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Wet torrefaction of forest residues – Combustion kinetics

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Abstract

Fresh branches of Norway spruce and birch were torrefied in hot compressed water at varied temperatures (175, 200, or 225 °C) and for 30 minutes. The combustion of untreated and torrefied branches in synthetic air (21% O₂ and 79% N₂) was experimentally studied by means of a thermogravimetric analyzer, followed by a kinetic analysis adopting the distributed activation energy model. It appears that, wet torrefaction has significant effects on the combustion reactivity of forest residues. Compared with the raw materials, wet-torrefied branches are less reactive during devolatilization, but more reactive in the char combustion stage.

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Keywords: Combustion kinetics; Kinetic modelling; Wet torrefaction; Forest residues.

1. Introduction

Forest residues, mainly tree branches and tops remaining after forest harvesting, is a relatively low-cost resource compared to stem wood. To use this resource as fuel is important for bioenergy deployment due to the fact that it contributes to meet the growing demand of bioenergy without increasing the volume of stem wood to be harvested. However, the use of forest residues as fuel is challenging due to their high moisture content, low homogeneity and low bulk density, which require pretreatments to make the residues suitable for use as fuel.

Wet torrefaction (WT) is a promising pretreatment method to overcome the shortcomings of using forest residues as fuel. The process involves the use of hot compressed water, in the temperature range of 180–260 °C [1–3] as reaction media, converting solid biomass to a hydrophobic solid fuel (*hydrochar*) with much better grindability, lower moisture content and higher calorific value compared with the raw material. Study on WT of biomass for energy applications has been quite active [1–4]. However, the reactivity of wet torrefied biomass solids in subsequent thermal conversion processes including combustion has not been investigated yet. The objective of the present work is to investigate effects of

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WT on combustion reactivity of forest residues, by analysing the combustion kinetics of forest residues before and after treatment via wet torrefaction.

2. Materials and methods

2.1. Materials

Fresh branches of Norway spruce and birch were torrefied in hot compressed water at different temperatures (175, 200 and 225 °C), for 30 min. The WT procedure reported in our previous study [1] was adopted for this present work. Proximate and ultimate analyses are shown in Table 1.

Table 1. Fuel properties of raw and torrefied biomass.

	Spruce				Birch			
	Raw	175°C	200°C	225°C	Raw	175°C	200°C	225°C
Proximate analysis, % w/w								
Ash	0.23	0.11	0.12	0.14	0.28	0.09	0.09	0.13
Volatile matter	86.5	85.72	83.92	74.74	89.46	88.57	85.15	73.78
Fixed carbon	13.27	14.17	15.95	25.12	10.26	11.34	14.76	26.09
Ultimate analysis, % w/w								
C	50.31	51.34	52.55	56.99	48.94	49.42	51.25	56.92
H	6.24	6.18	6.15	5.87	6.35	6.38	6.18	5.86
N	0.07	0.07	0.06	0.07	0.11	0.12	0.11	0.09
O	43.38	42.42	41.23	37.07	44.6	44.07	42.46	37.13
HHV, MJ/kg	20.42	20.81	21.33	22.97	19.94	20.21	20.78	22.93

Prior to the thermogravimetric analysis, raw and torrefied fuel samples were ground by an IKA MF 10 cutting mill with a closed bottom to obtain fine powder. Particles less than 90 µm were collected for the combustion kinetic study in a Mettler Toledo TGA/SDTA851e to ensure that the experiments would be in the kinetic control regime. A synthetic air (consisting of 79% nitrogen and 21% oxygen in volume) with a flow rate of 80 ml/min was used for all experiments. For each experiment, an amount of sample less than 0.5 mg was used. The experiment starts from room temperature, being heated to 105 °C and held at this temperature for 1h for drying. Thereafter, temperature was increased to 700 °C at a constant heating rate of 10 °C per minute.

2.2. Kinetic modeling

It is generally agreed that the combustion of solid biomass fuels undergoes two main steps: devolatilization of the fuel to produce char and the char burn-off (combustion of char) [5, 6]. The first step can be described by multi parallel-reactions, which is known as pseudo-component model [7-9], whereas the second step can be represented by the power rate law with an n-order and the Arrhenius equation for the rate constant coefficient. For the first step, the sample is regarded as a sum of M pseudo-components, where M is usually between 2 and 4 [10]. For each component, the distributed activation energy model (DAEM) with a first-order proposed by Pitt [11] can be applied. A general form for DAEM is given in Eq. 1

$$1 - \frac{V}{V^*} = \int_0^{\infty} \exp\left(-A \int_0^t e^{-\frac{E_a}{RT}} dt\right) f(E) dE \quad (1)$$

where the $f(E)$ is the distribution function of activation energy. Several forms of $f(E)$ are reported in literature including Gaussian, Weibull, and Gamma distribution [12]. Among those, the Gaussian function (Eq. 2), which show a mean activation value (E_0) and a standard deviation σ , has been widely used for studying the combustion kinetics of various biomass materials [13-15].

$$f(E) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(E - E_0)^2}{2\sigma^2}\right) \quad (2)$$

Latter an n^{th} -order DEAM was developed by Braun et al. [16]. The first application of DAEM for biomass materials was published by Avni et al. [17]. Recently, the DAEM was employed to study the combustion kinetics of torrefied biomass [15]. This model of a first-order was adopted for this present study with $M = 4$, being hemicelluloses, cellulose, lignin, and char.

2.3. Numerical method

The data from the TGA experiments are differentiated to obtain the DTG data, which show the conversion rate versus time ($\frac{d\alpha}{dt}$). The mathematical simulation and optimization of DTG curves are based on the least squares method, which aims to minimize the sum of the square differences between experimental and calculated data. The objective function is given in Eq. 3:

$$S = \sum_{i=1}^N \left[\left(\frac{d\alpha_i}{dt} \right)_{exp} - \left(\frac{d\alpha_i}{dt} \right)_{cal} \right]^2 \quad (3)$$

In order to evaluate the models, the fit quality between actual and simulated data is calculated according Eq. 9:

$$Fit (\%) = \left(1 - \frac{\sqrt{S}}{\left[\left(\frac{d\alpha_i}{dt} \right)_{exp} \right]_{max}} \right) \cdot 100\% \quad (4)$$

The simulation was run until the maximum fit value is reached, at which the convergence criteria of the optimization process are achieved.

3. Results and discussions

3.1. Combustion reactivity of untreated branches

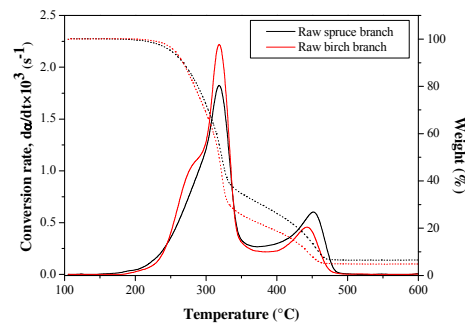


Figure 1. TG and DTG curves for untreated forest residues

Figure 1 represents the mass losses (TG) and conversion rate (DTG) curves for the raw branches during air combustion in the temperature range of 100-600 °C. The peak values and temperatures for each stage taken from the DTG curves are tabulated in Table 2. For both types of feedstock, the conversion

rates increase rapidly from almost zero at 150 °C to reach the peak values at 318.5 °C, and then decrease dramatically to $0.37 \times 10^{-3} \text{ s}^{-1}$ for birch branch and $0.42 \times 10^{-3} \text{ s}^{-1}$ for spruce branch at around 340 °C. This marks the end of the devolatilization and the beginning of the char combustion.

Table 2. Peak conversion rates and temperatures of untreated forest residues

Peak value	Spruce				Birch			
	Raw	175°C	200°C	225°C	Raw	175°C	200°C	225°C
$\left(\frac{d\alpha}{dt}\right)_{dev}^{peak}, \times 10^3 \text{ s}^{-1}$	1.824	1.934	2.156	1.793	2.221	2.444	2.421	1.983
$T_{dev}^{peak}, \text{ }^\circ\text{C}$	318.5	318.0	317.0	315.7	318.5	320.8	322.3	323.2
$\left(\frac{d\alpha}{dt}\right)_{comb}^{peak}, \times 10^3 \text{ s}^{-1}$	0.602	0.653	0.654	0.766	0.455	0.416	0.572	0.573
$T_{comb}^{peak}, \text{ }^\circ\text{C}$	451.7	478.2	473.2	464.3	442.5	440.5	471.5	480.8

From Figure 1, it can also be seen that the DTG curve of raw birch branch has a clear shoulder in the devolatilization stage, which is addressed to hemicellulose decomposition, whereas a similar behaviour in the DTG curve of raw spruce branch is missing, indicating a less hemicellulose content in spruce than birch. The char combustion of both feedstocks has much lower conversion rates than in the devolatilization. On the other hand, Table 2 shows that char formed from raw spruce branch has a higher peak temperature and higher peak conversion rate than birch branch. This indicates that the reactivity of birch branch is lower than that of spruce branch in the char burn-off stage.

3.2. Combustion reactivity of torrefied branches

3.2.1. Thermogravimetric analysis

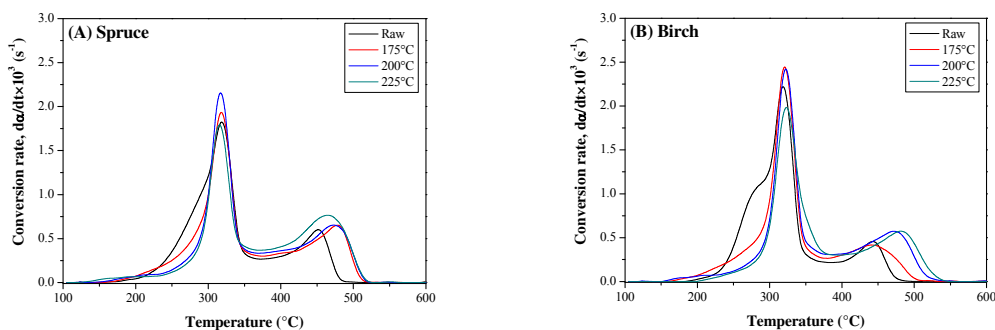


Figure 2. DTG curves for raw and torrefied (A) spruce and (B) birch branches

The combustion behavior of spruce branch torrefied in compressed water at different temperatures is presented in Figure 2A. The DTG curve for raw spruce is also included in this figure for comparison. It can be seen that the torrefied fuels are less reactive than the raw one at temperatures below 300 °C. However, the peak temperature, presented in Table 2, of raw material is higher than those of the torrefied materials. Moreover, the conversion rate peaks of torrefied spruce branch shift down to a lower temperature with increasing torrefaction temperature. The highest conversion rate peaks is found for the sample torrefied at 200 °C ($2.2 \times 10^{-3} \text{ s}^{-1}$), while the lowest peak ($1.8 \times 10^{-3} \text{ s}^{-1}$) is for the fuels treated at 225 °C. It can also be observed that the combustion peaks vary in a wide range of temperature (451.7-464.3

°C) and the peak temperature increases with increasing WT temperature. The behaviour of torrefied birch branch in the combustion stage (Figure 2B) show trends similar to that of torrefied spruce.

3.2.2. Kinetic evaluation

Figure 3 presents results from the kinetic evaluation. The partial conversions are also generated from the model, assigning to the hemicellulose, cellulose, lignin, and char. It can be seen that the predicted data fit nicely to the experimental data for both types of feedstock. Extracted kinetic parameters for both raw and torrefied samples are listed in Table 3.

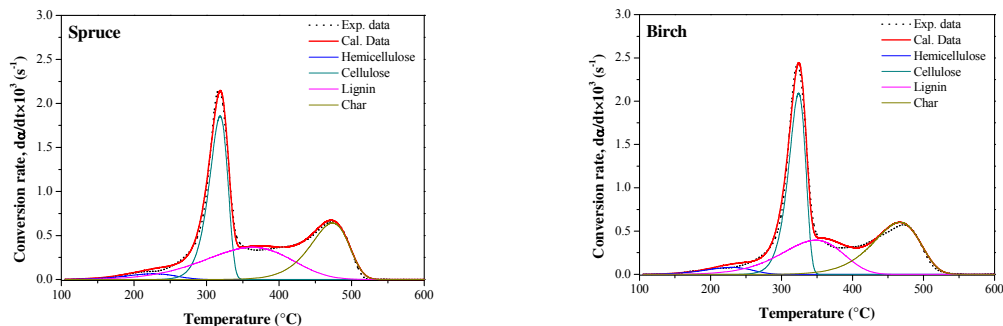


Figure 3. Curve fitting for spruce and birch branches torrefied in mid conditions (200°C)

Compared with the raw fuels, the mass fractions of hemicellulose in all torrefied fuels are reduced dramatically with increasing WT severity, from 0.17 to 0.03 for spruce and from 0.21 to nil for birch sample. Compared with the raw materials, the cellulose fraction of both spruce and birch samples torrefied at lower temperature increases. But an opposite trend is observed for the sample torrefied at 225°C. However, there is no clear correlation trend between the mass fraction of lignin in raw and torrefied fuels. Finally, the char fraction is increased gradually with increasing torrefaction temperature, i.e. more severe conditions produce more char.

Table 3. Kinetic data for raw and torrefied forest residues

	Spruce				Birch			
	Raw	175°C	200°C	225°C	Raw	175°C	200°C	225°C
E_{hemi} , KJ/mol	105.33	106.66	55.50	42.46	131.37	69.04	60.88	–
σ_{hemi} , KJ/mol	14.53	14.35	14.35	15.41	26.66	18.26	13.60	–
A_{hemi} , s^{-1}	4.68E+07	1.69E+08	2.81E+03	2.54E+02	2.42E+10	3.92E+04	1.03E+04	–
c_{hemi}	0.17	0.05	0.03	0.03	0.21	0.08	0.04	–
E_{cell} , KJ/mol	218.77	213.99	230.35	237.57	234.78	217.17	250.72	242.57
σ_{cell} , KJ/mol	43.59	43.66	43.46	43.67	43.67	43.83	43.86	43.66
A_{cell} , s^{-1}	2.13E+17	9.24E+16	2.88E+18	1.45E+19	6.28E+18	1.39E+17	1.22E+20	2.15E+19
c_{cell}	0.29	0.34	0.37	0.28	0.38	0.45	0.39	0.27
E_{lign} , KJ/mol	43.06	36.91	51.36	56.71	54.39	49.34	69.73	90.92
σ_{lign} , KJ/mol	16.94	16.53	17.02	17.79	16.57	16.33	16.37	16.40
A_{lign} , s^{-1}	1.26E+01	2.13E+00	4.21E+01	1.67E+02	1.38E+02	4.64E+01	2.65E+03	2.84E+05
c_{lign}	0.33	0.41	0.33	0.31	0.27	0.24	0.26	0.33
E_{char} , KJ/mol	177.21	197.74	172.92	143.01	213.67	116.94	133.58	96.17
σ_{char} , KJ/mol	34.98	35.12	35.12	35.12	35.12	33.68	35.12	38.09
A_{char} , s^{-1}	4.70E+10	4.63E+11	7.82E+09	6.92E+07	3.39E+13	1.43E+06	1.33E+07	2.09E+04
c_{char}	0.20	0.20	0.26	0.38	0.15	0.23	0.31	0.40
n_{char}	1.02	1.01	1.04	1.02	1.05	1.08	1.01	1.01
Fit, %	98.48	98.75	98.71	98.56	98.71	98.63	98.56	97.46

Along with the reduction in hemicellulose content, the activation energy of this component is also decreased dramatically after WT, being from 105.3 to 42.7 kJ/mol torrefied spruce and from 131.4 to 60.9 kJ/mol for birch. However, activation energy for cellulose exhibits insignificant changes by torrefaction. The average value is around 227.3 kJ/mol for torrefied spruce branch and 236.8 kJ/mol for torrefied birch sample. Activation energy for lignin has an increasing trend with increasing torrefaction temperature, while that for char shows an opposite tendency. Although an n^{th} -order reaction has been chosen for the char burn-off, the simulation result gives the value of reaction order close to 1.

4. Conclusion

Combustion kinetics of spruce and birch branches, raw and treated via wet torrefaction, has been studied. The results showed that WT has significant effects of on the combustion reactivity of forest residues. Compared with the raw materials, wet-torrefied branches are less reactive during devolatilization, but more reactive in the char combustion stage. The amount of char in the wet-torrefied samples is increased gradually with increasing severity of WT, whereas the reactivity of char increases.

Acknowledgements

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