



Effects of wet torrefaction on reactivity and kinetics of wood under air combustion conditions



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HIGHLIGHTS

- Torrefaction temperature and holding time significantly influence the combustion reactivity and kinetics of woody biomass.
- The effect of torrefaction pressure is insignificant.
- Mass fraction and activation energy of hemicellulose are reduced by wet torrefaction.
- Activation energy of cellulose is increased by wet torrefaction.

ARTICLE INFO

Article history:

Received 24 March 2014

Received in revised form 18 June 2014

Accepted 5 August 2014

Available online 19 August 2014

Keywords:

Wet torrefaction

Wood reactivity

Combustion kinetics

Kinetic modelling

Biofuel pretreatment

ABSTRACT

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

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1. Introduction

Wet torrefaction (WT), which may be defined as treatment of biomass in hydrothermal media (HM) or hot compressed water (HCW) at temperatures within 180–260 °C [1–5], is a promising method for production of high quality solid fuels from low cost wet biomass resources such as forest residues, agricultural waste, aquatic energy crops, and sewage sludge. The concept of WT is very similar to “hydrothermal carbonization” (HTC) [6–15] and

sometimes is discussed under the general term “hydrothermal conversion” [15–19] or “hydrothermal treatment” [20–25]. Although the terminologies of WT and HTC have sometimes been used interchangeably, there is a significant difference between them. While WT aims at producing upgraded solid fuels for energy applications only, HTC is employed mainly for producing charcoal, with much higher carbon content, which can be used not only as fuel but also as activated carbon, soil enhancer, fertilizer, etc. Clearly, energy efficiency of the process, fuel properties and combustion properties of the product are more critical for WT than for HTC, and thus the former tends to be performed at lower temperatures (180–260 °C) than the latter (from 300 °C).

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Like dry torrefaction (DT), which may be defined as thermal treatment of biomass in an inert environment at atmospheric pressure and temperatures within the range of 200–300 °C [26–28], WT results in the following main improvements in the fuel properties of biomass: (1) increased heating value due to a reduction in the O/C ratio; (2) intrinsic transformation from hygroscopic into hydrophobic nature of biomass; (3) better grindability coupling with less energy requirement for size reduction of the fuel. After WT, the wet hydrophobic solid product can be effectively made dry by mechanical and/or natural dewatering, which is an attractive option capable of dramatically reducing the energy requirement for the post-drying step. In addition to the solid fuel product, many valuable organic compounds including acetic acid, formic acid, lactic acid, glycolic acid, levulinic acid, phenol, furfural, HMF, and sugars are found in the aqueous phase products of WT, making up approximately 10 wt% of the feedstock [4,6]. The potential use of these water-soluble organic fractions for production of valuable products may contribute to further improving the economy of the WT process.

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

Despite various advantages of WT over DT, only a few studies on WT have been reported [1–5] compared to a sharply increasing number of studies on DT during the last few years [26–34]. In addition, most WT studies focused on the effects of process parameters on the yield and fuel properties of the solid product. To our knowledge, no study of using solid fuel obtained from WT for energy applications has been reported so far. Combustion is currently the most important energy application of biomass solid fuel, considering its contribution to more than 90% of the global bioenergy deployment [35–39]. It is therefore important and necessary to investigate into the effects of WT on combustion reactivity and kinetics of biomass solid fuels.

Several studies on combustion of dry torrefied biomass have been reported [30,40–43], which would be beneficial for studying combustion behavior of wet torrefied biomass fuel. Pimchua et al. [40] and Bridgeman et al. [30], for example, studied the combustion of biochars obtained from DT of different biomass materials. They found that the combustion of dry torrefied husks and herbaceous biomass released more heat than that of the raw materials due to the higher fixed carbon content of the biochars. However, no kinetic data was reported from these studies. Arias et al. [41] applied a simple first-order kinetic model to estimate the activation energy and pre-exponential factor of raw and dry-torrefied eucalyptus samples in a two-stage combustion process (devolatilization followed by combustion). The results showed that both kinetics parameters (the activation energy and pre-exponential factor) increased in stage 1 and decreased in stage 2 after DT.

Nevertheless, the model was based on an empirical method which was not validated because the model itself could not either reproduce simulated curves or give any information about the fit quality between the predicted and experimental data. Recently, studies on the combustion kinetics of dry torrefied woody biomass materials using multi pseudo-component models have been reported by Broström et al. [42] and Tapasvi et al. [43]. The former employed a global kinetic model and the latter employed a distributed activation energy model (DAEM). The results from the two approaches showed that DT had little effect on the kinetic parameters of the torrefied biomass regardless of the treatment conditions. Broström et al. [42] reported that the activation energy values of hemicellulose, cellulose and lignin were constant at 100.6, 213.1, and 121.3 kJ/mol, respectively for both raw and dry-torrefied spruce. Tapasvi et al. [43] found that the activation energy values for cellulose, non-cellulosic part and char remained at 135, 160 and 153 kJ/mol, respectively for different types of feedstock and DT conditions.

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

2. Materials and methods

2.1. Materials

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

Stem wood from Norway spruce (softwood) and birch (hardwood) were selected as feedstock for the study since they are the main wood species in Norwegian forests. The samples were cut into 1 cm cubes for WT in hot compressed water, using a 250 ml Parr reactor series 4650 (Parr Instrument, USA) at different temperatures (175, 200, 225 °C), pressures (15.54, 70, 160 bar) and holding times (10, 30, 60 min). The corresponding vapour pressures of water at 175, 200, and 225 °C are 8.93, 15.54, and 25.50 bar, respectively. However, in order to keep more water in the liquid phase, the pressure of 70 bar was used for all of the WT experiments, except for the investigation of the pressure effect at 200 °C [1]. For this investigation, the pressures of 15.54, 70 and 160 bar were employed. Distilled water was used as the reaction media. The ratio of dry feedstock over water was 1:5 by weight.

After WT, the wet solid products were dried at 105 °C for 48 h and then stored in a desiccator for further analyses. The proximate and ultimate analyses of the samples used for this work are presented in Table 1. The proximate analyses were performed according to ASTM standards: ASTM E871, ASTM E872 and ASTM D1102 for moisture content, volatile matter and ash content, respectively. The ultimate analyses were determined (on a dry basis) by means of an “EA 1108 CHNS-O” elemental analyzer (Carlo Erba Instruments). The higher heating values (HHVs) were calculated on dry and ash free basis, according to Channiwalla and Parikh [46].

2.2. Thermogravimetric analysis method and procedure

A thermogravimetric analyzer (Mettler Toledo TGA/SDTA851e) was employed for this study. The biomass solid fuels were first

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	
<i>Spruce</i>										
Raw	–	0.23	86.50	13.27	50.31	6.24	0.07	43.38	<0.02	20.42
175 °C, 30 min	88.27	0.11	85.72	14.17	51.34	6.18	0.07	42.42	<0.02	20.81
200 °C, 10 min	82.48	0.14	84.64	15.22	51.21	6.39	0.06	42.35	<0.02	21.02
200 °C, 30 min	78.45	0.12	83.92	15.95	52.55	6.15	0.06	41.23	<0.02	21.33
200 °C, 60 min	73.28	0.09	81.87	18.03	53.69	5.89	0.06	40.36	<0.02	21.51
225 °C, 30 min	69.74	0.14	74.74	25.12	56.99	5.87	0.07	37.07	<0.02	22.97
<i>Birch</i>										
Raw	–	0.28	89.46	10.26	48.94	6.35	0.11	44.60	<0.02	19.94
175 °C, 30 min	79.53	0.09	88.57	11.34	49.42	6.38	0.12	44.07	<0.02	20.21
200 °C, 10 min	66.42	0.08	87.97	11.94	49.61	6.16	0.13	44.10	<0.02	20.01
200 °C, 30 min	64.64	0.09	85.15	14.76	51.25	6.18	0.11	42.46	<0.02	20.78
200 °C, 60 min	63.06	0.10	82.64	17.27	51.34	5.94	0.13	42.59	<0.02	20.51
225 °C, 30 min	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.

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

2.3. Kinetic model selection

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

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



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

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

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

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

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 the total mass of released volatiles and v is the mass of released volatiles at any time.

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

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

2.4. Numerical method

Data collected from the TGA experiments was differentiated to obtain the DTG data, and presented in the form of conversion (mass loss) rate ($\frac{d\alpha}{dt}$) versus temperature T . A mathematical model corresponding to the selected model was then employed for

simulation and comparison with the experimental DTG data. The optimization of the predicted DTG curves was based on the non-linear least squares method, which minimized the sum of the square differences between the experimental and calculated data. The objective function is given in Eq. (8):

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

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

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

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

The actual simulation was run until the maximum fit value was found, at which the convergence criteria of the optimization process are achieved. The extracted kinetic parameters are: the activation energies (E_1 – E_4), the pre-exponential factors (A_1 – A_4), the mass fractions (c_1 – c_4), and the reaction orders (n_1 – n_4) for each pseudo-component. Totally, there are 12 kinetic parameters for the 1st order model and 16 parameters for the n th order model.

3. Results and discussions

3.1. Thermogravimetric analysis of spruce and birch wood in air

Fig. 1 shows the TG and DTG curves, representing the thermal behavior of the raw spruce and birch woods in the temperature range of 100–600 °C. The standard deviation of the conversion rate data for the tested samples was $1.38 \times 10^{-5} \text{ s}^{-1}$. For both types of feedstock, the decomposition starts at around 180 °C with a low conversion rate. Then the decomposition rate increases rapidly from around 250 °C to the devolatilization peaks ($\approx 2.3 \times 10^{-3} \text{ s}^{-1}$) at 321–324 °C, from which the rate decreases quickly, down to $0.30 \times 10^{-3} \text{ s}^{-1}$ for the spruce wood and $0.25 \times 10^{-3} \text{ s}^{-1}$ for the birch wood at around 350 °C. This marks the end of the devolatilization and the beginning of the char combustion, which has much lower rates than the devolatilization. In addition, a clear shoulder in the devolatilization stage is observed for the raw birch wood, but not for the raw spruce. This is because the hemicelluloses content of birch (hardwood) is normally higher than that of spruce

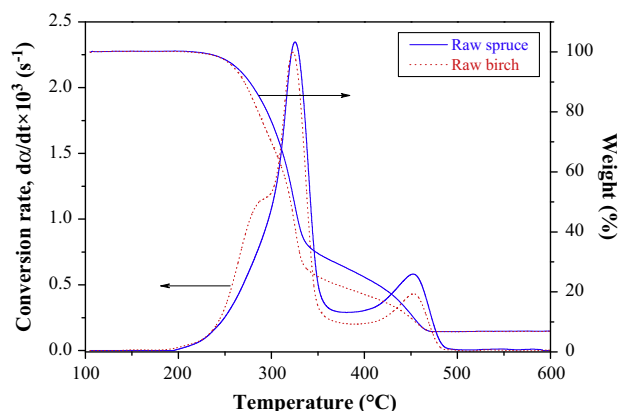


Fig. 1. TGA and DTG curves in air for raw spruce and birch woods.

(softwood) [54]. Also, hemicellulose of hardwood usually contains more xylan than softwood, which is the most reactive compound in the temperature range of the devolatilization (200–350 °C) [54].

In the char combustion stage, the birch wood char exhibits lower reactivity than that of spruce 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 the spruce.

3.2. Effects of torrefaction conditions on reactivity of wood in air combustion

3.2.1. The effect of torrefaction temperature

The woods torrefied at three different temperatures (175, 200, and 225 °C), in the common conditions of 30 min as holding time and 70 bar as pressure were used for this test. The test results are presented in Fig. 2, which includes the data collected for the raw woods for comparison. Fig. 2A is for the spruce wood and Fig. 2B for the birch wood. As can be seen, the torrefied woods start decomposing at temperatures around 150 °C, somehow lower than those for the raw woods (around 180 °C). However, the conversion rates in this early stage are very low, approximately being less than $0.2 \times 10^{-3} \text{ s}^{-1}$ in all cases. A slightly higher reactivity of the torrefied woods than their origins in the early decomposition stage may be due to the higher reactivity of a small amount of remaining organic compounds, with low molecular weights, produced from the degradation of hemicellulose during the WT processes [55,56]. Most of these organic compounds were washed out and collected in the water-soluble product portion, but some of them

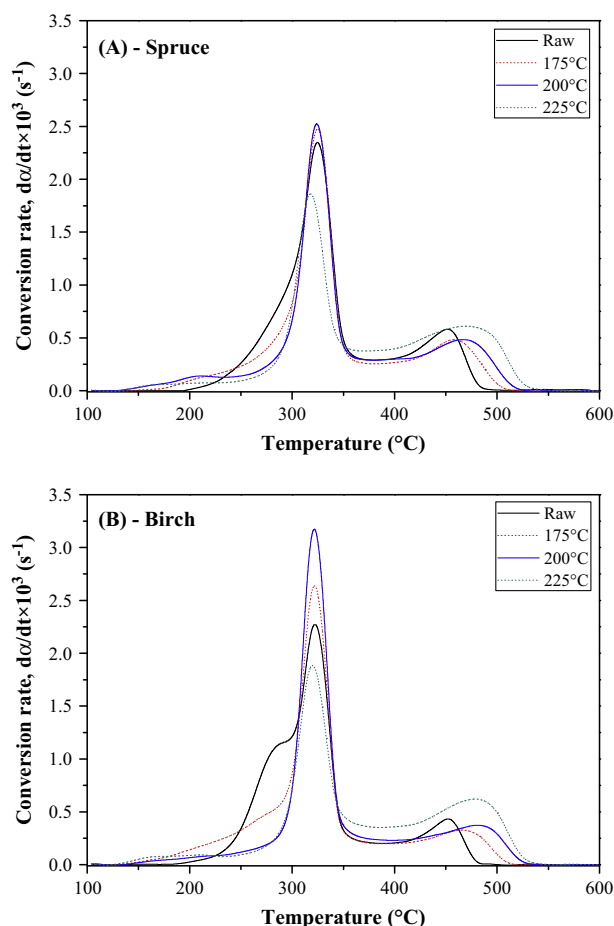


Fig. 2. DTG analyses in air for spruce (A) and birch (B) woods torrefied at 70 bar for 30 min.

may have been trapped in the pores and/or adsorbed on the surface of the torrefied biomass. At temperatures from 250 °C up to 310 °C, the torrefied woods become less reactive than their origins. This is probably due to the degradation of hemicellulose in the raw woods as discussed earlier in Section 3.1, considering that torrefied woods contain less or no hemicellulose compared to their origins. At temperatures above 310 °C, the devolatilization peaks, mainly contributed by cellulose decomposition [57,58], are established. The peaks for the woods torrefied at 175 °C and 200 °C are higher than those for the raw woods, but occur at the same location (around 321–324 °C). In addition, the peaks for the woods torrefied at 200 °C are higher than those for the woods torrefied at 175 °C. However, the peaks for the woods torrefied at 225 °C are the lowest and the peak locations slightly shifted to the left, at around 317 °C.

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

3.2.2. The effect of torrefaction time

Fig. 3 presents the effect of holding time (10, 30, and 60 min) during WT on the combustion behavior for the woods torrefied at 200 °C and 70 bar as the common conditions. Fig. 3A is for the spruce wood and Fig. 3B for the birch wood. The figures indicate that increases in WT holding time make the woods less reactive at TGA temperatures below 300 °C and more reactive during the char combustion stage. Again, similar explanations based on the role of the hemicellulose and fixed carbon content of the tested samples can be applied for these observed trends. In addition, inconsistencies in the devolatilization peak heights, which are similar to those for the effect of torrefaction temperature, were also observed.

3.2.3. The effect of torrefaction pressure

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

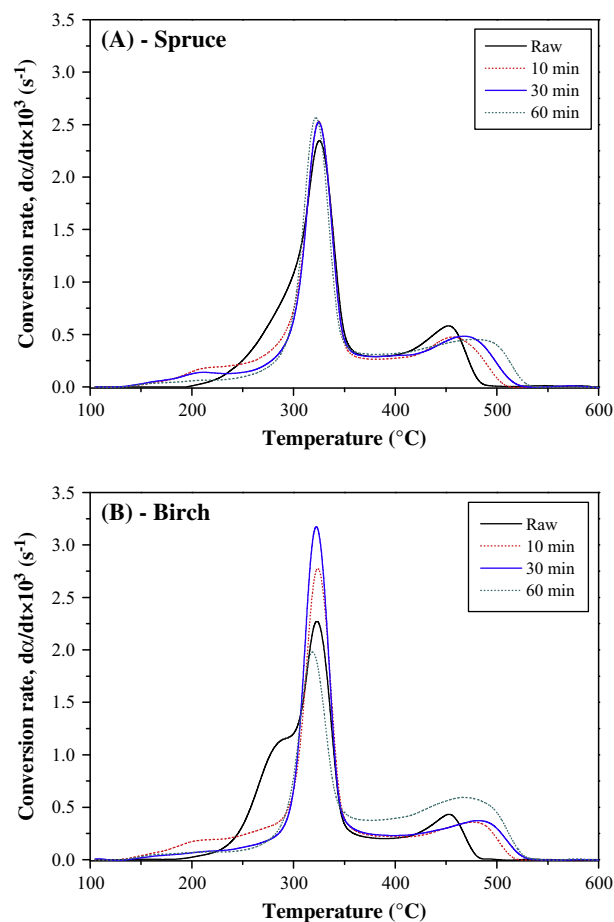


Fig. 3. DTG analyses in air for spruce (A) and birch (B) torrefied at 200 °C and 70 bar.

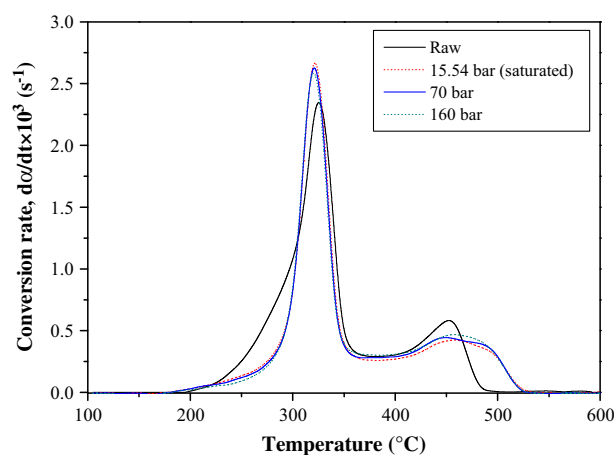


Fig. 4. DTG curves in air for spruce torrefied in the condition of 200 °C, 10 min at different pressures.

3.3. Kinetic analysis

A kinetic analysis employing the four-pseudo-component model with different reaction orders ($n = 1$ and $n \neq 1$) was performed for a quantitative evaluation of the effects of WT on the combustion reactivity of wood. Because the effect of pressure during WT on the reactivity of wood in air combustion is not significant, only the wood samples torrefied at a constant pressure of

Table 2

Combustion kinetic data for spruce fuels.

Torrefaction condition		First order reactions				nth order reactions				
		<i>E</i> (kJ/mol)	<i>A</i> (s ^{−1})	<i>c</i>	Fit (%)	<i>E</i> (kJ/mol)	<i>A</i> (s ^{−1})	<i>c</i>	<i>n</i>	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, 30 min	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, 10 min	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, 30 min	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, 60 min	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, 30 min	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.

70 bar (at different temperatures and with different holding times) were selected for the kinetic analysis. The selection of this pressure was based on the recommendation discussed in our previous study [1]. In total, 12 experimental data sets were analyzed kinetically, of which 6 were for the spruce wood and 6 for the birch wood. The kinetic data extracted from this analysis are presented in Tables 2 and 3 for the spruce and birch, respectively. The quality of the fit between the experimental and predicted data is also included in the tables. In addition, for a graphical demonstration of the fit quality, curves fittings for the raw woods and the woods torrefied at 200 °C for 30 min (at 70 bar) are presented in Figs. 5 and 6, respectively. In these figures, the actual conversion rates from the experiments are presented by the black dotted curves. The red solid curves denote the predicted rates. The other four curves are presenting the conversion rates of the three main components of wood (hemicellulose, cellulose, and lignin) and the char formed from the devolatilization step. The figures show good fits between the experimental and modelled results. The fit quality numerically presented in Tables 2 and 3 is within 98–99% in all cases.

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

It can be seen that, while there is no clear trend for the effect of WT on the pre-exponential factor, the activation energy of hemicellulose is reduced dramatically by WT, e.g. decreases from 103.76 to 44.82 kJ/mol and from 144.68 to 41.29 kJ/mol for the spruce and birch, respectively, by WT at 225 °C (and 70 bar) for 30 min. This effect can also be observed from the hemicellulose curves in Figs. 5 and 6, which show clearly that WT caused a shift of the hemicellulose curves to a lower temperature range. This is in agreement with the literature [61] and can be explained by that

during WT the hemicellulose component of the wood was decomposed and cracked into smaller molecules such as polysaccharides [55,56], which remained in the solid products.

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

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

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

The mass fraction of hemicellulose is reduced by WT. In addition, the mass fraction is decreased gradually with increasing WT severity, from 0.15 for the raw spruce to 0.05 for the spruce torrefied at 225 °C and 30 min; and from 0.23 for the raw birch to 0.06 for the birch torrefied at 225 °C and 30 min. From the conditions of 200 °C and 30 min to more severe conditions (higher temperatures or longer holding times), the hemicellulose mass fraction of the torrefied fuel is small, less than 10% of the total mass. With the reduction of hemicellulose fraction, the mass fraction of the other component fractions in the torrefied biomass fuels (cellulose, lignin, and char) are relatively increased compared with the raw materials, as presented in Tables 2 and 3.

Table 3
Combustion kinetic data for birch fuels.

Torrefaction condition		First order reactions				nth 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, 30 min	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, 10 min	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, 30 min	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, 60 min	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, 30 min	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.

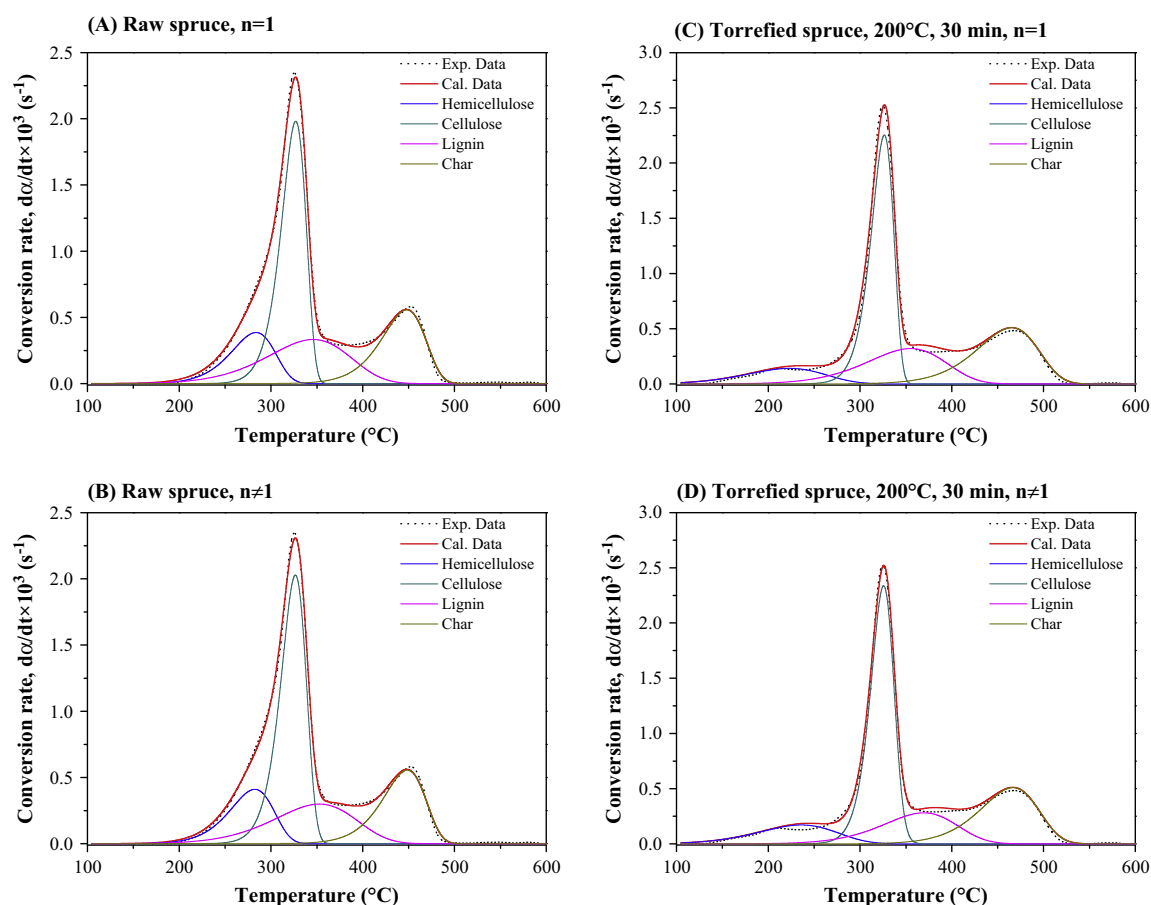


Fig. 5. Curve fitting for raw and torrefied spruce fuels.

The mass fraction of cellulose in the torrefied fuels from both feedstocks increased to a maximum value, 0.47 and 0.56 for spruce and birch torrefied at 200 °C and 30 min, and then

decreased with either increasing temperature or holding time. The contribution of cellulose fractions is in good agreement with the heights of the devolatilization peaks shown in Figs. 2 and 3.

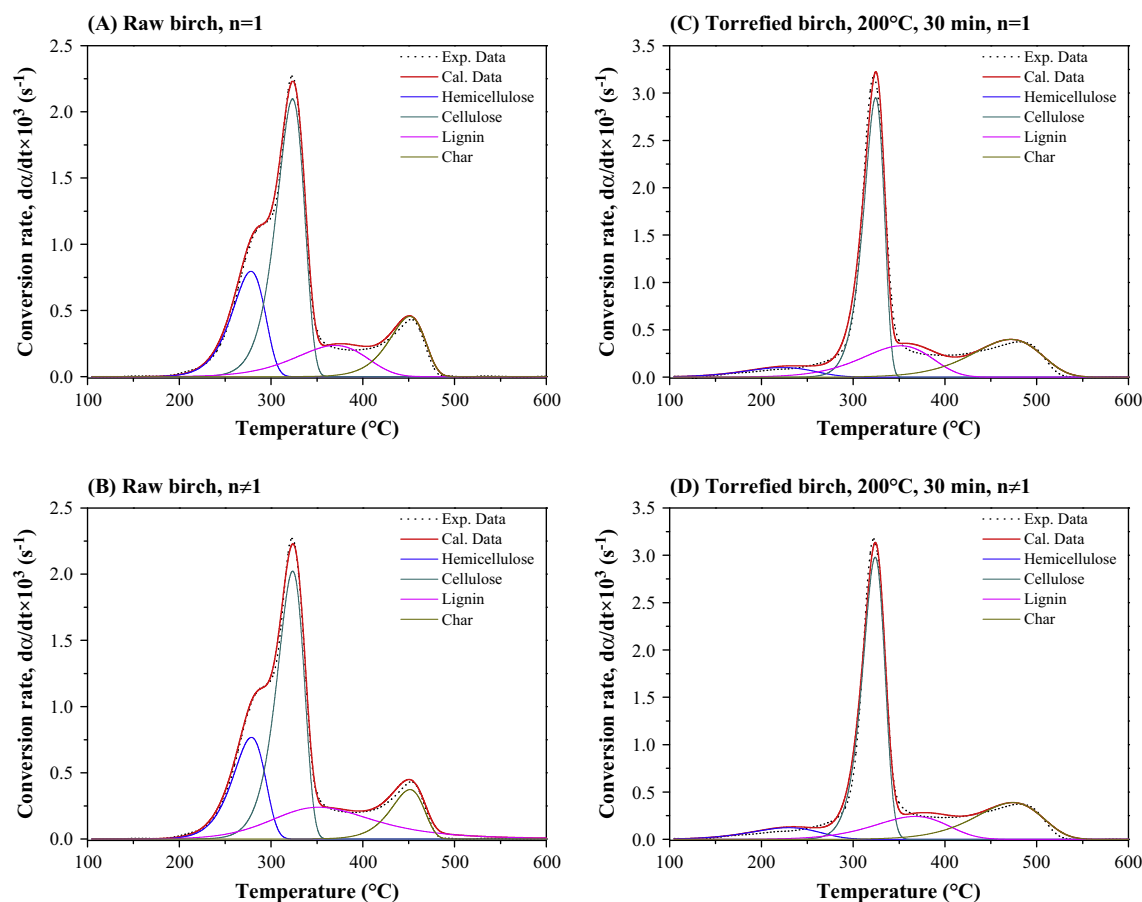


Fig. 6. Curve fitting for raw and torrefied birch fuels.

The higher cellulose fraction is, the higher devolatilization peak is observed. This helps confirm the suspicion and explain the inconsistent trend in the effects of WT temperature or holding time on the devolatilization peaks height as observed and discussed earlier in this paper.

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

4. Conclusions

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

- WT pressure had insignificant effects on the combustion reactivity of the woods.
- WT temperature and holding time had similar effects on the combustion reactivity of the woods. Increasing either temperature or holding time make the woods more reactive in the devolatilization stage, but less reactive in the char combustion stage. However, too severe WT conditions (from 225 °C and 30 min) made the trends reversed due to the decomposition

of cellulose in the devolatilization stage and the competition between catalyzing and inhibiting effects of char ash on the char combustion stage.

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

Acknowledgements

This work is financially supported by the Research Council of Norway and industry partners through the KMB project STOP (STable OPERating conditions for biomass combustion plants), which is gratefully acknowledged.

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