.05 for spruce and from
16 0.23 to 0.06 for birch). The amount of char in the torrefied woods increased gradually with
17 increasing torrefaction temperature or holding time (from 0.24 to 0.40 for spruce, and from 0.18
18 to 0.34 for birch).

19
20 **Keywords:** Wet torrefaction; wood reactivity; combustion kinetics; kinetic modelling; biofuel
21 pretreatment.

22

1 **1 Introduction**

2 Wet torrefaction (WT), which may be defined as treatment of biomass in hydrothermal media
3 (HM) or hot compressed water (HCW) at temperatures within 180-260°C [1-5], is a promising
4 method for production of high quality solid fuels from low cost wet biomass resources such as
5 forest residues, agricultural waste, aquatic energy crops, and sewage sludge. The concept of WT
6 is very similar to “hydrothermal carbonization” (HTC) [6-15] and sometimes is discussed under
7 the general term “hydrothermal conversion” [15-19] or “hydrothermal treatment” [20-25].
8 Although the terminologies of WT and HTC have sometimes been used interchangeably, there is
9 a significant difference between them. While WT aims at producing upgraded solid fuels for
10 energy applications only, HTC is employed mainly for producing charcoal, with much higher
11 carbon content, which can be used not only as fuel but also as activated carbon, soil enhancer,
12 fertilizer, etc. Clearly, energy efficiency of the process, fuel properties and combustion properties
13 of the product are more critical for WT than for HTC, and thus the earlier tends to be performed
14 at lower temperatures (180-260°C) than the latter (from 300°C).

15 Like dry torrefaction (DT), which may be defined as thermal treatment of biomass in an inert
16 environment at atmospheric pressure and temperatures within the range of 200-300°C [26-28],
17 WT results in the following main improvements in the fuel properties of biomass: (1) increased
18 heating value due to a reduction in the O/C ratio; (2) intrinsic transformation from hygroscopic
19 into hydrophobic nature of biomass; (3) better grindability coupling with less energy requirement
20 for size reduction of the fuel. After WT, the wet hydrophobic solid product can be effectively
21 made dry by mechanical and/or natural dewatering, which is an attractive option capable of
22 dramatically reducing the energy requirement for the post-drying step. In addition to the solid
23 fuel product, many valuable organic compounds including acetic acid, formic acid, lactic acid,

1 glycolic acid, levulinic acid, phenol, furfural, HMF, and sugars are found in the aqueous phase
2 products of WT, making up approximately 10 wt% of the feedstock [4, 6]. The potential use of
3 these water-soluble organic fractions for production of valuable products may contribute to
4 further improving the economy of the WT process.

5 Recently, an assessment of WT for energy applications (combustion, gasification, and pyrolysis)
6 in comparison with DT has been reported by our research group [1]. The assessment includes a
7 literature review of past studies relevant to WT, which will not be repeated in this present work.
8 A core theme of the assessment was to investigate the effects of process parameters including
9 pressure, reaction temperature, holding time, and feedstock particle size on the yield and fuel
10 properties of the solid product. For reaction temperature and holding time, positive trends of their
11 effects on the yield and fuel properties of the solid products were observed, which are similar to
12 those for DT. However, pressure and feedstock particle size only have minor effects. More
13 interestingly, the ash content of biomass fuel is significantly reduced by WT. This suggests that
14 WT can be employed to produce “cleaner” biomass solid fuels as well, with respect to inorganic
15 elements. In addition, a comparison between WT and DT supported by regression analyses and
16 numerical prediction showed that WT can produce solid fuel with greater heating value, higher
17 energy yield, and better hydrophobicity at much lower temperatures and holding times than DT
18 [1].

19 Despite various advantages of WT over DT, only a few studies on WT have been reported [1-5]
20 compared to a sharply increasing number of studies on DT during the last few years [26-34]. In
21 addition, most WT studies focused on the effects of process parameters on the yield and fuel
22 properties of the solid product. To our knowledge, no study of using solid fuel obtained from WT
23 for energy applications has been reported so far. Combustion is currently the most important

1 energy application of biomass solid fuel, considering its contribution to more than 90% of the
2 global bioenergy deployment [35-39]. It is therefore important and necessary to investigate into
3 the effects of WT on combustion reactivity and kinetics of biomass solid fuels.

4 Several studies on combustion of dry torrefied biomass have been reported [30, 40-43], which
5 would be beneficial for studying combustion behavior of wet torrefied biomass fuel. Pimchuai et
6 al. [40] and Bridgeman et al. [30], for example, studied the combustion of biochars obtained from
7 DT of different biomass materials. They found that the combustion of dry torrefied husks and
8 herbaceous biomass released more heat than that of the raw materials due to the higher fixed
9 carbon content of the biochars. However, no kinetic data was reported from these studies. Arias
10 et al. [41] applied a simple first-order kinetic model to estimate the activation energy and pre-
11 exponential factor of raw and dry-torrefied eucalyptus samples in a two-stage combustion process
12 (devolatilization followed by combustion). The results showed that both kinetics parameters (the
13 activation energy and pre-exponential factor) increased in stage 1 and decreased in stage 2 after
14 DT. Nevertheless, the model was based on an empirical method which was not validated because
15 the model itself could not either reproduce simulated curves or give any information about the fit
16 quality between the predicted and experimental data. Recently, studies on the combustion
17 kinetics of dry torrefied woody biomass materials using multi pseudo-component models have
18 been reported by Broström et al. [42] and Tapasvi et al. [43]. The former employed a global
19 kinetic model and the latter employed a distributed activation energy model (DAEM). The results
20 from the two approaches showed that DT had little effect on the kinetic parameters of the
21 torrefied biomass regardless of the treatment conditions. Broström et al. [42] reported that the
22 activation energy values of hemicellulose, cellulose and lignin were constant at 100.6, 213.1, and
23 121.3 kJ/mol, respectively for both raw and dry-torrefied spruce. Tapasvi et al. [43] found that

1 the activation energy values for cellulose, non-cellulosic part and char remained at 135, 160 and
2 153 kJ/mol, respectively for different types of feedstock and DT conditions.

3 This present study is a follow-up of our first assessment of WT for energy applications [1],
4 which has been published as mentioned earlier. The objective of the present work was to assess
5 the effects of WT conditions (temperature, holding time and pressure) on the combustion
6 reactivity and kinetics of biomass solid fuels. Thermogravimetric analysis (TGA) was employed
7 for this work as it is a proven method for studying devolatilization and combustion of biomass in
8 the kinetic regime [44, 45].

9 **2 Materials and methods**

10 **2.1 Materials**

11 As mentioned in the introduction, the present work is a follow-up of our first report on
12 comparative assessment of WT for energy applications. The biomass materials used for this work
13 were obtained from the previous work, in which the full details about materials and experimental
14 methods were presented and can be found elsewhere [1]. For a convenience, a brief extraction is
15 imported in this present work.

16 Stem wood from Norway spruce (softwood) and birch (hardwood) were selected as feedstock for
17 the study since they are the main wood species in Norwegian forests. The samples were cut into 1
18 cm cubes for WT in hot compressed water, using a 250 ml Parr reactor series 4650 (Parr
19 Instrument, USA) at different temperatures (175, 200, 225°C), pressures (15.54, 70, 160 bar) and
20 holding times (10, 30, 60 min). The corresponding vapour pressures of water at 175, 200, and
21 225°C are 8.93, 15.54, and 25.50 bar, respectively. However, in order to keep more water in the
22 liquid phase, the pressure of 70 bar was used for all of the WT experiments, except for the

1 investigation of the pressure effect at 200°C [1]. For this investigation, the pressures of 15.54, 70
2 and 160 bar were employed. Distilled water was used as the reaction media. The ratio of dry
3 feedstock over water was 1:5 by weight.

4 After WT, the wet solid products were dried at 105°C for 48h and then stored in a desiccator for
5 further analyses. The proximate and ultimate analyses of the samples used for this work are
6 presented in Table 1. The proximate analyses were performed according to ASTM standards:
7 ASTM D4442-07, ASTM E872 and ASTM D1102 for moisture content, volatile matter and ash
8 content, respectively. The ultimate analyses were determined (on a dry basis) by means of an
9 “EA 1108 CHNS-O” elemental analyzer (Carlo Erba Instruments). The higher heating values
10 (HHVs) were calculated on dry and ash free basis, according to Channiwala and Parikh. [46].

11 **2.2 Thermogravimetric analysis method and procedure**

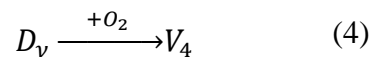
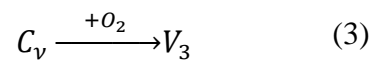
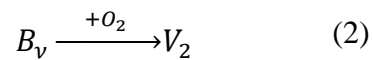
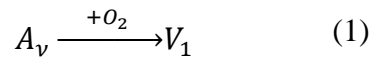
12 A thermogravimetric analyzer (Mettler Toledo TGA/SDTA851e) was employed for this study.
13 The biomass solid fuels were first ground using an IKA MF 10 cutting mill. Then the particles
14 passing through a 125 µm sieve (Fritsch Analysette 3 Pro) were collected for the kinetic study to
15 ensure the experiments to be in the chemical reaction kinetic regime [47, 48]. For each TGA run,
16 an amount of about 0.5 mg sample was spread in a 150 µl alumina pan located inside the TGA
17 reactor. It is worth noting that the buoyancy effect plays a significant role for such a small sample
18 weight. Therefore, it is mandatory to run a blank TGA (mass loss versus temperature) curve first.
19 The weight change of the blank experiment was subtracted from the experimental curves
20 automatically. The experiment started from room temperature, the fuel sample was heated to
21 105°C and held at this temperature for 1h for drying. Thereafter, the sample was heated to 700°C
22 at a constant heating rate of 10 °C/min. A synthetic air flow rate of 80 ml/min was applied for all

1 experiments. Moreover, three repetitions were run for each fuel sample, and the average kinetic
2 values are reported.

3 **2.3 Kinetic model selection**

4 Branca and Di Blasi [49] proposed and examined two different models to describe the
5 combustion of biomass fuel. They are series- and parallel-reaction models, of which each model
6 consists of four reactions (3 reactions for the devolatilization of the three main components of
7 lignocellulosic biomass, and 1 reaction for the char burn-off). It was concluded that both models
8 gave similar results for the estimated kinetic parameters. However, the parallel-reaction
9 mechanism, or the pseudo-component model, is favorable and widely used [42, 50, 51] because it
10 can describe the possible overlapped reactions of the lumped components in biomass. According
11 to this model, the biomass sample is regarded as a sum of four pseudo-components, and the
12 activation energies were assumed to be constant during the reactions to simplify the simulation
13 process.

14 For the present study, the parallel-reaction model proposed by Branca and Di Blasi [49] was
15 adopted. The four parallel reactions applied for the model are as follows:



16 where A_v , B_v , C_v and D_v are the pseudo-components; and V_i ($i = 1, 2, 3, 4$) is the lumped volatiles
17 and/or gases released from the thermal degradation of the respective pseudo-component. The

1 three first reactions (Eq. 1-3) are associated with the devolatilization of the three main
 2 components of biomass including hemicellulose, cellulose and lignin, respectively. The rates of
 3 these reactions can be presented by the general power law (n -order) expression, although $n = 1$ is
 4 usually used [42, 49, 51, 52]. The last reaction (Eq. 4) represents the char combustion, for which
 5 the rate law is generally related the partial pressure of oxygen through an empirical exponent and
 6 the char porosity. Due to a relatively small amount of the sample tested in an air flow, it is
 7 reasonable to assume that the oxygen mass fraction remains constant during the reaction process.
 8 Consequently, the general power law (n -order) expression can also be applied to represent the
 9 char combustion. Overall, the conversion rate of these four reactions can be described by the
 10 following Arrhenius expression:

$$\frac{d\alpha_i}{dt} = A_i \exp\left(-\frac{E_i}{RT}\right) (1 - \alpha_i)^{n_i}, \quad i = 1, \dots, 4 \quad (5)$$

11 where A is the pre-exponential factor, E is the activation energy of the reaction, R is the universal
 12 gas constant, T is the absolute temperature, n is the reaction order, and i is for the i^{th} pseudo-
 13 component. The conversion degree (α) is defined as the mass fraction of decomposed solid or
 14 released volatiles:

$$\alpha = \frac{m_0 - m}{m_0 - m_f} = \frac{v}{v_f} \quad (6)$$

15 where m_0 and m_f are the initial and final masses of solid, m is the mass of solid at any time; v_f is
 16 the total mass of released volatiles and v is the mass of released volatiles at any time.

17 The overall conversion rate is the sum of the partial conversions, where c_i indicates the mass
 18 fraction of each pseudo-component in the following equation:

$$\frac{d\alpha}{dt} = \sum_{i=1}^4 c_i \frac{d\alpha_i}{dt} \quad (7)$$

1 2.4 Numerical method

2 Data collected from the TGA experiments was differentiated to obtain the DTG data, and
 3 presented in the form of conversion (mass loss) rate $\left(\frac{d\alpha}{dt}\right)$ versus temperature T . A mathematical
 4 model corresponding to the selected model was then employed for simulation and comparison
 5 with the experimental DTG data. The optimization of the predicted DTG curves was based on the
 6 non-linear least squares method, which minimized the sum of the square differences between the
 7 experimental and calculated data. The objective function is given in Eq. 8:

$$S = \sum_{j=1}^N \left[\left(\frac{d\alpha_j}{dt} \right)_{exp} - \left(\frac{d\alpha_j}{dt} \right)_{cal} \right]^2 \quad (8)$$

8 where $\left(\frac{d\alpha_j}{dt}\right)_{exp}$ and $\left(\frac{d\alpha_j}{dt}\right)_{cal}$ represent the experimental and calculated conversion rates,
 9 respectively; and N is the number of experimental points.

10 In order to validate the optimization or the curve fitting process in other words, the fit quality
 11 between actual and modelled data is calculated according to Eq. 9 [49, 53]:

$$Fit (\%) = \left(1 - \frac{\sqrt{\frac{S}{N}}}{\left[\left(\frac{d\alpha_j}{dt} \right)_{exp} \right]_{max}} \right) \cdot 100\% \quad (9)$$

12 The actual simulation was run until the maximum fit value was found, at which the convergence
 13 criteria of the optimization process are achieved. The extracted kinetic parameters are: the
 14 activation energies ($E_1 - E_4$), the pre-exponential factors ($A_1 - A_4$), the mass fractions ($c_1 - c_4$),

1 and the reaction orders ($n_1 - n_4$) for each pseudo-component. Totally, there are 12 kinetic
2 parameters for the 1st order model and 16 parameters for the n^{th} order model.

3 **3 Results and discussions**

4 **3.1 Thermogravimetric analysis of spruce and birch wood in air**

5 Figure 1 shows the TGA and DTG curves, representing the thermal behavior of the raw spruce
6 and birch woods in the temperature range of 100-600°C. The standard deviation of the
7 conversion rate data for the tested samples was $1.38 \times 10^{-5} \text{ s}^{-1}$. For both types of feedstock, the
8 decomposition starts at around 180°C with a low conversion rate. Then the decomposition rate
9 increases rapidly from around 250°C to the devolatilization peaks ($\approx 2.3 \times 10^{-3} \text{ s}^{-1}$) at 321-324°C,
10 from which the rate decreases quickly, down to $0.30 \times 10^{-3} \text{ s}^{-1}$ for the spruce wood and $0.25 \times 10^{-3} \text{ s}^{-1}$
11 for the birch wood at around 350°C. This marks the end of the devolatilization and the
12 beginning of the char combustion, which has much lower rates than the devolatilization. In
13 addition, a clear shoulder in the devolatilization stage is observed for the raw birch wood, but not
14 for the raw spruce. This is because the hemicelluloses content of birch (hardwood) is normally
15 higher than that of spruce (softwood) [54]. Also, hemicellulose of hardwood usually contains
16 more xylan than softwood, which is the most reactive compound in the temperature range of the
17 devolatilization (200-350°C) [54].

18 In the char combustion stage, the birch wood char exhibits lower reactivity than that of spruce
19 wood char. The char combustion rate peak is only $0.38 \times 10^{-3} \text{ s}^{-1}$ for the birch, but $0.53 \times 10^{-3} \text{ s}^{-1}$ for
20 the spruce.

1 **3.2 Effects of torrefaction conditions on reactivity of wood in air combustion**

2 **3.2.1 The effect of torrefaction temperature**

3 The woods torrefied at three different temperatures (175, 200, and 225°C), in the common
4 conditions of 30 min as holding time and 70 bar as pressure were used for this test. The test
5 results are presented in Figure 2, which includes the data collected for the raw woods for
6 comparison. Figure 2A is for the spruce wood and Figure 2B for the birch wood. As can be seen,
7 the torrefied woods start decomposing at temperatures around 150°C, somehow lower than those
8 for the raw woods (around 180°C). However, the conversion rates in this early stage are very
9 low, approximately being less than $0.2 \times 10^{-3} \text{ s}^{-1}$ in all cases. A slightly higher reactivity of the
10 torrefied woods than their origins in the early decomposition stage may be due to the higher
11 reactivity of a small amount of remaining organic compounds, with low molecular weights,
12 produced from the degradation of hemicellulose during the WT processes [55, 56]. **Most of these**
13 **organic compounds were washed out and collected in the water-soluble product portion, but some**
14 **of them may have been trapped in the pores and/or adsorbed on the surface of the torrefied**
15 **biomass.** At temperatures from 250°C up to 310°C, the torrefied woods become less reactive than
16 their origins. This is probably due to the degradation of hemicellulose in the raw woods as
17 discussed earlier in section 3.1, considering that torrefied woods contain less or no hemicellulose
18 compared to their origins. At temperatures above 310°C, the devolatilization peaks, mainly
19 contributed by cellulose decomposition [57, 58], are established. The peaks for the woods
20 torrefied at 175°C and 200°C are higher than those for the raw woods, but occur at the same
21 location (around 321-324°C). In addition, the peaks for the woods torrefied at 200°C are higher
22 than those for the woods torrefied at 175°C. However, the peaks for the woods torrefied at 225°C
23 are the lowest and the peak locations slightly shifted to the left, at around 317°C.

1 At temperatures above 350°C, where the char formed from the devolatilization stage starts
2 combusting, the situation is reversed. The char combustion stage of the torrefied woods starts at
3 temperatures somehow lower than the raw woods, with the combustion peaks clearly shift to the
4 right. The woods torrefied at 225°C (the highest one among the temperatures employed for the
5 WT) exhibit the highest reactivity with the highest combustion rate peaks ($0.50 \times 10^{-3} \text{ s}^{-1}$) and the
6 longest DTG tails (last until 550°C) compared with the others. This is probably due to the highest
7 fixed carbon content of the woods torrefied at 225°C (Table 1). However, the combustion peaks
8 of the woods torrefied at 175°C and 200°C are lower than that of the raw woods. Nevertheless,
9 the combustion stages of the woods torrefied at 175°C and 200°C last longer than those of the
10 raw woods. This inconsistent trend, together with the inconsistency observed for the
11 devolatilization peaks, makes it hard to identify a general trend for the effect of WT temperature
12 on the reactivity of wood in air combustion, and therefore no firm conclusion on this can be
13 drawn at this stage. Nevertheless, it is suspected that severer WT conditions would cause higher
14 devolatilization peaks. However, when the WT severity factor is too high, such as at WT
15 temperatures of 225°C, cellulose starts to decompose (about 10% at 225°C for 30 min [2, 56]).
16 Consequently, the devolatilization peak heights of the DTG curves for the woods torrefied in
17 these conditions are lower than the others, even those of their origins.

18 3.2.2 *The effect of torrefaction time*

19 Figure 3 presents the effect of holding time (10, 30, and 60 min) during WT on the combustion
20 behavior for the woods torrefied at 200°C and 70 bar as the common conditions. Figure 3A is for
21 the spruce wood and Figure 3B for the birch wood. The figures indicate that increases in WT
22 holding time make the woods less reactive at TGA temperatures below 300°C and more reactive
23 during the char combustion stage. Again, similar explanations based on the role of the

1 hemicellulose and fixed carbon content of the tested samples can be applied for these observed
2 trends. In addition, inconsistencies in the devolatilization peak heights, which are similar to those
3 for the effect of torrefaction temperature, were also observed.

4 3.2.3 *The effect of torrefaction pressure*

5 Figure 4 presents DTG curves for the combustion of the spruce wood torrefied at various
6 pressures: 15.54 (the vapour pressure of water at 200°C), 70 and 160 bar, in the common
7 conditions of 200°C and 10 min. Changes in the conversion rate were observed to be within 7.11-
8 $14.35 \times 10^{-5} \text{ s}^{-1}$. These indicate that the effect of WT pressure on the reactivity of the woods was
9 insignificant. Increasing pressure made the wood slightly less reactive during the devolatilization,
10 but somewhat more reactive in the char combustion stage, considering the peaks height.
11 However, the peaks locations were almost at the same temperatures.

12 3.3 *Kinetic analysis*

13 A kinetic analysis employing the 4-pseudo-component model with different reaction orders ($n =$
14 1 and $n \neq 1$) was performed for a quantitative evaluation of the effects of WT on the combustion
15 reactivity of wood. Because the effect of pressure during WT on the reactivity of wood in air
16 combustion is not significant, only the wood samples torrefied at a constant pressure of 70 bar (at
17 different temperatures and with different holding times) were selected for the kinetic analysis.
18 The selection of this pressure was based on the recommendation discussed in our previous study
19 [1]. In total, 12 experimental data sets were analyzed kinetically, of which 6 were for the spruce
20 wood and 6 for the birch wood. The kinetic data extracted from this analysis are presented in
21 Table 2 and Table 3 for the spruce and birch, respectively. The quality of the fit between the
22 experimental and predicted data is also included in the tables. In addition, for a graphical
23 demonstration of the fit quality, curves fittings for the raw woods and the woods torrefied at

1 200°C for 30 min (at 70 bar) are presented in Figure 5 and Figure 6, respectively. In these
2 figures, the actual conversion rates from the experiments are presented by the black dotted
3 curves. The red solid curves denote the predicted rates. The other four curves are presenting the
4 conversion rates of the three main components of wood (hemicellulose, cellulose, and lignin) and
5 the char formed from the devolatilization step. The figures show good fits between the
6 experimental and modelled results. The fit quality numerically presented in Table 2 and Table 3
7 is within 98-99% in all cases.

8 Table 2 and Table 3 show that the modelling with different reaction orders generated quite
9 similar kinetic data. The data of the activation energy and pre-exponential factor are comparable
10 with those reported in the literature [45, 49, 53, 59, 60]. In addition, most of the calculated n
11 values are close to 1. However, the n^{th} order model still exhibits somehow better fit and gives
12 more information about the reaction order. Therefore, the kinetic data obtained from the n^{th} order
13 model are chosen for further assessments hereafter.

14 It can be seen that, while there is no clear trend for the effect of WT on the pre-exponential
15 factor, the activation energy of hemicellulose is reduced dramatically by WT, e.g. decreases from
16 103.76 to 44.82 kJ/mol and from 144.68 to 41.29 kJ/mol for the spruce and birch, respectively,
17 by WT at 225°C (and 70 bar) for 30 min. This effect can also be observed from the hemicellulose
18 curves in Figure 5 and Figure 6, which show clearly that WT caused a shift of the hemicellulose
19 curves to a lower temperature range. This is in agreement with the literature [61] and can be
20 explained by that during WT the hemicellulose component of the wood was decomposed and
21 cracked into smaller molecules such as polysaccharides [55, 56], which remained in the solid
22 products.

1 However, the effect trend of WT on the activation energy of lignin is not clear. Similar
2 observations were described by Biwas et al. [61], which reported that the thermal reactivity of
3 woody lignin may either increase or decrease due to hydrothermal pretreatment, depending on the
4 severity of the pretreatment conditions which may result in condensation and re-polymerization
5 reactions.

6 In contrast to hemicellulose, the activation energy of cellulose is increased by WT. This is
7 presumably due to the increased crystallinity of cellulose caused by hydrothermal treatment [62-
8 64]. It is because that during thermal degradation, crystalline cellulose was reported to have much
9 higher activation energy than non-crystalline cellulose due to the increased cross linking [65].

10 Similar to hemicellulose, the activation energy of char combustion is decreased by WT (from
11 183.09 kJ/mol for the raw spruce to 109.38 kJ/mol for spruce torrefied at 225°C and 30 min;
12 from 222.00 kJ/mol for raw birch to 132.26 kJ/mol for birch torrefied at 225°C for 30 min). This
13 is presumably due to the changes in ash content of the woods after WT since it was reported in
14 the literatures [66-69] that the ash content and ash composition of char from biomass would both
15 enhance or inhibit the char reactivity. It is because both mass transfer limitations and catalytic
16 effects of the ash.

17 The mass fraction of hemicellulose is reduced by WT. In addition, the reduction is decreased
18 gradually with increasing WT severity, from 0.15 for the raw spruce to 0.05 for the spruce
19 torrefied at 225°C and 30 min; and from 0.23 for the raw birch to 0.06 for the birch torrefied at
20 225°C and 30 min. From the conditions of 200°C and 30 min to more severe conditions (higher
21 temperatures or longer holding times), the hemicellulose mass fraction of the torrefied fuel is
22 small, less than 10% of the total mass. With the reduction of hemicellulose fraction, the mass

1 fraction of the other component fractions in the torrefied biomass fuels (cellulose, lignin, and
2 char) are relatively increased compared with the raw materials, as presented in Table 2 and Table
3 3.

4 The mass fraction of cellulose in the torrefied fuels from both feedstocks increased to a maximum
5 value, 0.47 and 0.56 for spruce and birch torrefied at 200°C and 30 min, and then decreased with
6 either increasing temperature or holding time. The contribution of cellulose fractions is in good
7 agreement with the heights of the devolatilization peaks shown in Figure 2 and Figure 3. The
8 higher cellulose fraction, the higher devolatilization peak is observed. This helps confirm the
9 suspicion and explain the inconsistent trend in the effects of WT temperature or holding time on
10 the devolatilization peaks height as observed and discussed earlier in this paper.

11 The mass fraction of lignin varies in a narrow range (0.17-0.23 for torrefied spruce and 0.15-0.25
12 for torrefied birch) because the hydrothermal media within the WT conditions has little effects on
13 the overall degradation of lignin [22]. On the other hand, the mass fraction of char is increased
14 gradually (from 0.20 and 0.14 for raw spruce and birch to 0.40 and 0.34 for spruce and birch
15 torrefied at 225°C and 30 min, respectively) with torrefaction temperature and holding time.

16 **4 Conclusions**

17 The effects of WT on the reactivity and kinetics of woods under air combustion conditions were
18 investigated using thermogravimetric method and kinetic modelling. Two types of woody
19 biomass, Norway spruce and birch woods were used as feedstock. The following conclusions can
20 be drawn from this study:

- 21 - WT pressure had insignificant effects on the combustion reactivity of the woods.

1 - WT temperature and holding time had similar effects on the combustion reactivity of the
2 woods. Increasing either temperature or holding time make the woods more reactive in
3 the devolatilization stage, but less reactive in the char combustion stage. However, too
4 severe WT conditions (from 225°C and 30 min) made the trends reversed due to the
5 decomposition of cellulose in the devolatilization stage and the competition between
6 catalyzing and inhibiting effects of char ash on the char combustion stage.

7 In addition, the kinetic analysis using the four-pseudo-component model with $n \neq 1$ showed that
8 the activation energy of hemicellulose and char was reduced, but that of cellulose was increased
9 by WT. The activation energy of hemicellulose was reduced from 103.8 to 44.8 kJ/mol for the
10 spruce wood, and from 144.7 to 41.3 kJ/mol for the birch wood. That of char was from 183.1 to
11 109.4 kJ/mol for the spruce and from 222.0 to 132.3 kJ/mol for the birch. The activation energy
12 of the cellulose was increased from 221.5 to 239.0 kJ/mol for the spruce, and from 204.7 to 236.7
13 kJ/mol for the birch. The mass fraction of hemicellulose was reduced by WT (from 0.15 to 0.05
14 for the spruce and from 0.23 to 0.06 for the birch), but that for char was increased gradually (0.20
15 to 0.40 for spruce and 0.14 to 0.34 for birch).

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9

10

1 Table 1. Proximate and ultimate analyses of raw and wet torrefied fuels (dry and ash free)

Sample		Solid yield ^a	Proximate analysis			Ultimate analysis					HHV ^b
			Ash ^a	VM ^a	FC ^a	C ^a	H ^a	N ^a	O ^a	S ^a	
Spruce	Raw	–	0.23	86.50	13.27	50.31	6.24	0.07	43.38	< 0.02	20.42
	175°C, 30min	88.27	0.11	85.72	14.17	51.34	6.18	0.07	42.42	< 0.02	20.81
	200°C, 10min	82.48	0.14	84.64	15.22	51.21	6.39	0.06	42.35	< 0.02	21.02
	200°C, 30min	78.45	0.12	83.92	15.95	52.55	6.15	0.06	41.23	< 0.02	21.33
	200°C, 60min	73.28	0.09	81.87	18.03	53.69	5.89	0.06	40.36	< 0.02	21.51
	225°C, 30min	69.74	0.14	74.74	25.12	56.99	5.87	0.07	37.07	< 0.02	22.97
Birch	Raw	–	0.28	89.46	10.26	48.94	6.35	0.11	44.60	< 0.02	19.94
	175°C, 30min	79.53	0.09	88.57	11.34	49.42	6.38	0.12	44.07	< 0.02	20.21
	200°C, 10min	66.42	0.08	87.97	11.94	49.61	6.16	0.13	44.10	< 0.02	20.01
	200°C, 30min	64.64	0.09	85.15	14.76	51.25	6.18	0.11	42.46	< 0.02	20.78
	200°C, 60min	63.06	0.10	82.64	17.27	51.34	5.94	0.13	42.59	< 0.02	20.51
	225°C, 30min	58.01	0.13	73.78	26.09	56.92	5.86	0.09	37.13	< 0.02	22.93

VM: volatile matter, FC: fixed carbon, HHV: higher heating value

^a wt%, ^b MJ/kg

2

1 Table 2. Combustion kinetic data for spruce fuels

Torrefaction condition		First order reactions				n th order reactions				
		E (kJ/mol)	A (s ⁻¹)	c	Fit (%)	E (kJ/mol)	A (s ⁻¹)	c	n	Fit (%)
Raw	H	103.80	3.70E+07	0.14	99.27	103.76	3.89E+07	0.15	1.01	99.28
	C	221.58	2.43E+17	0.42		221.53	2.46E+17	0.44	1.06	
	L	66.17	1.33E+03	0.23		68.40	1.80E+03	0.21	1.01	
	Char	178.49	5.90E+10	0.21		183.09	1.27E+11	0.20	1.01	
175°C, 30min	H	66.23	1.47E+03	0.12	98.90	66.97	1.47E+03	0.12	1.01	98.90
	C	241.17	1.31E+19	0.40		241.13	1.32E+19	0.41	1.03	
	L	40.60	1.39E+01	0.23		40.27	1.40E+01	0.23	1.01	
	Char	132.50	1.58E+07	0.24		132.58	1.58E+07	0.24	1.01	
200°C, 10min	H	47.11	2.32E+02	0.12	98.92	47.41	2.35E+02	0.13	1.01	98.96
	C	239.33	9.59E+18	0.44		239.46	1.00E+19	0.45	1.06	
	L	66.55	1.48E+03	0.21		67.12	1.47E+03	0.18	1.01	
	Char	135.34	2.49E+07	0.24		135.50	2.53E+07	0.24	1.01	
200°C, 30min	H	43.98	1.54E+02	0.09	98.69	46.75	2.27E+02	0.11	1.01	98.93
	C	243.41	2.21E+19	0.43		259.18	5.93E+20	0.47	1.20	
	L	71.70	3.35E+03	0.21		82.85	2.20E+04	0.17	1.04	
	Char	131.32	9.46E+06	0.26		142.27	5.78E+07	0.25	1.04	
200°C, 60min	H	43.32	1.63E+02	0.04	98.49	43.93	1.63E+02	0.05	1.01	98.61
	C	247.46	6.34E+19	0.43		247.27	6.34E+19	0.46	1.12	
	L	71.32	3.05E+03	0.22		72.45	3.05E+03	0.19	1.01	
	Char	111.63	2.77E+05	0.31		111.77	2.77E+05	0.30	1.01	
225°C, 30min	H	44.03	2.90E+02	0.04	98.32	44.82	2.89E+02	0.05	1.01	98.41
	C	238.92	1.44E+19	0.30		238.97	1.54E+19	0.33	1.18	
	L	67.72	1.60E+03	0.25		68.78	1.62E+03	0.21	1.01	
	Char	109.03	1.94E+05	0.41		109.38	2.01E+05	0.40	1.01	

H: hemicellulose, C: cellulose, L: lignin

2

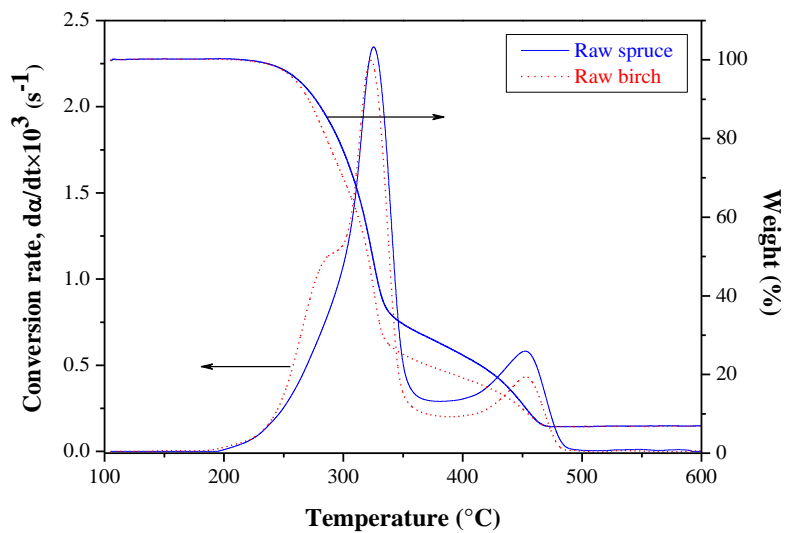
1 Table 3. Combustion kinetic data for birch fuels

Torrefaction condition		First order reactions				n th order reactions				
		E (kJ/mol)	A (s ⁻¹)	c	Fit (%)	E (kJ/mol)	A (s ⁻¹)	c	n	Fit (%)
Raw	H	138.17	1.14E+11	0.22	98.79	144.68	4.69E+11	0.23	1.01	98.98
	C	194.25	1.13E+15	0.50		204.71	9.71E+15	0.48	1.01	
	L	83.96	2.71E+04	0.14		83.51	2.77E+04	0.16	1.06	
	Char	221.99	8.74E+13	0.14		222.00	8.87E+13	0.14	1.04	
175°C, 30min	H	58.34	2.66E+03	0.17	98.59	64.69	1.12E+04	0.18	1.01	98.76
	C	246.38	4.84E+19	0.44		263.00	1.54E+21	0.46	1.16	
	L	65.14	1.20E+03	0.20		65.80	1.20E+03	0.18	1.08	
	Char	127.47	5.48E+06	0.19		127.71	5.51E+06	0.18	1.01	
200°C, 10min	H	49.02	4.61E+02	0.13	98.49	48.99	4.60E+02	0.13	1.01	98.55
	C	254.86	2.43E+20	0.46		254.85	2.43E+20	0.46	1.04	
	L	61.56	4.42E+02	0.23		68.70	2.13E+03	0.23	1.28	
	Char	152.51	2.77E+08	0.18		150.04	1.81E+08	0.18	1.01	
200°C, 30min	H	50.30	8.01E+02	0.06	98.31	52.71	1.25E+03	0.07	1.01	99.11
	C	267.74	3.85E+21	0.52		263.29	1.62E+21	0.56	1.14	
	L	80.54	2.24E+04	0.19		82.31	2.08E+04	0.15	1.03	
	Char	118.13	8.26E+05	0.23		123.53	1.93E+06	0.22	1.01	
200°C, 60min	H	50.31	1.21E+03	0.05	98.24	50.78	1.19E+03	0.05	1.02	98.42
	C	235.27	6.95E+18	0.33		237.06	1.04E+19	0.35	1.14	
	L	79.94	2.03E+04	0.22		81.18	2.30E+04	0.20	1.10	
	Char	104.16	9.15E+04	0.41		104.91	1.02E+05	0.40	1.01	
225°C, 30min	H	40.88	1.33E+02	0.06	98.22	41.29	1.26E+02	0.06	1.01	98.48
	C	231.51	2.66E+18	0.32		236.66	8.13E+18	0.34	1.18	
	L	67.79	1.39E+03	0.27		71.58	2.56E+03	0.25	1.08	
	Char	129.38	4.98E+06	0.36		132.26	7.80E+06	0.34	1.01	

H: hemicellulose, C: cellulose, L: lignin

2

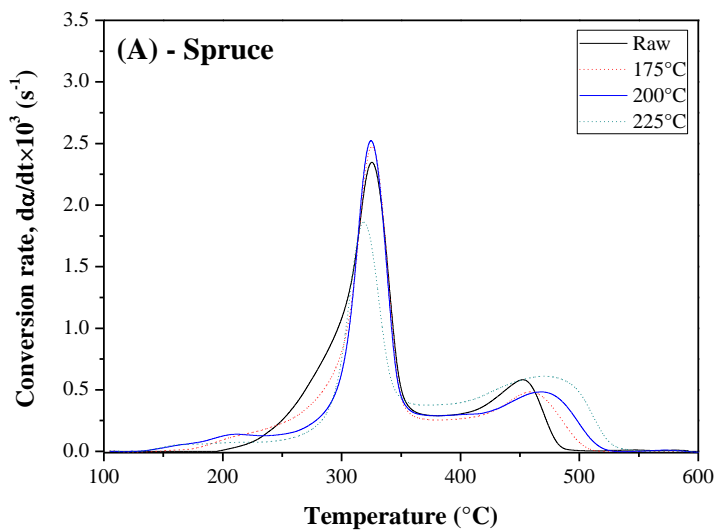
1 Figure 1. TGA and DTG curves in air for raw spruce and birch woods



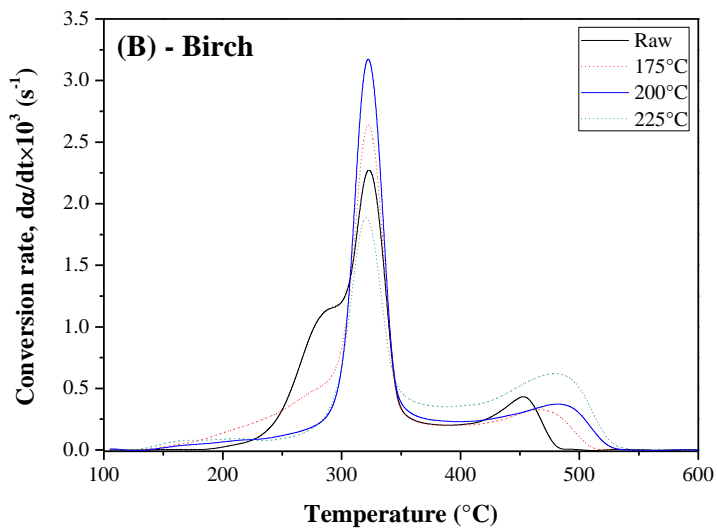
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1 Figure 2. DTG analyses in air for spruce (A) and birch (B) woods torrefied at 70 bar for 30 min

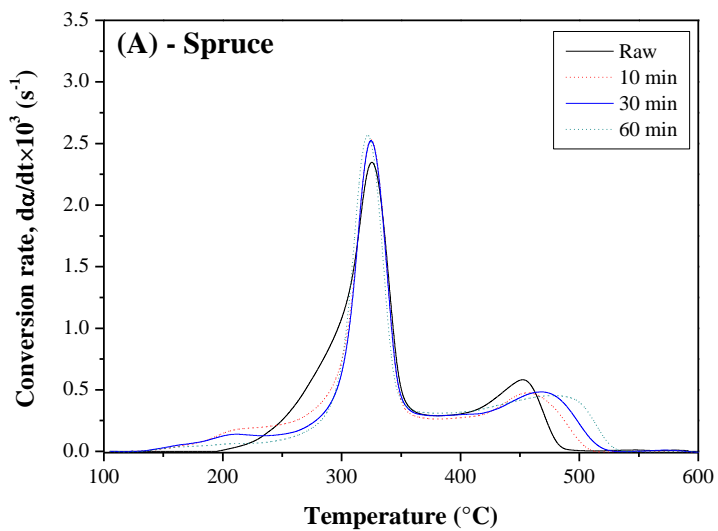


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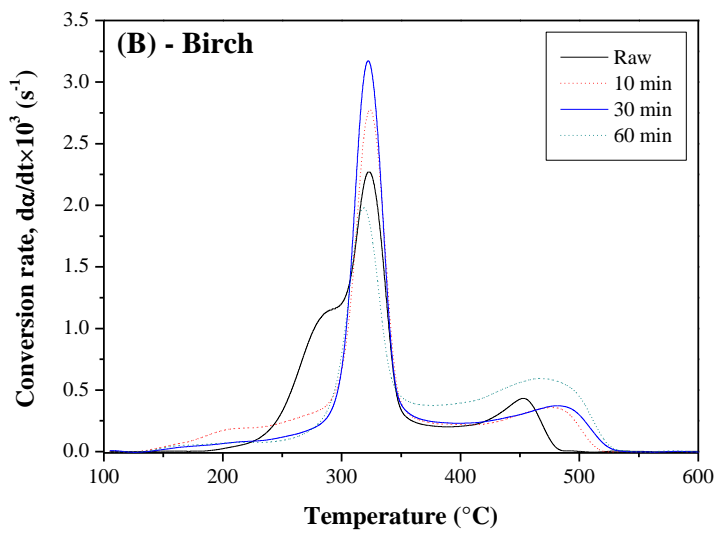


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1 Figure 3. DTG analyses in air for spruce (A) and birch (B) torrefied at 200°C and 70 bar



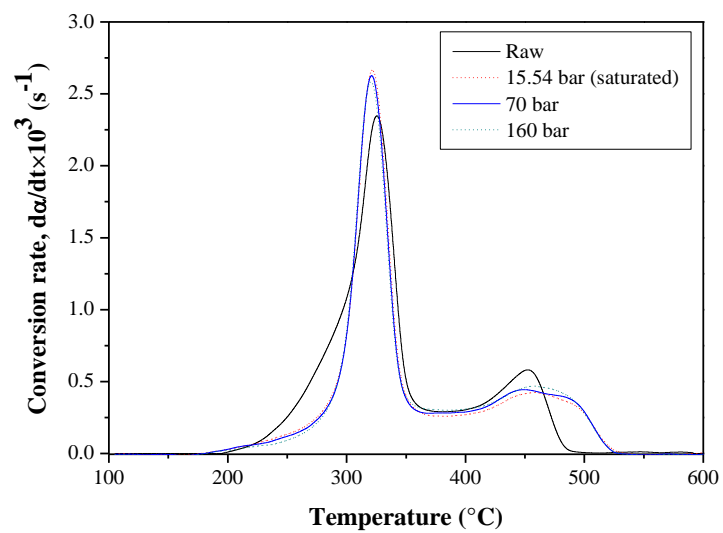
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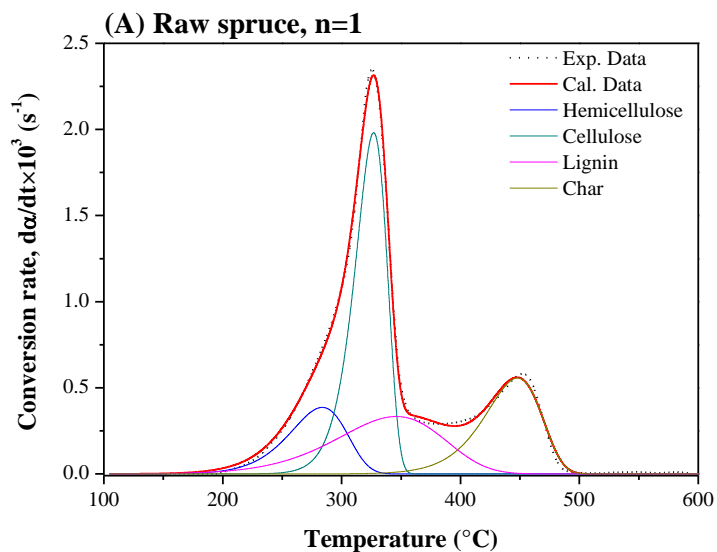
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- 1 Figure 4. DTG curves in air for spruce torrefied in the condition of 200°C, 10 minutes at different
- 2 pressures

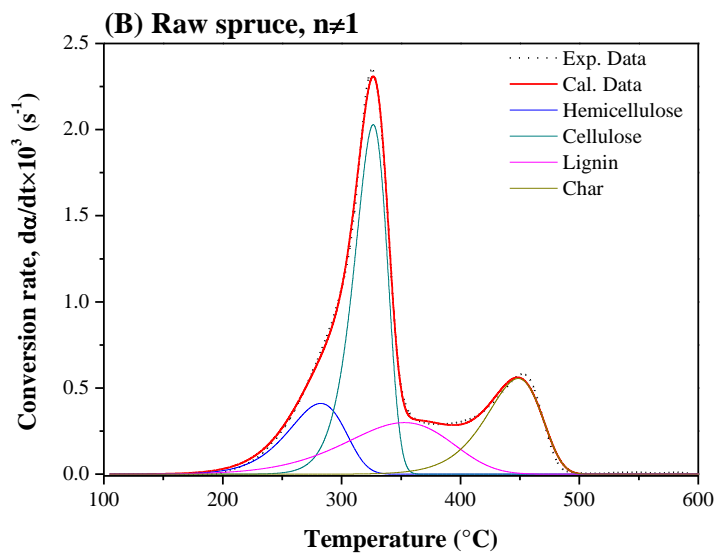


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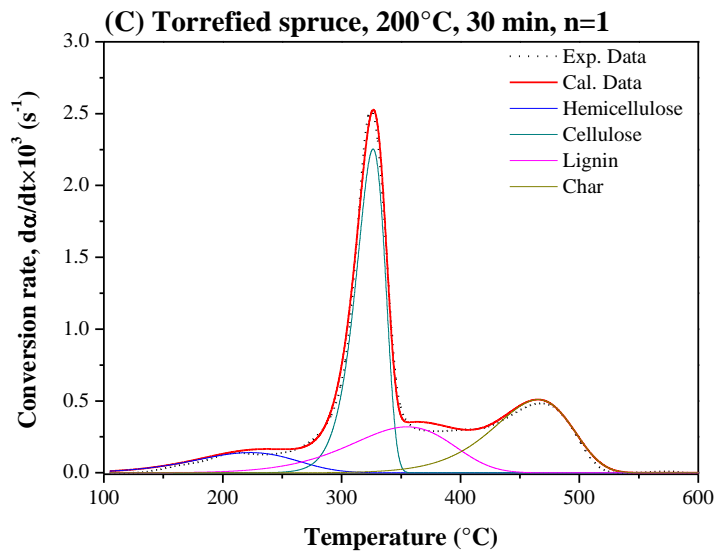
1 Figure 5. Curve fitting for raw and torrefied spruce fuels



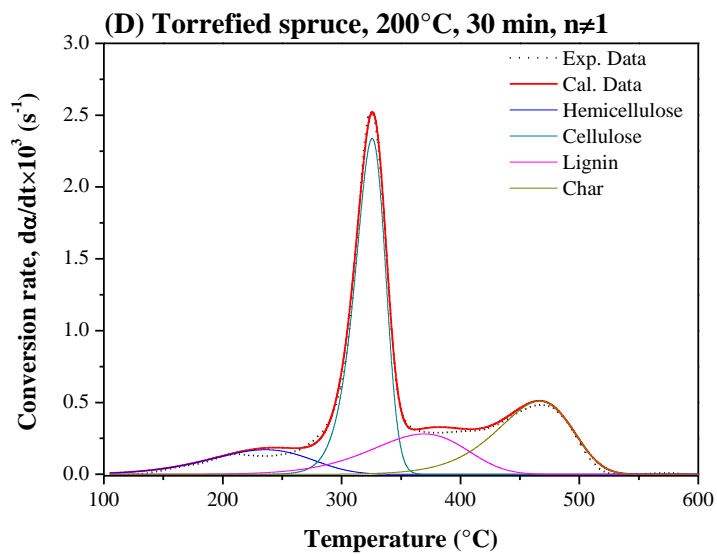
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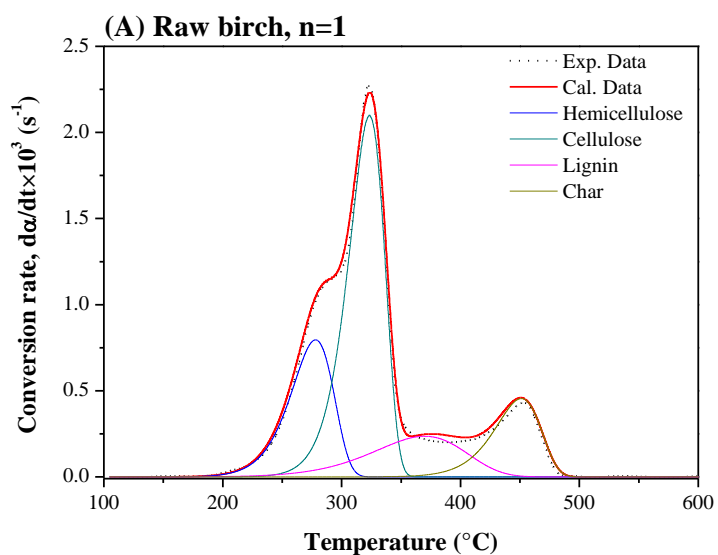


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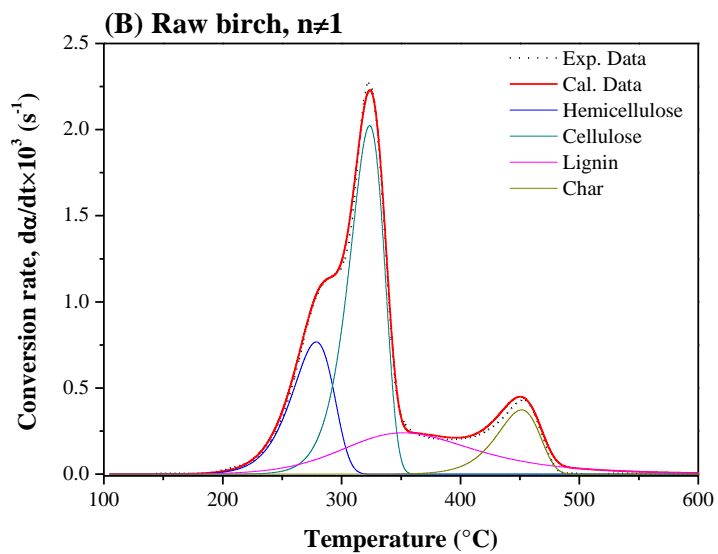


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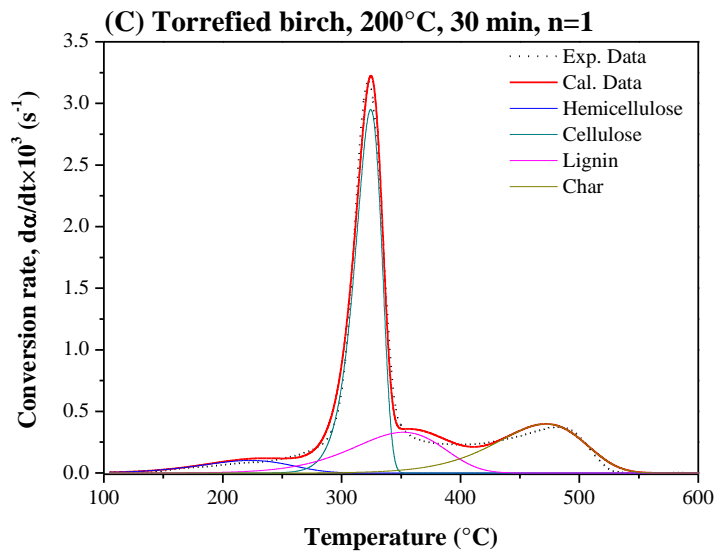
1 Figure 6. Curve fitting for raw and torrefied birch fuels



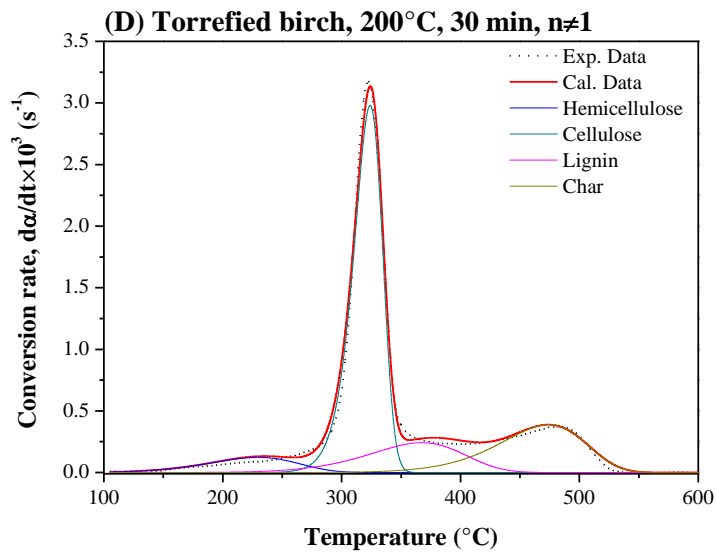
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