

Torrefaction of spruce biomass under different conditions and characterising the formation of volatiles during thermodegradation

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Introduction

Wood heat treatment by torrefaction is used to improve wood properties, such as its decay durability and dimensional stability. These new properties result from chemical and physical modifications of wood cell wall polymers during thermal treatments. Knowledge of wood thermodegradation mechanisms is of great interest to reveal important parameters applicable to industrial/commercial wood heat treatment processes and will help design recommendations regarding operating temperature and residence time to improve and control properties of heat-treated wood (Candelier *et al.*, 2013).

Previous studies have shown that thermodesorption coupled to GC–MS is a robust and reliable method for identifying and quantifying volatile degradation products generated during wood torrefaction and pyrolysis (Candelier *et al.*, 2013, Chen *et al.*, 2018). Thus, this method can be used to obtain valuable information about the mechanisms of the thermodegradation of wood. One way of modifying the chemical and physical properties of biomass is to apply torrefaction as a pre-treatment (Chen *et al.*, 2021). Torrefaction is a thermal treatment that has been explored for the pretreatment of biomass to increase the heating value and hydrophobicity in the temperature range of 200–300 °C. The resulting product is intermediate between wood and charcoal and exhibits certain advantages when compared to the original material (dimensional stabilisation, increased biological resistance to decay, etc. (Almeida *et al.*, 2010; Chen *et al.*, 2015).

In conjunction with TGA/DSC and FTIR methods, the use of thermodesorption combined with GC–MS enables the identification and quantification of volatile degradation products formed during thermodegradation of wood, which allows obtaining indirect information about the stability of the polymers from which these products are formed.

This work aims to use thermodesorption in conjunction with GC–MS to study the kinetics of the formation and degradation of hemicellulose and cellulose molecules at different temperatures and torrefaction delay times.

Material and methods

Torrefaction and thermogravimetric analyses were performed using a thermal analyser TGA/DSC 2 (Mettler Toledo). TGA is an inevitable step in the experimental investigation of the thermal decomposition mechanism and is often used to determine the optimal process conditions. Samples weighing about 10 mg were heated in 70 μ L Al₂O₃ crucibles from room temperature to 200, 250, 300, and 350 °C at a heating rate of 30 °C/min and held for 60 and 120 min. Nitrogen gas with a flow rate of 20 mL/min was used as a carrier.

The presence of organic compounds in the raw and torrefied samples was identified and quantified by pyrolysis gas chromatography – mass spectrometry with thermal desorption (TD-GC/MS). The unit is equipped with TD2+ pyrolyser Gerstel (Muelheim, Germany) directly attached to the Agilent 7890 chromatograph (Agilent Technologies, USA) with MS detector Agilent 5975C. First, the sample was heated up in thermal desorption (TD) and consequently pyrolysed. It is a standard technique for Gerstel pyrolysis. TD2+: initial temperature of 50 °C (1 min), end temperature of 350 °C (5 min), heating rate 60 °C/min. CIS inlet: initial temperature 10 °C (0.1 min) – 300 °C (10 min), rate 10 °C/s. Separation of the released organic compounds was performed in a nonpolar column HP 5 ms (60 m, 250 μ m, 0.25 μ m), the temperature programme: 40 °C (4 min) to 310 °C (4 min), with a heating rate of 6 °C/min.

Results and discussion

Figure 1 shows that torrefaction temperature and duration have the most significant effect on sample mass loss. The results obtained in this study showed that torrefaction temperatures (300–350 °C) and residence time (60–120 min) have the greatest influence, mass loss was in the range of 73–76% at 350 °C and 42–55% at 300 °C was also the most affected by the dwell time. This showed that there was a higher reactivity or more extensive devolatilisation and decarbonisation of the hemicellulosic and cellulosic fraction of the biomass at 350 °C than at 300 °C and at a residence time of 2 h than 1 h. This is due to the initial decomposition of cellulose occurring above

270 °C along with hemicellulose, which is responsible for the higher mass loss during torrefaction of the sample at 300 and 350 °C.

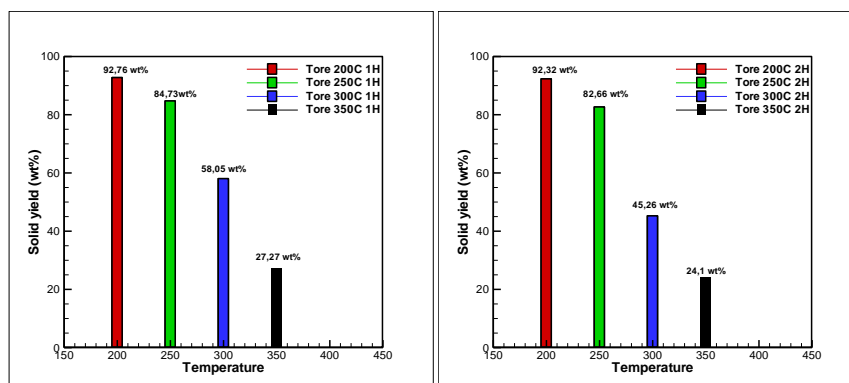


Figure 1 Mass loss caused by different torrefaction conditions (left-1h, right-2h) treatments in an inert atmosphere, in presence of N₂

FTIR analysis was performed to check the chemical changes in the biomass caused by torrefaction. FTIR spectra of raw and torrefied biomass are shown in Figure 2. In order to explain some important structural changes, some well-defined peaks were assigned to different functional groups as follows: 3300–3500 cm⁻¹ for O-H bond vibration, 2900 cm⁻¹ for C-H stretching in lignin, 1750–1800 cm⁻¹ for unconjugated C=O valence vibrations of aromatic rings, 1400–1350 cm⁻¹ for C-H bond vibrations, and 1000 cm⁻¹ for C-O, C=C, and C-C-O groups present in cellulose, hemicellulose, and lignin. The figure shows apparent changes in the IR spectrum of torrefied biomass compared to raw biomass, and a decrease in the intensity of all peaks was observed as the process conditions intensified. The decrease in intensity of various peaks in the torrefied samples compared to the virgin biomass confirms the structural changes of various chemical compounds present in the biomass, such as ketones, aromatic compounds, esters, aldehydes, etc.

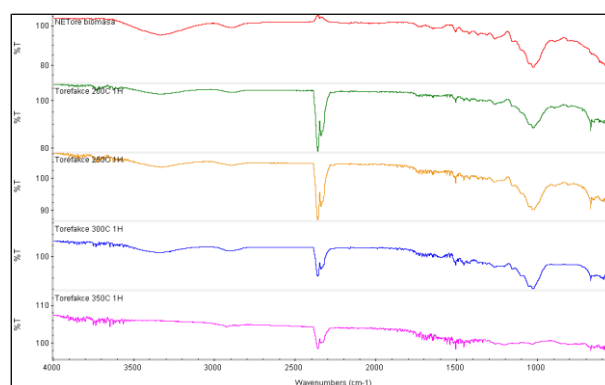


Figure 2 FTIR spectra of raw and torrefied biomass at 200, 250, 300, and 350 °C.

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