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Energy Procedia 75 (2015) 150 – 155

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The 7<sup>th</sup> International Conference on Applied Energy – ICAE2015

# Dry and wet torrefaction of woody biomass – A comparative study on combustion kinetics

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## Abstract

The combustion kinetics of Norway spruce woody treated via wet or dry torrefaction were studied and compared. Dry and wet torrefaction of wood were performed in compatible conditions on the basis of a common mass yield. The combustion experiments were studied thermogravimetrically, followed by a kinetic evaluation assuming a four-pseudo-component model. The results show that dry-torrefied wood is less reactive in the devolatilization step but more reactive in the char combustion, compared to wet-torrefied one. Dry torrefaction removes more hemicellulose from Norway spruce wood than wet torrefaction, in compatible conditions. The activation energy and pre-exponential factor of cellulose and lignin in the devolatilization step are increased by both torrefaction methods. However, in the char combustion the activation energy and pre-exponential factor are increased by dry torrefaction, but decreased after wet torrefaction.

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Peer-review under responsibility of Applied Energy Innovation Institute

Keywords: Dry torrefaction; Wet torrefaction; Fuel upgrading; Combustion kinetics

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## 1. Introduction

Biomass is an important renewable and carbon neutral energy resource which has a high potential for replacing fossil fuels. Nevertheless, the use of biomass for energy applications is not straightforward. Inherent disadvantages of biomass include the low bulk density, high moisture content, low heating value, and poor grindability. Torrefaction is recognized as a pretreatment method for upgrading the solid biomass fuel, which has been paid attention for last decades. There are two torrefaction techniques, dry

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and wet torrefaction. Dry torrefaction (DT) is thermal treatment of biomass in an inert environment at atmospheric pressure and temperatures within the range of 200-300°C [1-3]. Wet torrefaction (WT) may be defined as treatment of biomass in a hydrothermal media, or hot compressed water, at temperatures within 180-260°C [4, 5]. The two techniques have their own pros and cons. For example, WT is more suitable for lower cost biomass resources such as forest residues, agricultural wastes, and even aquatic energy crops, which normally have very high moisture content. In addition, WT is capable of reducing the ash content of biomass as well, while DT is not. However, WT requires more advanced reactors capable to work at elevated pressures, and thus higher investments.

A quantitative comparison between WT and DT was reported in our previous study [4]. This has been performed for different criteria, including fuel properties such as proximate and ultimate analysis, grindability, and hydrophobicity. However, a comparison for the reactivity of these fuels in subsequent combustion is still missing, which is the motivation and objective of this study. The present work aims at investigating and comparing the combustion behaviors and kinetics of spruce wood torrefied by dry and wet method on the basis of the same solid product yield.

## 2. Materials and methods

Stem wood from Norway spruce was selected as feedstock since they are the main wood species in Norwegian forests. The wood samples, which were cut into cube with 1 cm side, were obtained from a local supplier in Trondheim, Norway. DT and WT procedures and characterization methods have been reported in our previous studies [2, 4]. Characteristics of raw and torrefied spruce used in this study are listed in Table 1. Thermogravimetric analysis (TGA), a proven technique for studying the biomass combustion in the kinetic regime [6-9], was employed in this work. TGA data collection was reported in another paper [10].

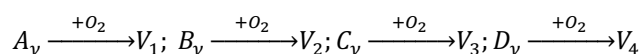
Because WT is different from DT in the reaction medium and pressure, it is challenging to carry out any comparison between them. However, since torrefaction is basically developed for upgrading of solid biomass fuels, the solid yield is a critical indicator. Keeping this in mind, it is reasonable to assume a common solid yield as a compatible basis for comparing fuel properties of solids obtained from WT or DT of the same biomass source. That was in our previous study that a common solid yield of 74% approximately was achieved by either DT in the at 275°C for 60 min, or WT at 222°C for 5 min, as well as well WT at 210°C for 30 min, as presented in Table 1.

Table 1. Characteristics of raw spruce and dry- and wet-torrefied spruce

| Torrefaction condition                | Solid yield <sup>a</sup> | Proximate analysis |                 |                 | Ultimate analysis |                |                |                | HHV <sup>b</sup> |
|---------------------------------------|--------------------------|--------------------|-----------------|-----------------|-------------------|----------------|----------------|----------------|------------------|
|                                       |                          | Ash <sup>a</sup>   | VM <sup>a</sup> | fC <sup>a</sup> | C <sup>a</sup>    | H <sup>a</sup> | N <sup>a</sup> | O <sup>a</sup> |                  |
| <b>Raw</b>                            | –                        | 0.23               | 86.50           | 13.27           | 50.31             | 6.24           | 0.07           | 43.38          | 20.42            |
| <b>DT-275</b><br>(DT, 275 °C, 60 min) | 74.0                     | 0.20               | 75.65           | 24.15           | 55.33             | 5.73           | 0.09           | 38.80          | 22.05            |
| <b>WT-210</b><br>(WT, 210 °C, 30 min) | 73.8                     | 0.08               | 82.56           | 17.36           | 55.27             | 5.99           | 0.07           | 38.67          | 22.35            |
| <b>WT-222</b><br>(WT, 222 °C, 5 min)  | 74.1                     | 0.10               | 81.51           | 18.39           | 55.75             | 6.05           | 0.06           | 38.14          | 22.64            |

<sup>a</sup> wt%, <sup>b</sup> MJ/kg

For kinetic modelling, a 4-pseudo-component model was adapted from Branca and Di Blasi [7, 11, 12] 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 conversion rate of these four reactions can be described by the following Arrhenius expression:

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

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  $i^{\text{th}}$  pseudo-component. Three first reactions represent the devolatilization of three main biomass components (hemicellulose, cellulose and lignin) and thus they are first order. The last reaction represents the char combustion, which is  $n^{\text{th}}$  order.

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:

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

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 as:

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

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, respectively; and  $N$  is the number of experimental points.

The fit quality between actual and modelled data is calculated as:

$$Fit (\%) = \left( 1 - \frac{\sqrt{\frac{OF}{N}}}{\left[ \left( \frac{d\alpha_j}{dt} \right)_{exp} \right]_{max}} \right) \times 100\%.$$

### 3. Results and discussions

#### 3.1. Thermogravimetric analysis

Figure 1 shows the thermogravimetric (TG) and differential thermogravimetric (DTG) curves for raw and torrefied spruce. It can be seen that the wet-torrefied spruce start decomposing from 150°C, which are earlier than both raw and dry-torrefied spruce. From 200°C, raw and dry-torrefied spruce are degraded. Among the tested samples, raw biomass is degraded fastest, which is due to that the raw biomass contains more hemicellulose than any torrefied biomass. Moreover, DTG curves show that the devolatilization peak of sample DT-275 is slightly shifted to a lower temperature, while the peaks of raw spruce and wet-torrefied spruce have similar positions. The peak height of sample WT-210 is the highest and that of sample DT-275 is the lowest, raw sample and sample WT-222 have the same heights in between. This observation indicates that higher dry torrefaction temperature (275°C) and longer residence time (60 min) may result to partial degradation of cellulose and show lower devolatilization peak.

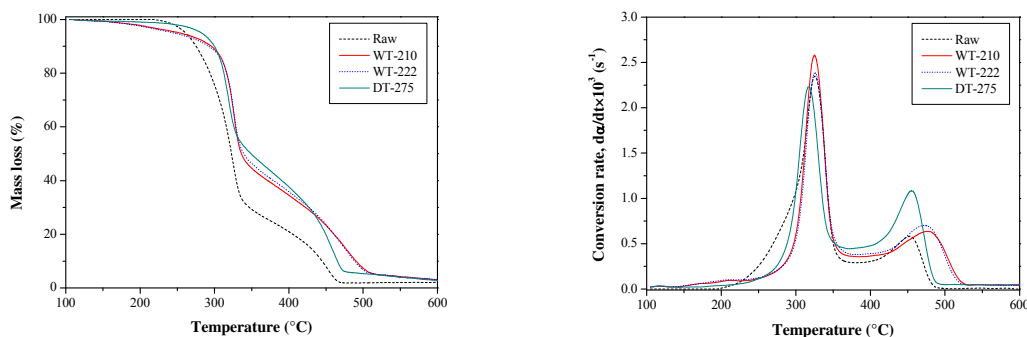


Figure 1. TG and DTG curves for raw and torrefied spruce

In the combustion stage, raw spruce exhibits the lowest peak and its combustion also ends earliest. The combustion stage of sample DT-275 shows the highest rate and lasts slightly longer than raw sample but still earlier than wet-torrefied samples. Samples WT-210 and WT-222 have similar combustion stages: slightly higher rate than raw sample but significantly lower than DT-275; moreover, their combustion stage last longest. In addition, between the two wet-torrefied fuels, sample WT-222 has slightly higher combustion peak than sample WT-210, which is opposite to the devolatilization peak.

### 3.2. Kinetic analysis

Table 2. Kinetic analysis for raw and torrefied spruce

|               |                        | Hemicellulose | Cellulose | Lignin   | Char     | Fit quality |
|---------------|------------------------|---------------|-----------|----------|----------|-------------|
| <b>Raw</b>    | $E$ (kJ/mol)           | 103.80        | 221.58    | 66.17    | 178.48   | 99.26%      |
|               | $A$ (s <sup>-1</sup> ) | 3.70E+07      | 2.43E+17  | 1.33E+03 | 5.92E+10 |             |
|               | $c$                    | 0.14          | 0.42      | 0.23     | 0.21     |             |
|               | $n$                    | 1             | 1         | 1        | 1.01     |             |
| <b>DT-275</b> | $E$ (kJ/mol)           | -             | 237.78    | 72.78    | 202.75   | 97.95%      |
|               | $A$ (s <sup>-1</sup> ) | -             | 1.32E+19  | 4.25E+03 | 3.12E+12 |             |
|               | $c$                    | 0.00          | 0.36      | 0.30     | 0.34     |             |
|               | $n$                    | -             | 1         | 1        | 1.01     |             |
| <b>WT-210</b> | $E$ (kJ/mol)           | 47.01         | 250.49    | 83.68    | 127.32   | 98.27%      |
|               | $A$ (s <sup>-1</sup> ) | 2.88E+02      | 9.17E+19  | 3.63E+04 | 4.27E+06 |             |
|               | $c$                    | 0.04          | 0.43      | 0.20     | 0.33     |             |
|               | $n$                    | 1             | 1         | 1        | 1.01     |             |
| <b>WT-222</b> | $E$ (kJ/mol)           | 51.49         | 247.92    | 81.30    | 134.06   | 98.21%      |
|               | $A$ (s <sup>-1</sup> ) | 9.53E+02      | 5.39E+19  | 2.26E+04 | 1.43E+07 |             |
|               | $c$                    | 0.04          | 0.40      | 0.22     | 0.34     |             |
|               | $n$                    | 1             | 1         | 1        | 1.01     |             |

Table 2 presents the kinetic analysis employing a 4-pseudo-component model for a quantitative evaluation of the effects of torrefaction method on the combustion reactivity of wood. A demonstration of the fit quality is also given in Figure 2. It can be seen from the table that the contribution factor of hemicellulose is reduced from 0.14 in raw spruce to 0.00 in sample DT-275, and 0.04 in sample WT-222 and WT-210. This indicates that hemicellulose is completely degraded during DT at 275 °C, while a small fraction of this component still remains in the fuels after WT at lower temperatures and shorter

holding times. The contribution factor of cellulose in wood is decreased but that of lignin is increased by DT. However, these changes are unpronounced after WT, i.e contribution factors of cellulose and lignin of wet-torrefied wood are quite similar to those for raw wood. Finally, the contribution factors of char in all torrefied woods are somehow equal (in the range of 0.33-0.34) and higher than raw wood (0.21).

Together with the reduction in contribution factor of hemicellulose, the activation energy and pre-exponential factor of this component are also significantly decreased after WT. The activation energy is reduced from 103.80 kJ/mol for raw spruce to 47.01-51.49 kJ/mol for wet-torrefied spruce, while pre-exponential factor is decreased from  $3.70\text{E}+07\text{ s}^{-1}$  for raw spruce to  $2.88\text{E}+02$  and  $9.53\text{E}+02\text{ s}^{-1}$ . On the other hand, the activation energy and pre-exponential factor of cellulose and lignin are increased after torrefaction (both dry and wet). This can lead to anticipation that the removal of hemicellulose during torrefaction can increase the crystallinity of cellulose and thus increase its activation energy in subsequent combustion. In addition, transformation/modification of lignin structure may occur and offer higher activation energy to this component. However, the activation energy and pre-exponential factor of cellulose and lignin in wet-torrefied fuels are higher than those in dry-torrefied fuel. It means that WT may have more effects on the structure modification of the two components than DT. Moreover, opposite trends are found for the activation energy and pre-exponential factor of char after DT and WT: they are increased after DT but decreases after WT.

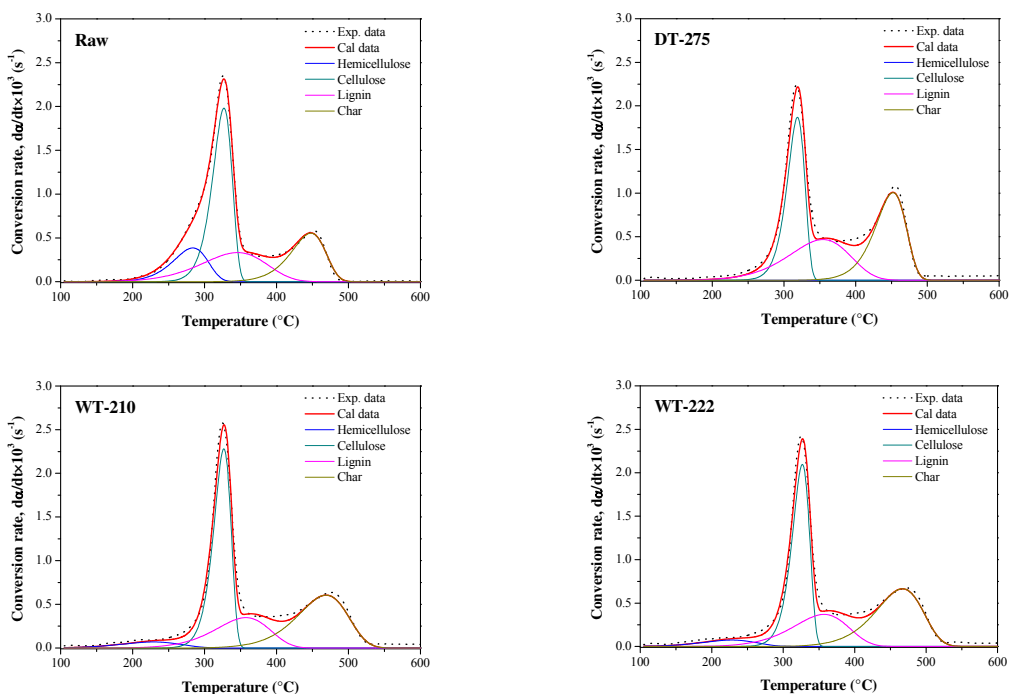


Figure 2. Curve fitting for raw and torrefied spruce

#### 4. Conclusion

Effects of torrefaction method, WT and DT, on the combustion kinetics of Norway spruce wood were thermogravimetrically investigated for samples torrefied in compatible conditions on the basis of a common mass yield. The results show that dry-torrefied wood is the least reactive in the devolatilization step but the most reactive in the char combustion, compared to wet-torrefied wood. Moreover, the wet-torrefied spruce has the longest combustion stage, among the tested fuels.

The kinetic analysis shows a dramatically reduction in the contribution factor of hemicellulose after WT, that of cellulose is even down to zero after DT at 275 °C. The contribution factor of cellulose is decreased but that of lignin is increased by DT; however, these changes are unpronounced after WT. Moreover, the contribution factors of char in torrefied woods are almost equal. The activation energy and pre-exponential factor of cellulose and lignin are increased after any torrefaction method, but they are higher in wet-torrefied fuels than in dry-torrefied one. Opposite trends are found for the activation energy and pre-exponential factor of char after DT and WT: they are increased after DT but decreased after WT.

#### 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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