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Comparative study on the thermal behavior of untreated and various torrefied bark, stem wood, and stump of Norway spruce

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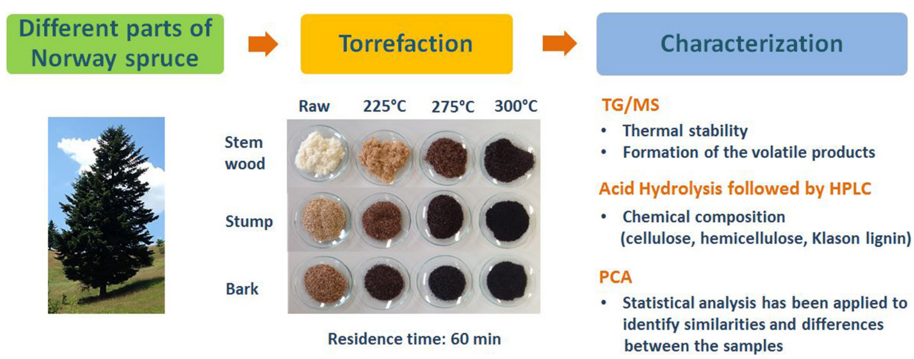
HIGHLIGHTS

- Comparative study on the thermal behavior of torrefied bark, stem wood and stump.
- Thermal stability of the samples is interpreted in terms of the chemical composition changes.
- The residence time has larger effect at higher torrefaction temperature.
- Hemicellulose side groups are split at milder torrefaction conditions compared to the galactomannan chain.
- Principal component analysis has been used to identify statistical correlations.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the torrefaction of different parts of Norway spruce (stem wood, bark, and stump) was studied. Three different torrefaction temperatures were applied: 225, 275, and 300 °C with 30 and 60 min isothermal periods. The thermal stability as well as the evolutions of the decomposition products of the untreated and torrefied samples were measured by thermogravimetry/mass spectrometry (TG/MS). The TG/MS results are interpreted in terms of the chemical composition, namely the cellulose, hemicellulose and Klason lignin content. The inorganic components of the samples were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) technique. It was found that the effect of torrefaction temperature was greater than the effect of residence time up to 275 °C, while at 300 °C the residence time had a significant influence on the composition of the torrefied samples due to the intensive decomposition of cellulose. Principal component analysis has been applied to find statistical correlations between the torrefaction temperature, the residence time, the chemical composition and the thermal parameters of the samples. The results of the principal component analysis confirmed that the chemical composition and hence the thermal properties of the studied samples changed to a greater extent at higher torrefaction temperature than at lower torrefaction temperature.
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Abbreviations

BA	bark
ST	stump
SW	stem wood
SW U	untreated stem wood
SW 225_60	torrefied stem wood obtained by torrefaction at 225 °C for 60 min isothermal period
DTG_{max}	maximum value of the −dm/dt curves
T_{start}	extrapolated temperature of the beginning of decomposition (on the DTG curve)
T_{peak}	temperature belonging to the DTG_{max}
T_{end}	extrapolated temperature of the end of cellulose decomposition (on the DTG curve)
Char	char residue at 900°C temperature
% m/m	mass percent
PCA	principal component analysis
TG/MS	thermogravimetry/mass spectrometry

1. Introduction

The Paris Agreement aims to involve all nations to combat climate change and to keep the global temperature rise this century well below 2 °C above the pre-industrial levels [1]. The Norwegian national energy strategy has a goal of reducing the domestic greenhouse gas emissions by 30% by 2020, and the long-term goal was to become climate neutral by 2050 [2], which was changed to 2030 later. This strategy indicates that the utilization of lignocellulosic biomass and biofuels (bioethanol, biodiesel, and biogas), as sources of energy, will have to increase substantially in the next few years. Biomass is a carbonaceous renewable energy source, and therefore, it has attracted considerable attention as a replacement for fossil fuels.

Various thermal conversion technologies exist to produce bioenergy from lignocellulosic biomass, such as combustion [3], gasification [4], pyrolysis [5], as well as co-firing of biomass and coal [6]. However, in energetic applications the properties of raw lignocellulosic materials create challenges for their efficient utilization. One of the main difficulties is the high moisture content of the untreated biomass, which reduces the efficiency of the conversion process and increases the fuel transportation costs. Some of the other problems with raw biomass materials are the following: low calorific value, low energy density, hydrophilic nature, and high oxygen content. Furthermore, the transportation, storage, and grinding are costly due to the low density and the fibrous nature of lignocellulose. Torrefaction is a mild thermal treatment method performed between 200 and 300 °C in an inert atmosphere for reducing the mentioned disadvantages [7]. A major goal of torrefaction is to upgrade the quality of the solid product by decreasing the moisture content and increasing the hydrophobicity, grindability, and energy density of biomass. The volumetric energy density of torrefied biomass can be increased by a combined grinding and pelletizing step after torrefaction [8,9]. In this way, the torrefied material can be handled and stored like coal.

While pelletization of lignocellulose is an established technology, torrefaction is still a developable process for the production of solid energy carriers. Recent research papers focus on the viability of torrefaction as a part of integrated approaches [10–13]. The major technical challenges are the predictability and consistency of the product quality, the flexibility related with using different input materials, and the densification of torrefied biomass [14]. The applied torrefaction condition (temperature and residence time) and the moisture content have significant influences on the pellet production (e.g., compression and friction energy) and pellet quality (e.g., strength) [15]. In order to estimate the feasibility of a commercial torrefaction system in a particular region, local and abundant biomass resources should be investigated.

During tree harvesting, stem wood is the main product, while the other parts of the tree (including bark and stump) are considered as by-products. According to the literature, stump constitutes 23–25% of the stem volume of a coniferous tree [16] and bark can reach 6–20% of the total volume of the stems [17]. These forest residues represent an abundant and underutilized source of renewable energy. Many studies have been carried out on the thermal characteristics of stem wood [7,18,19]. These papers focus on the effect of torrefaction on the properties of the solid product, such as mass yield, energy content, hydrophobicity, grindability, and particle-size distribution. Only a few papers are available on the thermal decomposition of forest residues, such as bark and stump. The thermal behavior of bark and wood of Eucalyptus tree has been studied during torrefaction [20,21]. Almeida et al. [20] concluded that the mass loss is an excellent indicator of the treatment severity. It was suggested [21] that the most feasible torrefaction temperature was between 298 and 310 °C for Eucalyptus wood and bark. The torrefaction of stump has been studied focusing on the kinetic evaluation [22] and the thermogravimetric results [16]. In the literature, there is a lack of papers, which compare the thermal behavior of different parts of the coniferous tree during torrefaction. A profound understanding of the thermal behavior of stump and bark is essential for the efficient utilization of these abundant energy sources in the future.

Thermoanalytical methods are suitable to determine similarities and differences between the compositions of the lignocellulosic materials without separating the main fractions [23]. Several factors may influence the thermal decomposition of lignocellulosic materials. The alkali ions are known to exert a great influence on the thermal decomposition of cellulose [23–25] and lignin [23,26,27]. As a consequence of the difference in the relative amounts of cellulose, hemicellulose, lignin, extractives, and inorganic materials, the different biomass materials behave differently during thermal decomposition. Therefore, monitoring the changes in the chemical composition is essential during torrefaction. Nevertheless, comparison of chemical analysis and thermal analysis results is rarely carried out in the biomass literature.

The aim of this work has been to gain information about the thermal behavior of untreated and various torrefied bark, stem wood and stump of Norway spruce, which is the most abundant wood species in Norway and in the Northern hemisphere. The thermal stability and the formation of the volatile products of untreated and torrefied samples have been studied by thermogravimetry/mass spectrometry (TG/MS). The main differences between the thermal decomposition of the studied samples are interpreted in terms of the chemical composition (cellulose, hemicellulose and Klason lignin) with the goal of understanding the mechanisms of the decomposition of biomass components during torrefaction. The obtained data were evaluated by principal component analysis (PCA) to identify correlations between the temperature of torrefaction, the residence time, the chemical composition and the thermal behavior of the studied samples.

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