INFLUENCE OF TORREFACTION PRETREATMENT ON THE COMPOSITION AND DECOMPOSITION OF LIGNOCELLULOSIC MATERIALS

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DOCTORAL THESIS

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LIST OF ABBREVIATIONS

AD  Anaerobic digestion
BA  Bark
BL  Black locust
BL 200 Torrefied black locust obtained by torrefaction at 200 °C
BL 200_W Washed torrefied black locust wood obtained by torrefaction at 200 °C
BL U Untreated black locust
Char Char residue at 950 °C temperature
CHP Combined heat and power
DTG Derivative thermogravimetric curve
DTG$_{\text{max}}$ Maximum value of the DTG curve (maximum decomposition rate)
FC  Fixed carbon
HHV Higher heating value
MC  Moisture content
PCA Principal Component Analysis
Py-GC/MS Pyrolysis-gas chromatography/mass spectrometry
RS  Rape straw
ST  Stump
SW  Stem wood
SW 225_60 Torrefied stem wood obtained by torrefaction at 225 °C for 60 minutes isothermal period
T$_{1\%}$ Temperature belonging to the 1% mass loss of the dried samples
T$_{\text{end}}$ Extrapolated temperature of the end of cellulose decomposition (on the DTG curve)
T$_{\text{peak}}$ Temperature of the maximum of the DTG curve
T$_{\text{start}}$ Extrapolated temperature of the beginning of decomposition (on the DTG curve)
TG/MS Thermogravimetry/mass spectrometry
VM  Volatile matter
WS  Wheat straw
LIST OF PUBLICATIONS

This thesis is based on the following scientific papers, which will be referred to in the text by their roman numerals. The papers are appended to the end of the thesis.


VI. **E. Barta-Rajnai, B. Babinszki, E. Jakab, Z. Sebestyén, Zs. Czégény: On the significance of chlorine and potassium content of lignocellulose during torrefaction.** Manuscript
Other related papers


Other papers


Oral presentations


**Poster presentations**


Conference proceedings


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1 Introduction

Lignocellulose is a primary type of renewable energy source, which is an abundant carbonaceous energy source on the Earth; hence, it has attracted considerable attention as a replacement for fossil fuels. The Paris Agreement aims to involve all nations to fight climate change and to keep the global temperature rise this century well below 2 °C above the pre-industrial levels [UNFCCC]. This strategy indicates that the utilization of lignocellulosic biomass and biofuels (bioethanol, biodiesel, and biogas), as sources of renewable energy, will have to increase significantly in the next few years.

Various thermal conversion technologies exist to produce bioenergy from lignocellulose, such as combustion, gasification, pyrolysis, as well as co-firing of biomass and coal. However, in energetic applications the properties of untreated lignocellulosic materials, such as the high oxygen content, low calorific value, low energy density, hydrophilic nature and high moisture content create challenges for their efficient utilization. Pretreatment of biomass is necessary prior to the thermochemical conversion processes; which can be mechanical, thermal, and chemical treatment and various combinations of these methods (Liu et al., 2017). Each pretreatment has its own effect; therefore, it is not possible to define the best pretreatment method as it depends on many factors, such as the type of lignocellulose and the desired products. Among many pretreatment technologies, torrefaction, a thermal treatment of biomass in the temperature range of 200 °C to 300 °C in the absence of oxygen has gained continuous interests in the past decade.

In order to estimate the feasibility of a commercial torrefaction system in a particular region, local and abundant biomass resources should be investigated. A profound understanding of the thermal behavior of the local biomass materials is essential for the efficient utilization of these energy sources in the future. Thermal analysis and pyrolysis are suitable methods to determine similarities and differences between the compositions of the lignocellulosic materials without separating the main fractions. The coupled techniques, such as thermogravimetry/mass spectrometry and pyrolysis-gas chromatography/mass spectrometry can provide detailed information about the volatile decomposition products of the samples.
1.1 Objectives of the thesis

The subject of the present thesis is torrefaction, which is a mild thermal pretreatment of lignocellulosic biomass prior to thermochemical conversion processes. The general aim of my work was to get new information about the thermal degradation process of torrefied herbaceous biomass materials, hardwood, and softwood with the goal of deeper understanding the structural changes taking place during torrefaction in the main biomass components. The characterization of the samples was carried out by both carbohydrate and lignin content determination and thermal decomposition techniques to get more comprehensive knowledge about the mechanisms of torrefaction.

The present thesis contains the results of the following studies:

- The first part includes the comprehensive compositional analysis of untreated and torrefied herbaceous materials (rape straw and wheat straw) and hardwood (black locust wood) samples. The impact of the reduction of inorganic ion contents on the thermal degradation process during torrefaction was investigated in detail. Furthermore, the effect of torrefaction on the biomass chlorine content was studied.
- The second part presents a comparative study on the composition and decomposition of untreated and various torrefied bark, stem wood, and stump samples of softwood (Norway spruce). Additionally, the effect of torrefaction on physiochemical characteristics of the stem wood, stump, and bark samples was investigated.

The work was carried out at the Renewable Energy Research Group of the Institute of Materials and Environmental Chemistry, Hungarian Academy of Sciences in cooperation with SINTEF (Trondheim, Norway) and Norwegian University of Science and Technology (NTNU, Trondheim, Norway). Torrefaction experiments of black locust wood, rape straw, and wheat straw were performed in Hungary, while the torrefaction experiments, ultimate and proximate analysis, and the particle size distribution study of Norway spruce were performed at SINTEF Energy Research and Norwegian University of Science and Technology in Norway. All other experiments (carbohydrate and lignin content determination, TG/MS, Py-GC/MS) and statistical calculations (PCA) presented in this thesis were performed in the Institute of Materials and Environmental Chemistry of the Research Centre for Natural Sciences (Hungarian Academy of Sciences) in Hungary.
2 Background

2.1 Lignocellulosic biomass

Lignocellulosic biomass is a carbonaceous renewable energy source, which involves various materials including herbaceous plants, energy crops, agricultural residues, woody biomass, forestry residues, etc. The major components of lignocellulose are cellulose, hemicellulose, and lignin (Figure 1). Cellulose is the fibrous component of plants, which ensures the strength, stability, and flexibility of the cell wall. Cellulose fibres are covered by lignin in order to be impermeable, rigid, and resistant to microbes and chemicals. Lignin and cellulose are chemically bonded by different types of hemicelluloses (Brandt et al., 2013). There are other minor constituents, such as extractives (resins, fats, terpenes, and flavonoids) and inorganic materials (calcium, potassium, magnesium, carbonates, silicates, oxalates, chlorides, and phosphates). Herbaceous plants, agricultural residues, and energy crops usually have a higher mineral content than wood (Leijenhorst et al., 2016, Monti et al., 2008). The relative amount of each compound varies from species to species, depending on the cell type and in response to environmental conditions (Vassilev et al., 2012).

![Figure 1 Composition of lignocellulose (Tumuluru et al., 2011).](image-url)
The typical composition of some biomass materials are summarized in Table 1. The carbohydrates give around 57-68% of the total dry mass of lignocelluloses. The main building blocks of polysaccharides of softwood are glucan and mannan, while in case of hardwoods, and herbaceous materials they are glucan and xylan.

<table>
<thead>
<tr>
<th>Species</th>
<th>Glucan</th>
<th>Xylan</th>
<th>Galactan</th>
<th>Arabinan</th>
<th>Mannan</th>
<th>Lignin</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spruce</td>
<td>44.0</td>
<td>6.0</td>
<td>2.3</td>
<td>2.0</td>
<td>13.0</td>
<td>27.5</td>
<td>1</td>
</tr>
<tr>
<td>Birch</td>
<td>41.5</td>
<td>15.0</td>
<td>2.1</td>
<td>1.8</td>
<td>3.0</td>
<td>25.2</td>
<td>2</td>
</tr>
<tr>
<td>Bagasse</td>
<td>39.0</td>
<td>21.8</td>
<td>0.8</td>
<td>1.8</td>
<td>N.D.</td>
<td>24.8</td>
<td>3</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>32.6</td>
<td>20.1</td>
<td>0.8</td>
<td>3.3</td>
<td>0</td>
<td>24.2</td>
<td>4</td>
</tr>
</tbody>
</table>

N.D. not detected, ¹Hackl and Harvey, 2015, ²Chandel et al., 2010, ³Templeton et al., 2010, ⁴Linde et al., 2008

2.1.1 Cellulose

Cellulose, the most abundant organic polymer on Earth, is a homopolymer of β-D-glucopyranose units, which are connected with β-1,4 glycosidic bonds. In the chain direction, the repeating unit is a disaccharide, cellobiose (Figure 2), and every second glucose unit is rotated by 180° to the main axis of the chain. Cellulose is a high molecular weight polysaccharide, the average degree of polymerization ranges from 500 units for pulp to more than 15000 units for cotton (Sjöström, 1993).

![Cellobiose unit](image)

**Figure 2** Cellobiose is the repeating unit of cellulose (Moldoveanu, 1998).

Each glucose unit has three hydroxyl groups at C2, C3 and C6 positions. These hydroxyl groups play an important role in the crystallinity as well as the solubility issues of cellulose. The hydroxyl groups form both intramolecular and intermolecular hydrogen bonds in the cellulose molecule. Intramolecular hydrogen bonds are formed between the hydroxyl group of C3 and the oxygen of C5 within
the adjacent glucose molecule. Bundles are formed from cellulose fibers, which are stabilized by intermolecular hydrogen bonds between the cellulose chains (Sjöström, 1993). These bundles are aggregated together in the form of microfibrils, in which highly ordered crystalline sections and less ordered amorphous sections are combined. Microfibrils form macrofibrils and then cellulose fibers. Cellulose is hydrophilic, however insoluble in water and alkalis (Fengel and Wegener, 1989).

2.1.2 Hemicellulose

The hemicelluloses differ from cellulose by the composition of various sugar units, by the lower degree of polymerization (about 200 for hardwood and 100 for softwood) and by the branching of the chain molecules (Fengel and Wegener, 1989). The amount of hemicelluloses in the dry lignocelluloses is usually between 15-30%, which mainly consists of various hexoses, such as D-glucose, D-mannose, D-galactose and pentoses, such as D-xylose and D-arabinose (Sjöström, 1993). The hemicellulose units can be acetylated, i.e. the hydroxyl groups either at C2 or C3 positions are replaced partially by O-acetyl groups. The O-acetyl groups occur to the extent of 3–17% in hemicelluloses and have the highest content in hardwoods. The acetyl groups are much more easily cleaved by alkali than by acid, and released as acetic acid (Ren and Sun, 2010). Hemicellulose is more hydrophilic than cellulose. The composition and structure of hemicelluloses are different in herbaceous plants (Figure 3), hardwoods, and softwoods (Figure 4). Arabinoxylans are the main hemicellulose units of herbaceous plants, containing arabinose as the primary side groups, which are attached to the xylan backbone. The major hemicellulose unit of hardwood is O-acetyl-4-O-methyl-glucoronoxylan, which has a β-1,4 linked xylan backbone with 4-O-methylglucuronic acid and glucuronic acid as primary side groups attached to the backbone structure. About 70% of the xylose residues contain an O-acetyl group at C2 or C3 positions. Hemicellulose in softwoods contains mainly of galactoglucomannans. The main chain of galactoglucomannans are built up from β-1,4-linked D-glucopyranose and D-mannopyranose backbone with α-1-6-linked D-galactopyranose groups attached to some of the D-mannopyranose units (Fengel and Wegener, 1989, Zhou et al., 2016).
Herbaceous plants:
arabinoxylan

![Figure 3 Structure of hemicellulose in herbaceous plants.](image)

Hardwoods:
4-O-methyl-glucoronoxylan

![Figure 4 Structure of hemicelluloses in hardwoods and softwoods.](image)

Softwoods:
galactoglucomannan

![Figure 4 Structure of hemicelluloses in hardwoods and softwoods.](image)
2.1.3 Lignin

Lignin is a high molecular weight polymer, which has a complex three-dimensional cross-linked structure. The main building blocks of lignin are 4-hydroxyphenylpropane, guaiacylpropane, and syringylpropane subunits, which have mostly hydroxyl groups on the propane groups. These monolignol units are differing in their degree of methoxylation. During the biosynthesis of lignins, the precursors are p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (Figure 5). The relative abundance of monolignols and their linkages varies depending on the biomass types. Coniferyl alcohol is the main lignin monomer found in softwoods. Both coniferyl and sinapyl alcohols are the building blocks of hardwood lignin. Herbaceous plants (e.g. agricultural residues and energy crops) are built up of all three building monomers (Sjöström, 1993, Zhou et al., 2016).

The building blocks of lignin are connected with different linkages; the seven major linkages in lignin identified by Dorrestijn et al. (2000) are the following: β-O-4, α-O-4, 4-O-5, 5-5, β-β, β-1, and β-5.

![Figure 5 Structural segment and building units of lignin.](Wikimedia Commons)
2.1.4 Lignocellulosic materials studied

Wheat straw
Wheat (*Triticum aestivum*) is one of the main crops of the World with an annual production of 761 million metric tons reported for 2017 (FAO, 2018). Wheat straw, as an abundant byproduct of wheat harvesting, is considered as one of the potential raw materials for bioenergy production. The ratio of grain to straw is about 1.0:1.3 on dry weight basis (Milbrandt, 2005). In 2017, 5237 thousand tons of wheat grain was harvested in Hungary according to the Hungarian Central Statistical Office. Approximately 30-40% of the straw is left on the field for soil protection; hence more than 3 million tons/year surplus of wheat straw could be collected in Hungary.

Rape straw
Rapeseed (*Brassica napus*) is grown for the production of edible vegetable oils, biodiesel, and animal feed (Jahreis and Schäfer, 2011). Global rapeseed production has undergone continuous growth over the past decades; an annual harvest of oilseed production is around 450 million tons, which accounts for 20% of the world grain production (Carré and Pouzet, 2014). There are five major producers of rapeseed in the World: Canada, China, India, Germany, and France (FAOSTAT, 2017, Applewhite, 1993). In Hungary, the amount of harvested rape seed increased from 290 thousand tons to 680 thousand tons from 2004 to 2014; while in 2016, 882 thousand tons of rape seed was harvested according to the Hungarian Central Statistical Office. The increased production of rapeseed has resulted in a large surplus of rape straw, which can be a favorable source for energy production.

Black locust wood
Black locust wood (*Robinia pseudoacacia*) is the third most planted hardwood tree in the world, only eucalypts and hybrid poplars are more cultivated (DeGomez and Wagner, 2001). It is a North American species, which is adapted in Europe, temperate Asia, Australia, New Zealand, northern and southern Africa and temperate South America. It is cultivated worldwide because of the high-quality wood properties, high tolerance to many sites and climates; however this nitrogen fixing deciduous tree is very invasive (Vítková et al., 2015, Vítková et al., 2017). Its fragrant white blossoms are a nectar source for bees, yielding a high quality honey. Some parts of the wood are toxic, especially the bark (Veitch et al., 2010). Black locust wood was introduced into Hungary between 1710 and 1720 (Keresztesi, 1983). At present, the area of black locust forests is representing almost 24% of the total forest area (Rédei et al., 2008; Hungarian Central Statistical Office, 2018); half
of all black locust forests in the European Union can be found in Hungary (Hungarian Spectrum Website, 2018). It is grown mainly in the south and southwest Transdanubia, in the Danube-Tisza interfluve and in north-east Hungary. The area planted with black locust wood is still increasing (Rédei and Osvath-Bujtas, 2001). The black locust tree (Hungarian acacia) and its acacia honey became a Hungaricum in 2014 (Silvanus Forestry Website, 2018). Black locust wood can be a promising biomass for future energy production because of its high growth rate and promising fuel characteristics, such as high heating value and low ash content.

**Norway spruce**

Norway spruce (*Picea abies*) is a large evergreen softwood tree, which is the most important timber species in Central Europe, native to montane and boreal European forests, ranging from the European Alps to the Balkan and Carpathian Mountains, and extending north into Scandinavia and northern Russia. It is widely distributed in the United States, Canada and Alaska (Barnes and Wagner, 2003, Seppa et al., 2009). This tree is one of the most economically important coniferous species in Europe, it is used in the pulp and paper- and the sawmill industries, furthermore is esteemed as a source of tonewood for musical instruments. It is also widely planted for use as a Christmas tree (Brändström, 2001). Early growth of Norway spruce is slow, increasing to maximal rates from 20 to 60 years of age, and it lives up to 300 to 400 years (Köstler, 1956). During tree harvesting, stem wood is the main harvested 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 (Tran et al., 2013) and bark can reach 6-20% of the total volume of the stems (Liepiņš and Liepiņš, 2015). These forest residues represent an abundant and underutilized source of renewable energy.

### 2.2 Conversion of biomass into energy

Biomass is a primary type of renewable energy source, which is one of the most abundant energy sources on the Earth. Adoption and utilization of renewable energy sources are important for the modern society, considering the ever increasing energy demands and severe global warming due to the use of fossil fuels. 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 (UNFCCC, 2017). This agreement 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 energy source, and therefore, it has attracted considerable attention as a replacement for fossil fuels. 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 of lignocelluloses are costly due to the low energy density and the fibrous nature (Gupta et al., 2014).

Lignocelulosic materials can be converted via different conversion routes into various energy sources (Figure 6), which can be in the form of solid, liquid or gas (Basu, 2013). Biochemical conversion of lignocelluloses requires the use of bacteria, microorganisms and enzymes to break down biomass into gaseous or liquid fuels, such as biogas or bioethanol (Demirbas, 2009). The most general biochemical technologies are anaerobic digestion and fermentation (Basu, 2013). Several thermal conversion technologies exist to produce bioenergy from lignocellulosic biomass, such as combustion (Hupa et al., 2017), gasification (Sarker et al., 2015), liquefaction (Chornet and Overend, 1985), pyrolysis (Kan et al., 2016), as well as co-firing of biomass and coal (Miedema et al., 2016).

![Figure 6 Classification of the main biomass conversion routes (Gent et al., 2017). (CHP: Combined heat and power)](image_url)
2.2.1 Pyrolysis of biomass

Three main processes are applied within the thermochemical conversion: fast pyrolysis, slow pyrolysis (carbonization), and gasification. Table 2 shows process conditions and product yields obtained from these mentioned thermochemical processes. Gasification is used to convert lignocelluloses or other carbon containing materials into synthetic gas. The synthetic gas can then be used in a gas engine for the production of electricity and heat (Richardson Y et al., 2015). Pyrolysis is used to convert a solid material into condensable oil, carbonaceous char, and gases. Charcoal is produced generally by slow pyrolysis and it has been commonly used for a wide range of purposes, such as activated carbon and charcoal briquettes as a household or grill fuel, however the most important use is as a metallurgical fuel. The slow heating rate maximizes the production of the solid carbonaceous material and production of water from the dehydration reactions. The fast pyrolysis method was developed in the 1960’s, which is a high temperature process, in which biomass is rapidly heated in the absence of oxygen using very small particles (less than 2 mm). The pyrolysis oil (also known as tar) is a mixture of chemicals that are released in vapor phase. Fast pyrolysis generates more vapors and aerosols and less charcoal than slow pyrolysis. To minimize the secondary reactions, liquid production requires very low vapor residence time (typically 1s), while acceptable yields can be enhanced at residence times of up to 5s if the vapor temperature is set below 400 °C (Bridgewater et al., 1999). The maximum liquid yields can be reached with high heating rates, at reaction temperatures around 500 °C (Pecha and Garcia-Perez, 2015, Bridgewater et al., 1999). The dark brown liquid obtained has a heating value about half of that of conventional fuel oil. The pyrolysis of lignocellulosic biomass, such as straw and wood, is now considered a promising way to generate renewable fuels and chemical products. In the last decades, an increasing interest can be observed for torrefaction, which is a milder form of slow pyrolysis.
Table 2 Typical process conditions and product yields in wt%, obtained from different types of thermochemical processes (Ronsse, 2016).

<table>
<thead>
<tr>
<th></th>
<th>Dry processes</th>
<th>Wet processes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fast pyrolysis</td>
<td>Carbonisation (slow pyrolysis)</td>
</tr>
<tr>
<td>Temperature/Heating rate</td>
<td>– 500°C</td>
<td>&gt; 400°C</td>
</tr>
<tr>
<td></td>
<td>Fast, up to 1000°C/min</td>
<td>&lt; 80°C/min</td>
</tr>
<tr>
<td>Reaction time/Pressure</td>
<td>Few seconds</td>
<td>Hours to days</td>
</tr>
<tr>
<td></td>
<td>Atmospheric (and vacuum)</td>
<td>Atmospheric (or elevated up to 1 MPa)</td>
</tr>
<tr>
<td>Medium</td>
<td>Oxygen-free</td>
<td>Oxygen-free or oxygen-limited</td>
</tr>
<tr>
<td>Bio-oil</td>
<td>75%</td>
<td>30%</td>
</tr>
<tr>
<td>Permanent gases</td>
<td>13%</td>
<td>35%</td>
</tr>
<tr>
<td>Char (solids)</td>
<td>12%</td>
<td>35%</td>
</tr>
</tbody>
</table>


2.2.2 Torrefaction

Torrefaction is a mild thermal treatment method performed between 200 and 300 °C in an inert atmosphere for the partial conversion of biomass (Chen et al., 2015). The process name is adopted from the French “torrefier”, which is roasting of coffee beans at lower temperature in the presence of air (oxygen). The principles of torrefaction were first reported regarding to woody biomass in 1930’s (Bergman et al., 2005_a). In the 1980’s, studies reported that torrefied wood could be an efficient energetic source for combustion as well as for gasification (Armines, 1981, Bartholin et al., 1985, Beaumont et al., 1985, Bourgois and Guyonnet, 1986). Since then, torrefaction has gained attention again; when it was recognized that torrefied wood could be used as a reducing agent in metallurgic applications (Bergman, 2005). In the last decades, the number of publications has increased rapidly due to
the recognition that the thermal pretreatment has an economic significance in the enhancement of efficient biomass conversion technologies. There are different process settings applied for the various reactor models; however, the basic concept for torrefaction and densification routes is the same and usually incorporates heat integration, as can be seen in Figure 7. The thermal energy required for the drying and torrefaction process can be implemented in the following ways: recirculation of flue gas for direct or indirect process heating, recirculation of torrefaction gas for process heating, and recirculation of steam for direct or indirect process heat. It is important to dry the biomass before it goes into the torrefaction reactor, since moisture entering the torrefaction reactor results in wet torrefaction gas, which lowers the adiabatic flame temperature. For this reason, the moisture content of incoming biomass to the torrefaction reactor should not exceed 15%. One possibility to increase the global efficiency is adding residual heat from another process (e.g. gas engine, waste incinerator) to dry the lignocellulose feedstock (Koppejan et al., 2012).

![Figure 7 Process diagram of torrefaction (Acharya et al., 2015).](image)

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 (Bergman and Kiel, 2005). The torrefaction processes can be classified into light, mild, and severe torrefaction, where the temperatures are approximately 200-235, 235-270, and 270-300 °C, respectively. The torrefaction
aims to maximize the energy and mass yields by minimizing oxygen to carbon and hydrogen to carbon ratios; generally the torrefied product retains about 70% of the initial mass and up to 90% of its initial energy. About 30% of the initial mass is converted into volatiles, which contains about 10% of the energy of the lignocellulose (Boateng and Mullen, 2013). Slow heating rate is essential during torrefaction to increase the solid yield of the process. Typically the heating rate of torrefaction is less than 50 °C min\(^{-1}\). The volumetric energy density of torrefied biomass can be improved by a combined grinding and pelletizing step after torrefaction (Mišiljenovic et al., 2014, Khalil et al., 2013). In this way, the torrefied material can be handled and stored like coal. Torrefied pellet is a high quality fuel, which has characteristics compatible with coal, as Table 3 illustrates. During torrefaction, the moisture content of biomass is removed and the acidic functional groups of the hemicellulose component are cleaved. These reactions result in the increase of the calorific value and the higher stability against biodegradation of the torrefied biomass.

### Table 3

<table>
<thead>
<tr>
<th>Property</th>
<th>Wood</th>
<th>Wood pellets</th>
<th>Torrefaction pellets</th>
<th>Charcoal</th>
<th>Coal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content (% wt)</td>
<td>30 – 46</td>
<td>7 – 10</td>
<td>1 – 5</td>
<td>1 – 5</td>
<td>10 – 15</td>
</tr>
<tr>
<td>Lower heating value (MJ/kg)</td>
<td>9 – 12</td>
<td>15 – 16</td>
<td>20 – 24</td>
<td>30 – 32</td>
<td>23 – 28</td>
</tr>
<tr>
<td>Volatile matter (% db)</td>
<td>70 – 75</td>
<td>70 – 75</td>
<td>55 – 65</td>
<td>10 – 12</td>
<td>15 – 30</td>
</tr>
<tr>
<td>Density (kg/l) Bulk</td>
<td>0.2 – 0.26</td>
<td>0.55 – 0.75</td>
<td>0.75 – 0.85</td>
<td>~ 0.20</td>
<td>0.8 – 0.85</td>
</tr>
<tr>
<td>Energy density (GJ/m(^3)) (bulk)</td>
<td>2.0 – 3.0</td>
<td>7.5 – 10.4</td>
<td>15.0 – 18.7</td>
<td>6 – 6.4</td>
<td>18.4 – 23.8</td>
</tr>
<tr>
<td>Dust</td>
<td>Average</td>
<td>Limited</td>
<td>Limited</td>
<td>High</td>
<td>Limited</td>
</tr>
<tr>
<td>Hydroscopic properties</td>
<td>hydrophobic</td>
<td>hydrophobic</td>
<td>hydrophobic</td>
<td>hydrophobic</td>
<td>hydrophobic</td>
</tr>
<tr>
<td>Biological degradation</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Grindability</td>
<td>Poor</td>
<td>Poor</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Handling</td>
<td>Special</td>
<td>Special</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Quality variability</td>
<td>High</td>
<td>Limited</td>
<td>Limited</td>
<td>Limited</td>
<td>Limited</td>
</tr>
</tbody>
</table>

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 (Adams et al., 2015, Sermyagina et al., 2016, Rudolfsson et al., 2016, Chai and Saffron, 2016). 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 (Rudolfsson et al., 2017). The applied torrefaction condition (temperature and residence time) and the moisture content
have significant influence on the pellet production (e.g., compression and friction energy) and pellet quality (e.g., strength) (Rudolfsson et al., 2015). In order to estimate the feasibility of a commercial torrefaction system in a particular region, local, inexpensive and abundant biomass resources such as agricultural and forest residues should be investigated. However, not all biomass resources are suitable as a feedstock for torrefaction. In addition, the torrefaction process needs to lead to substantial improvements in the physical properties of the biomass to enable for further processing. The chemical composition of the biomass material is an important factor, the quality and composition of torrefied biomass is influenced by the properties of the raw lignocelluloses. Because of the relatively low temperature of the torrefaction, the unfavourable inorganic components of lignocelluloses (alkali metal and chloride ions, Sulphur and nitrogen compounds, heavy metal ions) remain in the torrefied product after heat treatment (Keipi et al., 2014).

Recently, the definition of torrefaction has been extended to include studies carried out in the presence of oxygen and carbon dioxide (Eseltine et al., 2013, Thanapal et al., 2014, Saadon et al., 2014, Chen et al., 2014), and under elevated pressures (Wannapeera and Worasuwannarak, 2012, Nhuchhen and Basu, 2014). Furthermore, within the last decade, several studies investigated the effect of wet torrefaction process (Figure 8), which is a treatment of biomass in hydrothermal media or hot compressed water at temperatures within 180–260 °C (Yan et al., 2010, Bach et al., 2013, Bach et al., 2015).

![Figure 8 Process diagram of wet torrefaction](Acharya et al., 2015).
Wet torrefaction is developed from the concept of hydrothermal carbonization. During wet torrefaction, the samples are mixed with water prior to the reaction. The untreated material must be mixed with enough water to completely submerge the solid biomass (the biomass: water ratio is 1:6) before the process. This process is more complicated than conventional torrefaction, but it offers a number of advantages compared to dry torrefaction (Acharya et al., 2015, Bach and Skreiberg, 2016):

- it is capable to utilize wet (>15%) biomass resources;
- this process does not require predrying of the raw biomass;
- the fuel properties of the solid product are better (such as increased HHV, better grindability, and improved hydrophobicity);
- in order to produce the same solid yield, wet torrefaction needs significantly lower temperature and shorter residence time than dry torrefaction;
- wet process is capable of dissolving and washing out part of the inorganic components from lignocellulose, resulting in lower ash content in hydrochar than that in untreated biomass (Reza et al., 2013);
- after wet torrefaction, the wet product can be effectively made dry by mechanical and natural dewatering, which can reduce the energy requirement of the post-drying step.

The use of dry and wet torrefaction depends on the moisture contents of the raw biomass materials. Wet torrefaction is preferred for lignocellulosics with high moisture contents, so this process is more suitable for municipal waste, sewage slug, animal manures, and direct treatment of the biomass residue from the field. Wet torrefaction can be a promising pretreatment method; however, the process costs due to the necessity of high pressure and increased transportation costs of wet lignocellulosics, are limiting the development of this treatment (Acharya et al., 2015, Bach and Skreiberg, 2016).
2.3 Thermal decomposition of biomass materials

The pyrolytic properties of lignocelluloses are influenced by the chemical composition of the major components, including cellulose, hemicellulose, and lignin and the minor components, such as extractives and inorganic materials. The individual components of biomass have different thermal properties (Shafizadeh, 1982). Several complex, competing and consecutive reactions occur during the pyrolysis of biomass materials and provides various products (Shafizadeh and McGinnis, 1971). During the pyrolysis the polysaccharides form anhydrosugars, furans, aldehydes, ketones and carboxylic acids as their primary volatile products, while the volatiles from lignin mainly consist of the low molecular weight aromatic compounds with guaiacyl-units or phenolic-units (Colomba, 1998). The reaction pathways are influenced by the experimental parameters, including temperature, heating rate, pressure, particle size, ambient gas environment, and the presence of ash or additives (Antal 1983, Antal 1985). The formation of levoglucosan as a result of cellulose pyrolysis can be from 20% to 70%, while from lignocellulosic biomass the amount of levoglucosan is less than 5%, although the cellulose content is about 40% (Shafizadeh and Bradbury, 1979, Kwon et al., 2007, Jakab, 2015).

Many researchers have extensively studied the pyrolysis of the lignocellulosic biomass and proposed reaction models by assuming that pyrolysis of cellulose, hemicellulose and lignin takes place independently without interactions among the three components (Alen et al, 1996, Miller and Bellan, 1997, Teng and Wei, 1998, Orfalo, 1999). However, results for predicting the composition of the biomass in terms of cellulose, hemicellulose and lignin were not entirely adequate, possibly due to the lack of knowledge of interactions among the main components during pyrolysis (Shen et al., 2013). From the morphological view of the plant cell-wall the main chemical components (cellulose, hemicellulose and lignin) would not decompose individually without the intrinsic interactions during the pyrolysis of the whole biomass system [Fengel and Wegener, 1989, Hosoya et al., 2007, Dammstrom et al., 2009]. The interactions among the chemical components of lignocellulosic biomass under pyrolytic conditions are of growing interests in the last years, in order to gain better understanding of the pyrolytic mechanism of the whole lignocellulose system from the pyrolysis of individual component [Hosoya et al., 2007, Wang et al., 2008, Couhert et al. 2009].
2.3.1 Thermal decomposition of biomass constituents

Cellulose decomposition
Numerous pathways have been proposed for cellulose pyrolysis; the most widely accepted reactions are depolymerization (Figure 9), elimination (Figure 10), and fragmentation (Figure 11) (Shafizadeh, 1982, Kilzer and Broido, 1965, Jakab, 2015).

*Figure 9 Depolymerization of cellulose during pyrolysis (Jakab, 2015).*

The first reaction is depolymerization, where the cleavage of bonds between the monomer units leads to the formation of levoglucosan. Levoglucosan (1,6-anhydro-β-D-glucopyranose) is an important primary product during cellulose pyrolysis, which was first isolated and characterized by Tanret in 1894.
Figure 10  Formation of pyranone rings during cellulose pyrolysis (Jakab, 2015).

Figure 11  Reverse aldolization during cellulose pyrolysis (Jakab, 2015).
The formation of levoglucosan by the pyrolysis of cotton cellulose under vacuum was reported by Pictet and Sarasin in 1918; they obtained levoglucosan yield of about 30%. The maximum theoretical levoglucosan yield can be 73%, which was reported by Sandermann and Augustin in 1964 (Shafizadeh, 1968). Three different mechanisms for levoglucosan formation during cellulose pyrolysis have been studied by Zhang et al. in 2013, which are the free-radical mechanism, the glucose intermediate mechanism, and the levoglucosan chain-end mechanism. Figure 9 shows a free-radical mechanism with the chain scission of the macromolecule.

The second reaction is elimination (Figure 10), which occurs when depolymerization and dehydration of cellulose take place at the same time. This reaction is suggested to happen during cellulose decomposition to a smaller degree (Jakab, 2015). The third reaction is the fragmentation of the pyranose rings, which produces light volatile products (e.g. formaldehyde, acetaldehyde) and more char. Furthermore, significant amount of carbon monoxide, carbon dioxide and water releases during fragmentation. This pathway is more important at low temperatures and slow heating rates. A typical fragmentation product is hydroxyacetaldehyde (glycolaldehyde), which forms by reverse aldolization during cellulose pyrolysis (Figure 11).

**Hemiellulose decomposition**

Isolation of hemicelluloses from the raw biomass is rather difficult; moreover, their structure is highly diverse depending on the botanical origin and isolation procedure. Therefore, less information is available for the decomposition of hemicellulose comparing to cellulose. It is supposed that hemicellulose and cellulose decompose similarly; the main mechanisms during the decomposition of hemicellulose are depolimerization and fragmentation. Mannan represents the main hemicellulose in softwoods, which contains mannopyranose units, however it has glucopyranose and galactopyranose segments, as well. During pyrolysis, anhydro derivatives of the sugar units are formed from heteropolysaccharides (Helleur, 1987). The most common hemicellulose in hardwoods is O-acetyl-4-O-methylglucorono-xylan, which produces mostly 5,6-dihydro-4-hydroxy-2H-pyran-2-one, 1,4-anhydroxylopyranose, and 2-furanaldehyde. Figure 12 shows the possible reaction way of the formation of these products from the xylan backbone (Jakab, 2015).
Shen et al. (2010) studied the pyrolysis of O-acetyl-4-O-methylglucorono-xylan extracted from beech wood, and the evolution of acetic acid and carbon dioxide was attributed to the primary decomposition of O-acetylxylan units. Xylan is also the precursor for the formation of the two-carbon, three-carbon fragments and gases (carbon monoxide, hydrogen and methane). The evolution of methanol was mainly attributed to the primary reactions of 4-O-methylglucuronic acid unit, which could be further decomposed to almost all of the products generated from the xylan units. Recently, Werner et al. (2014) studied the thermal decomposition behavior of seven different commercially available hemicelluloses (β-glucan, arabinogalactan, arabinoxylan, galactomannan, glucomannan, xyloglucan, and xylan) with respect to mass loss rate, reaction heat and composition of evolved gases. It was observed that the gaseous (CO, CO₂, CH₄, H₂O) and other decomposition products differed and the product distribution was correlated to the monosaccharide composition of the polysaccharide.

**Lignin decomposition**

Due to its complex composition and structure, the degradation of lignin is strongly influenced by several factors; hence it is difficult to understand its pyrolysis mechanisms. Lignin thermally decomposes over a broad temperature range (230-550°C); the various functional groups of lignin have different thermal stabilities, their scissions occurring at different temperatures. The cleavage of functional
groups plays an important role leading to the evolution of low molecular weight products (20-25%), while the complete rearrangement of the backbone at higher temperatures leads to 30-50% char and to the release of volatile products (Brebu and Vasile, 2010). Several studies have been carried out to determine the possible reactions ways of lignin model compounds (Faix and Schweers, 1975, Faix et al., 1988, Britt et al., 1995, Britt et al., 2000_b). Britt et al. (2000_a) concluded that the thermal degradation of lignin occurs principally by a free-radical reaction pathway, and that the methoxyl substituents enhance the homolysis of the β-O-4 linkage. The methoxyl-substituted phenoxy radicals undergo a complex series of reactions, which are dominated by intramolecular hydrogen abstraction, rearrangement, and β-scission reactions. Jakab et al. (1995) found correlations between the abundance of volatile products and the type and amount of functional groups. They found that the terminal CH₂OH groups decompose by the release of both water and formaldehyde, which was demonstrated by the relationship between the aliphatic hydroxyl group content and the formaldehyde as well as the water evolution. Furthermore they concluded that the dependence of the methane yield on the methoxyl group content provided evidence that the scission of methoxyl groups results in the formation of methane as well as methanol (Jakab et al, 1995).

2.3.2 Effect of extractives and inorganic ions during the thermal decomposition

The lignocellulosic materials contain different amount of extractable materials and inorganic components. Mészáros et al. (2007) studied the effect of extractive materials, which partly evaporate and partly decompose during the thermal decomposition. They found that the extractives do not have considerable impact on the thermal decomposition mechanisms of the macromolecular components. However, during pyrolysis, the inherent inorganic components of biomass materials have significant effect on the decomposition mechanisms.

Herbaceous materials have high inorganic content (4-16%), while wood samples contain rather low amount of inorganic materials (0.5-1-5%), although, the bark of wood has significantly higher (2-5%) inorganic content comparing to the stem (Sjöström, 1993, Mészáros et al., 2004). Potassium and calcium are the main cations in lignocellulosic materials; other minor elements are magnesium, sodium, phosphorus, iron, and aluminum. Several studies have been investigated the effect of alkali ions on the pyrolysis of cellulose (Várhegyi et al., 1988_a, Sekiguchi and
Shafizadeh, 1984, Nishimura et al., 2009), model compounds (Nowakowski and Jones, 2008), and biomass materials (Várhegyi et al., 1988_b, Várhegyi et al., 1989). Of all the metals present in lignocelluloses, potassium has the greatest effect on the thermal decomposition mechanisms, and cellulose is the most sensitive component. The presence of potassium and sodium promotes gas and char formation during cellulose pyrolysis. The levoglucosan yield is reduced in the presence of alkali metal ions, indicating that the depolymerization reactions are hindered, while the fragmentation reactions of the sugar moieties to low molecular weight components are promoted (Várhegyi et al., 1988, Nowakowski and Jones, 2008, Jakab, 2015), leading to the decreased decomposition temperature and the increased char yield. Furthermore, the maximum rate of the decomposition is considerably lower in the presence of alkali ions (Sekiguchi and Shafizadeh, 1984, Tanczos et al., 2003). Sebestyén et al. (2011) studied the effect of alkali ion concentration in detail on the thermal decomposition of hemp. They concluded that the concentration of the potassium and sodium ions in the hemp sample determines the effect of alkali ions to a great extent. The largest alteration of the thermogravimetry/mass spectrometry (TG/MS) parameters was detected in the 0–0.2 mmol g\(^{-1}\) concentration range of the alkali ions. Nowakowski and Jones (2008) studied the pyrolysis of oat spelt xylan in the presence of potassium and they found that the alkali metal content has negligible effect on the decomposition of hemicellulose. The inorganic ions modify the decomposition of lignin, although to a lesser extent than that of cellulose. The impact of cations on the thermal decomposition of lignins was studied by Jakab et al. in 1993, 1997, and 2010. They found that the presence of sodium or zinc ions promotes the scissions of the \(\text{CH}_2\text{OH}\) group. The effect of potassium on the lignin pyrolysis was confirmed by Nowakowski and Jones (2008), which was indicated by the increased char yield and lower temperature decomposition in the presence of potassium.

The release of chlorine may cause fouling, slagging, and corrosion problems during thermochemical conversion. The concentration and the compounds of chlorine vary in different lignocellulosic materials. In woody biomass, the concentration of Cl\(^{-}\) is usually very low (<0.01%); however, in straws the concentration of Cl\(^{-}\) is much higher, ranging from 0.1 to 0.6% (Wang et al., 2017). Chlorine and potassium are usually present as KCl, which is the key inorganic constituent of lignocellulosic material (Saleh et al., 2014, Wang et al., 2017). Khazraie et al. (2013) found that torrefaction of birch wood at 240 °C resulted in 25% decrease in chlorine and 40% decrease in sulfur content, while torrefaction of birch at 280 °C resulted in 85% and
55% decrease in chlorine and sulfur contents, respectively, however they did not find potassium release during torrefaction. Jensen et al. (2000) pyrolyzed wheat straw in a nitrogen atmosphere in the temperature range of 200–1050 °C to study the release and transformation of potassium and chlorine as a function of a temperature. They observed that the Cl⁻ was released in two steps, more than half of the initial chlorine was released between 200–400 °C, and the other part of the chlorine was released between 700 and 900 °C. They also found that the potassium did not release below 700 °C. Björkman and Strömberg (1997) presented that less then 10% of the chlorine was evaporated at 200 °C, while 20–50% of the chlorine was released during pyrolysis of annual lignocelluloses below 400 °C. Keipi et al. (2014) studied the effect of torrefaction on the chlorine content of eight woody biomass materials. They torrefied the woody samples at 260 °C for 30, 60, and 90 min, and they concluded that torrefaction at 260 °C reduced the chlorine content of the investigated samples. The release of methyl chloride from leaves and woody biomass in the temperature range of 150-350 °C was observed by Hamilton et al. (2003); however, Knudsen et al. (2004) suggested that chlorine released as HCl gas during pyrolysis at temperatures below 500 °C. The release of chlorine during torrefaction and the pyrolysis of six biomass materials have been investigated in the temperature range of 150-500 °C by Saleh et al. (2014). They concluded that most of the chlorine content released at 350 °C as methyl chloride. They also found that lignocelluloses with lower chlorine content released relatively higher amount of chlorine during the pyrolysis process. This could indicate that the chlorine release is controlled by a reaction between KCl and the organic constituents. A recent study (Wang et al., 2017) presented that a significant amount of methyl chloride can be released from KCl-doped pine wood and lignin, although the release of methyl chloride from KCl-doped cellulose and xylan is negligible. They suggested that the methoxyl groups in pine wood and lignin are responsible for the reaction with KCl and the formation of methyl chloride. In the above mentioned publications, the relative release of chlorine was generally calculated by the use of a mass balance and by the analysis of the biomass chlorine content before and after the heat treatment, therefore qualitative (e.g. CH3Cl or HCl) and quantitative data of the amount of chlorine from the different biomass materials is limited. The formation of methyl chloride was detected by thermogravimetry/mass spectrometry by Czégény et al., (2015) during the thermal decomposition of polyvinylchloride (PVC) - wood and wood component mixtures and they concluded that the methoxyl groups on the phenolic rings of lignin are the methyl source of methyl chloride.
2.3.3 Impact of torrefaction on the decomposition of biomass

When lignocellulose is pretreated in a torrefaction reactor, it goes through five stages according to Gent et al. (2017) (Figure 13). At first, biomass needs to be heated through three stages (initial heating, drying and post-drying) before the real torrefaction temperature is reached, hence the residence time of lignocellulose in a torrefaction reactor is basically never equal to the time that the biomass materials are exposed to the torrefaction temperature (Bergman et al., 2005_a). Then the temperature further increases until it reaches the torrefaction temperature. This temperature is held (residence time) until the reactor is cooled again. During the heating section, the thermally most labile parts of the lignocellulose rapidly start to decompose. In contrast, the cooling period barely contributes to the decomposition of the biomass. After torrefaction, the solid product is much more thermally stable as the most reactive parts already decomposed, therefore it is expected that the decomposition reactions will stop as soon as the temperature is decreased (Bergman et al., 2005_b). The difficulty is that the highest energy efficiency and the best product properties are obtained in a narrow temperature window, which strongly depends on the nature of biomass. A recent study [Buorgonje et al., 2017] presented a novel method to determine the heating value of the torr-gas, by combusting the torr-gas and to measuring the produced heat as an indicator along with other product properties as they develop during the torrefaction process.

![Figure 13](image.png) Heating and cooling stages during torrefaction (Gent et al., 2017).
Several reactions take place during torrefaction and different reaction pathways can be defined. The degree of thermal degradation depends on the duration of the heating and the temperature. The possible reaction ways can be grouped to main reaction sections; however, for each polymer (hemicellulose, cellulose and lignin) different decomposition temperature ranges can be defined as shown in Figure 14 (Bergman et al., 2005_a, Bergman et al., 2005_b, Tumuluru et al., 2011).

**Figure 14** Main decomposition stages during torrefaction and pyrolysis.
(Biochar Factory Website, 2018)

From the three main polymeric constituents of biomass, hemicellulose is the most reactive polymer followed by lignin and cellulose. Between 50–150 °C, physical drying of lignocellulose occurs. It is a nonreactive drying zone, where most of the chemical constituents of the biomass remain intact. The evaporation of extractives starts in the temperature range of 150–220 °C. This temperature initiates the cleavage of the most labile bonds resulting in the emission of smaller organic molecules. A further increase in the temperature (200–300 °C) leads to depolimerization, limited devolatilisation and carbonisation of the biopolymer constituents. At lower temperatures, minor decomposition is to be expected for cellulose and lignin, while at higher temperature the thermal decomposition becomes more vigorous as hemicellulose extensively decomposes into volatiles and a char-like solid product, and additionally lignin and cellulose show limited devolatilisation and carbonisation. The exact temperature ranges of the processes depend on the type and properties of the lignocellulose. For lignin, also a temperature regime (120–150 °C) is defined, in which the lignin softens and makes the material more suitable for densification, as the softened lignin is a good binder.
2.4 Techno-economic status of torrefaction

The techno-economic optimization of the torrefaction process is necessary to become competitive with the conventional wood pellet production. The major technical challenges to the commercialization of torrefaction technology are the energy integration within the process and handling the volatile gases [Koppejan et al., 2012]. The torrefaction process still needs to be optimized with respect to heat integration and waste heat utilization [Batidzirai et al., 2013]. Furthermore, the integration of torrefaction process with other thermochemical and biochemical processes could be useful for the improved technical and economic performance. Sermyagina et al. [2016] studied the integration of torrefaction with a combined heat and power (CHP) plant and they found that higher utilization of CHP boiler was achieved during part-load operations. Arpiainen and Wilen [2014] examined the feasibility of integrating the torrefaction with CHP in case of saw mill and pulp and paper industry and concluded that integrating the torrefaction with CHP does not reduced the costs significantly. Kumar et al. [2017] investigated the integration of torrefaction as a downstream operation in a conventional biomass pelletization process. They concluded that capital investment can be reduced in an integrated approach in comparison with standalone torrefaction process. The integration of torrefaction with gasification through thermodynamic modeling was studied by Clausen [2014] and he found that the biomass to syngas conversion efficiency increased from 63 to 86% in an integrated approach. Fagernas et al [2015] investigated the possibility of condensing the volatiles and selling the torrefaction condensate as a feedstock for pesticides production, and they concluded that the increased selling price of the torrefaction condensate reduces the selling price of the torrefied biomass. Doddapaneni et al. [2017] and Liaw et al. [2015] studied the integration of torrefaction process with anaerobic digestion (AD) for the effective utilization of the torrefaction condensate. They found that the torrefaction condensate can be effectively converted into biogas though AD. Doddapaneni et al [2018] compared the techno-economic performance of the standalone torrefaction process with two different integrated process configurations. These two process configurations are using the biogas in a gas engine to produce electrical and heat energy as well as biogas upgrading into bio-methane applying high-pressure water scrubbing (HPWS) and pressure swing adsorption (PSA). They concluded that torrefaction process integrated with AD was economically more viable than a standalone torrefaction process.
2.5 Goals of this thesis in light of the scientific literature

The general aim of my work was to get new information about the thermal degradation process of torrefied herbaceous materials (rape straw and wheat straw), hardwood (black locust wood), and softwood (Norway spruce) with the goal of the better understanding the chemical reactions and the compositional changes during the low temperature thermal treatment. Several studies have been carried out on the thermal characteristics of wheat straw (Shang et al., 2012, Stelte et al., 2013, Satpathy et al., 2014, Bai et al., 2017, Bläsing et al., 2017). These papers focus on the effect of torrefaction on the properties of the solid product, such as mass yield, energy content, grindability, hydrophobicity, pelletization, and particle-size distribution. Only a few papers are available on the thermal decomposition of rape straw (Szamosi et al., 2017, Ma et al., 2017), and black locust wood (Mészáros et al., 2004). The explosion characteristics of raw and torrefied wheat straw and rape straw samples have been studied by Szamosi et al. (2017). Ma et al. (2017) investigated the properties and interactions during co-combustion of rape straw with bituminous coal. Young black locust, poplar and willow from a short rotation forestry plantation have been studied by Mészáros et al. (2004) to get information about their thermal behavior. Many studies have been carried out on the thermal characteristics of stem wood (Van der Stelt et al., 2011, Tapasvi et al., 2012, Strandberg et al., 2015); however, only a few papers are available on the thermal decomposition of forest residues, such as bark (Almeida et al., 2011, Arteaga-Perez et al., 2015) and stump (Tran et al., 2013, Tran et al., 2014). In the literature, there is a lack of papers, which investigate both the chemical composition and the thermal decomposition of biomass materials during torrefaction. A profound understanding of the compositional changes and the thermal behavior during torrefaction is essential for the efficient utilization of these abundant energy sources in the future.
3 Materials and Methods

3.1 Raw materials and sample preparation

In the experimental work wheat straw and rape straw were used as herbaceous materials; while black locust wood and Norway spruce were selected as hardwood and softwood, respectively.

Rape straw and wheat straw
Wheat straw (*Triticum aestivum*) was taken from Túrricse in Szabolcs-Szatmár-Bereg County, while rape straw (*Brassica napus*) was collected near Ócsa in Pest County during the harvest season of 2013. The raw samples were cut with a scissor to <4-5 cm and dried in an oven at 105 °C for 8 h to obtain samples of low moisture content for the experiments and to avoid biodegradation during storage. Then the untreated samples were ground to <1 mm particle size by a Retsch cutting mill.

Black locust wood
Black locust wood (*Robinia pseudoacacia*) was collected near Túrricse in Szabolcs-Szatmár-Bereg County in 2013. The wood was first cut to wedges, and then chopped into <1 cm pieces. The raw samples were dried in an oven at 105 °C for 8 h to obtain samples of similar moisture content for the experiments and to avoid biodegradation during storage. The untreated samples were ground to <1 mm particle size by a Retsch cutting mill.

Norway spruce
Different parts of a representative single Norway spruce (*Picea abies*) tree were selected for the torrefaction study: bark, stem wood and stump. The samples originated from a Norway spruce forest in South Norway. The trees in the forest site have high ages, more than one hundred years old on average. After harvested, the trees were divided into three parts: trunk, stump, and forest residues. The trunk was further debarked to obtain stem wood and bark. The stem wood was first cut to strips, and then further chopped into cubes with sides of 1 cm. The bark was chipped into pieces and those with length of around 5-7 cm were used for the torrefaction experiments. The stump was shredded into pieces and the pieces with length of 3-5 cm were torrefied. For further analyses, the untreated and torrefied samples were ground by a cutting mill to <1 mm particle size.
3.2 Torrefaction experiments

Torrefaction of wheat straw, rape straw and black locust

The torrefaction experiments of wheat straw, rape straw, and black locust were carried out in Hungary. The experiments were performed in a nitrogen atmosphere in a horizontal tube furnace (Figure 15). About 4-12 g samples were treated in a glass boat of 200 mm long. The flow rate of the nitrogen gas was set to a relatively low value of 20 mL min$^{-1}$ to avoid the blow out of the smaller particles from the boat. The torrefaction experiments were performed at 200, 225, 250, 275, and 300 °C temperatures using an isothermal period of 1 h. The untreated and variously torrefied wheat straw, rape straw and black locust samples can be seen in Figure 16. The color of the raw biomass turns from brown to black from 200 °C to 300 °C, which can be mainly attributed to chemical compositional changes.

![Figure 15](image1.png)

**Figure 15** Apparatus setup for the torrefaction of black locust and straw materials.

![Figure 16](image2.png)

**Figure 16** Raw and torrefied wheat straw, rape straw and black locust samples.
Washing procedure
In order to study the effect of inorganic content we washed the raw samples with hot water to remove the majority of the water soluble inorganic components. The untreated wheat straw, rape straw and black locust samples were ground by the cutting mill to <1mm and further ground to <0.12mm particle size. About 1 g of the ground sample was washed in 100 mL of 60 °C distilled water for 20 min. After washing the samples were separated by centrifugation. These washing and centrifugation steps were repeated two more times; then the washed raw materials were dried at 105 °C for 24 hours. The efficiency of the inorganic ion removal was monitored by inductively coupled plasma - optical emission spectrometry (ICP-OES) method. The untreated, washed, and various torrefied black locust and wheat straw samples can be seen in Figure 17.

![Washed black locust samples](image1)

![Original black locust samples](image2)

![Washed wheat straw samples](image3)

![Original wheat straw samples](image4)

**Figure 17** Original and washed black locust and wheat straw samples before and after torrefaction.
Torrefaction of Norway spruce

The torrefaction experiments of different parts of Norway spruce were performed in Norway. The experiments were carried out in a batch tube reactor placed in an electrical furnace (Figure 18) in nitrogen atmosphere using flow rates of 1 L min⁻¹.

Figure 18 Apparatus setup for the torrefaction experiments of Norway spruce.

Approximately 80 g of the untreated samples were heated up at a heating rate of 15 °C min⁻¹ to three final temperatures (225, 275 and 300 °C). The residence time for one sample at each final temperature was 30 and 60 min, respectively. For further experiments the untreated and torrefied samples were ground by the cutting mill to <1 mm particle size. The ground samples can be seen in Figure 19.
3.3 Characterization of the untreated and torrefied samples

3.3.1 General characterization of the samples

Proximate and ultimate analysis

The samples were characterized before and after torrefaction, using proximate and elemental (ultimate) analyses. The moisture and volatile contents of the untreated and torrefied black locust wood and straw samples were determined by TG, heating the samples from room temperature up to 950 °C using 20 °C min^{-1} heating rate. The amount of ash of these materials was measured using the standard method proposed by the National Renewable Energy Laboratory (NREL/TP-510-42622), applying 550 °C ashing temperature. The fixed carbon content was determined as the difference between the mass of the solid residue measured by TG in argon atmosphere at 900 °C and the ash content. The volatile matter and ash content of the stem wood, stump, and bark samples were determined according to procedures described in ASTM Standard E872 and D1102. The fixed carbon content of the samples is calculated by difference from one hundred and the sum of volatile matter and ash content. The carbon and hydrogen contents of the untreated and torrefied biomass samples were measured by an elemental analyzer. The oxygen content was determined by difference. Three parallel proximate and ultimate analyses were performed to validate repeatability of the results, which was found to be quite satisfactory with a maximum ±1% standard deviation.
Higher heating value (HHV) determination
The HHV was determined using an automatic IKA C 5000 bomb calorimeter. The combustion of about 0.5 g of dried sample in a pure oxygen atmosphere was performed under 30 bar pressure. Benzoic acid calibration was applied to determine the heat capacity of the calorimeter. All heating values were calculated from the averages of three replicates.

Inductively coupled plasma-optical emission spectrometry (ICP-OES)
ICP-OES measurements were applied to determine the inorganic contents of the samples. Approximately 2 g biomass samples were ashed at 550 °C in a furnace according to CEN/TS 14775:2004 standard method. The ashes were fused at 920 °C with a fusion blend (Li₂B₄O₇:LiBO₂, 2:1) and digested by 25 mL 33% nitric acid. The calcium, potassium, sodium, and magnesium contents of the samples were determined by a Spectro Genesis ICP-OES (Spectro Analytical Instruments) with axial plasma observation. The amounts of the ashes have been determined according to the CEN/TS 14775 EU standard method. All experimental data were determined using three replicates.

Grinding and particle size distribution
The raw and torrefied spruce samples were ground in a cutting mill (IKA MF 10.1). The grinding of one sample included two stages: pre-grinding and fine grinding. The powder samples produced in the fine grinding stage were sieved by a vibrating sieving machine (Fritsch Analysette 3 Pro) with the following mesh sizes: 1 mm, 0.5 mm, 0.3 mm, 0.2 mm, 0.1 mm and 0.063 mm. The sample particles collected from the different sieves were weighed and presented as a percentage of the initial sample mass.
3.3.2 Carbohydrate and lignin content determination

Chemical composition analysis is an efficient way to study chemical composition changes of biomass during thermal treatment. For untreated and torrefied biomass samples, the contents of carbohydrates were analysed according to the slightly modified method reported by Sluiter et al (2008_a). The untreated and torrefied biomass samples were milled to particles smaller than 1 mm. The milled samples were dried at 40 °C for 1 day. The samples were treated in a two-step acid hydrolysis with 72% H$_2$SO$_4$ for 2 h at room temperature, and then with 4% H$_2$SO$_4$ for 1 h at 121 °C. The obtained suspensions were filtered and washed with distilled water through G4 glass filter crucibles. The sugar concentrations (glucose, xylose, arabinose, mannose, galactose) of the filtered supernatants were analyzed with high-performance liquid chromatography (HPLC) using an Agilent 1260 system with a Hi-Plex H column at 65 °C. An eluent of 5 mM H$_2$SO$_4$ was used at a flow rate of 0.5 mL min$^{-1}$. The Klason lignin content was determined by gravimetric method. The solid residues obtained after washing were dried at 105 °C until a constant weight. The dried residues consisted of acid-insoluble organics and acid-insoluble ash. The amounts of acid-insoluble ash were determined by ashing the sample at 550 °C for 5 h until the sample weight was constant (Sluiter et al., 2008_b). The Klason lignin content was calculated by subtracting the acid-insoluble ash content from the acid-insoluble residue content. All experimental data were determined using three replicates.

3.3.3 Thermogravimetry-Mass spectrometry (TG/MS)

Thermogravimetry/mass spectrometry was applied to provide information about the thermal stability of and evolution profile of the volatile decomposition products of raw and pretreated biomass samples. Figure 20 shows the used TG/MS system, which consist of a modified Perkin-Elmer TGS-2 thermobalance and a Hiden HAL quadrupole mass spectrometer. About 4 mg sample was placed into the platinum sample pan and the furnace was flushed with the carrier gas at a flow rate of 140 mL min$^{-1}$ for 40 minutes before the experiments. Then the samples were analyzed in argon atmosphere from 25 to 900 °C at a rate of 20 °C min$^{-1}$. The evolved products were led through a glass-lined metal capillary heated at 300 °C using argon carrier gas. The ion source of the mass spectrometer was operated at 70 eV electron energy. The mass range of 2-150 Da was scanned. The ion intensities were normalized to the sample mass and to the intensity of the $^{38}$Ar isotope of the carrier gas (used as an internal standard).
Since the MS intensities of various products have different magnitudes, they have been scaled to gain comparable peak heights in the plots. The curves of the individual species developed from different samples are plotted using the same scale within each study.

Figure 20 Thermogravimetry-mass spectrometry instrument (Jakab, 2015).

Figure 21 The most important parameters of a TG and a DTG curves (Jakab, 2015).
The TG curve displays the mass loss profile, while the derivative thermogravimetric (DTG) curve shows the mass loss rate during the thermal decomposition of the sample as a function of the sample temperature or analysis time. The TG and DTG curves give information about the thermal stability of the sample; Figure 21 shows the most important parameters (DTG$_{\text{max}}$, T$_{1\%}$, T$_{\text{hc}}$, T$_{\text{peak}}$, T$_{\text{c}}$ and Char) of these curves. DTG$_{\text{max}}$ shows the maximum value of the $-\text{dm}/\text{dt}$ curve. Four temperatures are used for the characterization of the thermal decomposition: T$_{1\%}$ denotes the temperature belonging to 1% weight loss of the sample, T$_{\text{hc}}$ marks the extrapolated temperature of the beginning of the decomposition, T$_{\text{peak}}$ denotes the temperature of the maximal decomposition rate (DTG$_{\text{max}}$), while T$_{\text{c}}$ is an extrapolated temperature of the end of cellulose decomposition. Char is the residue at 900 °C.

3.3.4 Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS)

For the Py-GC/MS experiments the untreated and torrefied stem wood, stump, and bark samples (1 mm particle size) were further ground by a cryogrinding to obtain homogeneous, representative samples for the Py-GC/MS experiments.

Py-GC/MS measurements were carried out in a CDS Pyroprobe 2000 equipped with a platinum coil and quartz sample tube. The pyrolyzer was coupled to an Agilent 6890/5973 GC/MS instrument (Figure 22).

![Figure 22 Pyrolysis-gas chromatography/mass spectrometry instrument.](image-url)
Approximately 1.1 mg samples were pyrolyzed at 550 °C for 20 s in a quartz tube using helium carrier gas. The pyrolysis products were separated on an Agilent DB-1701 capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness). The pyrolysis interface and the GC injector were held at 280 °C. The GC oven was programmed to hold at 40 °C for 4 min and then increase to 280 °C at a rate of 6 °C min⁻¹. The mass range of m/z 14-500 was scanned by the mass spectrometer in electron impact mode at 70 eV. The identification of the pyrolysis products was based on NIST mass spectral library and literature data. The percentages of the compounds were estimated using the peak areas of the total ion current chromatograms.

3.4 Principal component analysis

Due to the large number of samples and experimental data, principal component analysis (PCA) using the Statistica 12 software was employed. The main purposes of a PCA analysis are to identify patterns in data and finding patterns to decrease the data dimensionality with minimal loss of information (Wold et al., 1987). PCA is a technique for reduction of data dimensionality, which allows detecting patterns and visualization of patterns retaining as much important information present in the original data as possible. PCA finds a new coordinate system; it transforms the original measured variables into new uncorrelated variables called principal components (Factors). Each principal component (Factor) is a linear combination of the original measured variables. Factor 1 accounts for the maximum of total variance. Factor 2 is uncorrelated with Factor 1 and accounts for the maximum of the residual variance, and so on for additional factors. Usually two or three Factors can satisfactorily reveal the major similarities and differences between the samples. For the PCA technique, the singular vectors and singular values are calculated from the covariance (or correlation) matrix. The axis corresponding to the principal singular vector is the one along which the variance of the data is maximized. The singular vector with the highest singular value is the first principle component of the data. The axis corresponding to the second singular vector (the singular vector corresponding to the second largest singular value) is the axis along which the variance of distances from the first axis is greatest, and so on. The results can be presented in the score plots, which place the samples in the space of Factor 1 and Factor 2 (the two principal components). Factor loadings show the correlation between the original measured data and the Factors (principal components).
4 Results and discussion

In this chapter, I present and discuss the main results published in papers I-VI. The first part (Paper I and Paper VI) describes a comparative study of untreated and torrefied hardwood and herbaceous samples, while the second part (Paper II-V) summarizes the results obtained by various experimental techniques to study the thermal behavior of different parts of softwood during torrefaction.

4.1 Compositional study of untreated and torrefied black locust wood, wheat straw, and rape straw

In this part, the torrefaction of black locust wood, wheat straw, and rape straw was studied, which are typical biomass products or byproducts in Hungary. As a consequence of the difference in the relative amount of cellulose, hemicellulose, lignin, inorganic content and extractives, the woody and herbaceous materials behave differently during thermal decomposition. One of the significant differences between the chemical composition of wood and herbaceous materials is the amount of inorganic ions: the mineral matter content is significantly higher in the herbaceous biomass materials than in the wood samples. Furthermore, the hemicellulose and lignin components are chemically different in wood and herbaceous samples. The main objective of this work was to study the thermal behavior of these raw and torrefied woody and herbaceous biomass materials in order to clarify the effect of different composition on the thermal degradation process during torrefaction. The torrefaction of black locust wood, rape straw, and wheat straw was carried out at five temperatures: 200, 225, 250, 275 and 300 °C using 1 h isothermal period. The thermal stability and the formation of the volatile products from the untreated and torrefied samples were studied by the thermogravimetry/mass spectrometry method. The degree of hemicellulose and cellulose decomposition during torrefaction at different temperatures was characterized by compositional analysis of the samples. The cellulose, hemicellulose, and Klason lignin contents of the untreated and torrefied biomass samples were determined by acidic hydrolysis and subsequent high-performance liquid chromatography analysis. In order to study the effect of inorganic content, we washed the raw samples with hot water to remove the majority of the water soluble inorganic components. The inorganic ion content of the original and washed raw materials was measured by the inductively coupled plasma optical emission spectrometry (ICP-OES) method. The thermal degradation properties of raw and washed samples have been compared. Principal component analyses (PCA) have
been applied to identify the similarities and differences between the untreated and various torrefied black locust wood, rape straw, and wheat straw samples.

4.1.1 Characterization of raw and torrefied wood and straw samples

Table 4 shows the solid yield, proximate and ultimate analysis data, and energy content of the raw and torrefied samples. During torrefaction, the moisture content and volatiles release from the sample, resulting in a decrease of the sample mass. Up to the temperature of 250 °C, the yield of the solid residue was quite similar for the three investigated samples. In comparison of the results gained at 250 and 275 °C, it can be recognized that a substantial decrease of the solid yield occurred in rape and wheat straw samples (15 and 20%, respectively), while the solid yield was reduced to a lesser extent in black locust wood (11%). This observation designates a higher degree of decomposition of straw samples at and over 275 °C. The proximate analysis data of the three samples show that the moisture content (MC) and volatile matter (VM) decreased, while the ash and fixed carbon (FC) contents increased in the samples prepared at a higher torrefaction temperature as a result of the progress of the thermal decomposition. Black locust wood had a higher volatile matter content and a lower fixed carbon yield than wheat and rape straw samples, prepared under the same torrefaction conditions. The ultimate analysis confirms that the increasing torrefaction temperature increased the carbon content and reduced the oxygen and hydrogen contents of the torrefied materials. Atomic O/C ratio decreases with increase of torrefaction severity. The calorific value of the torrefied samples increased with the increasing temperature. Torrefaction at 225 °C increased the higher heating value (HHV) of the samples by at least 3.5% in comparison to the value of the raw samples (17.6–18.2 MJ kg$^{-1}$). Torrefaction at 275 °C resulted in an increase of 19–27% of the HHV. The proximate and ultimate analysis data as well as the calorific values verify the gradual thermal decomposition of the lignocellulosic samples at an increasing temperature. Table 5 shows the most important data of the ICP-OES results. As the data illustrate, the two straw samples have an order of magnitude higher K$^+$ content than the wood sample. Furthermore, Na$^+$, Ca$^{2+}$ and Si contents of wheat straw and rape straw are also significantly higher comparing to the black locust sample.
<table>
<thead>
<tr>
<th>Samples</th>
<th>Solid yield (%)</th>
<th>Proximate analysis (% m/m, as received)</th>
<th>Ultimate analysis (% m/m, dry basis)</th>
<th>HHV (MJ kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MC</td>
<td>VM</td>
<td>Ash</td>
</tr>
<tr>
<td>Black locust (BL)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BL U</td>
<td>100</td>
<td>6.08</td>
<td>77.85</td>
<td>1.75</td>
</tr>
<tr>
<td>BL 225</td>
<td>87</td>
<td>3.25</td>
<td>76.87</td>
<td>1.91</td>
</tr>
<tr>
<td>BL 250</td>
<td>79</td>
<td>3.23</td>
<td>69.79</td>
<td>2.16</td>
</tr>
<tr>
<td>BL 275</td>
<td>68</td>
<td>3.42</td>
<td>65.83</td>
<td>2.92</td>
</tr>
<tr>
<td>BL 300</td>
<td>49</td>
<td>3.78</td>
<td>56.34</td>
<td>4.20</td>
</tr>
<tr>
<td>Rape straw (RS)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RS U</td>
<td>100</td>
<td>7.16</td>
<td>71.16</td>
<td>6.04</td>
</tr>
<tr>
<td>RS 225</td>
<td>85</td>
<td>4.62</td>
<td>68.99</td>
<td>6.36</td>
</tr>
<tr>
<td>RS 250</td>
<td>76</td>
<td>4.11</td>
<td>66.01</td>
<td>7.26</td>
</tr>
<tr>
<td>RS 275</td>
<td>61</td>
<td>4.57</td>
<td>53.61</td>
<td>9.36</td>
</tr>
<tr>
<td>RS 300</td>
<td>47</td>
<td>3.76</td>
<td>40.73</td>
<td>11.84</td>
</tr>
<tr>
<td>Wheat straw (WS)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WS U</td>
<td>100</td>
<td>5.58</td>
<td>70.55</td>
<td>5.68</td>
</tr>
<tr>
<td>WS 225</td>
<td>89</td>
<td>3.68</td>
<td>69.69</td>
<td>5.80</td>
</tr>
<tr>
<td>WS 250</td>
<td>80</td>
<td>3.62</td>
<td>66.20</td>
<td>6.92</td>
</tr>
<tr>
<td>WS 275</td>
<td>60</td>
<td>3.53</td>
<td>54.84</td>
<td>9.28</td>
</tr>
<tr>
<td>WS 300</td>
<td>44</td>
<td>2.37</td>
<td>38.12</td>
<td>12.52</td>
</tr>
</tbody>
</table>
Table 5: The most important inorganic components of the three studied materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si</th>
<th>K⁺</th>
<th>Na⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black locust</td>
<td>* N. D.</td>
<td>0.27</td>
<td>* N. D.</td>
<td>0.085</td>
<td>0.017</td>
</tr>
<tr>
<td>Rape straw</td>
<td>0.03</td>
<td>1.86</td>
<td>0.072</td>
<td>0.503</td>
<td>0.158</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>1.07</td>
<td>1.69</td>
<td>0.008</td>
<td>0.137</td>
<td>0.077</td>
</tr>
</tbody>
</table>

* N. D.: Not determined, below the detection limit

4.1.2 Chemical composition of the samples

The compositional analysis of black locust wood, wheat straw and rape straw samples was performed to understand better the thermal conversion process during torrefaction. The cellulose, hemicellulose, and Klason lignin contents of the untreated and torrefied biomass samples were determined by acidic hydrolysis and subsequent high-performance liquid chromatography analysis. The results can be seen in Table 6. The standard deviation values for the compositional analysis are also presented in Table 6. The glucan content of the samples mainly characterizes the cellulose component of lignocellulose, while the sum of the xylan and arabinan contents represents the hemicellulose fraction. The Klason lignin is defined as the acid-insoluble residue content of the samples without the acid-insoluble ash content. The fraction denoted “Other” in Table 6 represents the sum of the unquantified components and includes extractives, acid-soluble lignin, and acid-soluble minerals. To compare the degradation degree of cellulose, hemicellulose, and lignin in the torrefied samples, one has to take into consideration the mass loss during the torrefaction experiment as well. Therefore, Table 6 also shows the mass loss during the torrefaction at the different temperatures. The chemical composition of the three raw samples shows that black locust has the highest Klason lignin content (26%), while wheat straw has the highest hemicellulose (23%) content. The lignocellulose content (sum of cellulose, hemicellulose, and lignin) of black locust and wheat straw samples is around 76%, while that of the untreated rape straw is only 66%. The reason could be the higher amount of extractive compounds and the higher acid soluble mineral content of the rape straw sample. The later assumption is supported by the highest alkali and alkaline earth ion content of the rape straw sample, as shown in Table 5. During torrefaction, the lignocellulose materials decompose to different degrees depending upon the applied temperature. The variation of the amount of glucan, xylan, and arabinan in the torrefied samples (see Table 6) reflects the changes in the proportion of cellulose and hemicellulose in the samples. The decreasing carbohydrate yields indicate the progress of the thermal decomposition of hemicellulose and cellulose during
torrefaction at various temperatures. Comparing the changes of carbohydrate and Klason lignin content of the samples as a function of torrefaction temperature (Table 6) it can be concluded that hemicellulose (measured as the sum of arabinan and xylan) is the thermally least stable component of the lignocellulose fraction during torrefaction. The hemicellulose content of the torrefied samples is slightly decreased up to 225 °C for each studied sample. The samples torrefied at 250 °C have about half of the hemicellulose content of the untreated sample for each biomass. At higher torrefaction temperatures, the relative amount of hemicellulose drastically decreases and only traces of hemicellulose were measured in the samples torrefied at 300 °C. The changes in the relative amount of hemicellulose show a similar tendency as a function of the torrefaction temperature for each sample, indicating that the thermal stability of hemicellulose is similar in the studied wood and herbaceous samples. Hence, it can be concluded that the thermal decomposition of hemicelluloses does not show significant dependence on the amount of alkaline ions in the given concentration range. The variation of the cellulose content in the raw and torrefied samples is demonstrated by the amount of glucan (Table 6). As can be seen in Table 6, the cellulose content of black locust wood does not decrease considerably up to 275 °C torrefaction temperature. In the case of the two herbaceous samples, the degradation of cellulose is significant at this temperature; the relative decrease is almost 50% in both cases. At 300 °C torrefaction temperature, about 60% of the cellulose content of black locust decomposes, while cellulose almost disappears from rape and wheat straw samples. Hence, it can be concluded that the thermal stability of cellulose in the herbaceous samples is lowered by about 25 °C compared to wood. As Table 5 shows, the herbaceous samples have more than an order of magnitude higher alkali ion content than wood. The catalytic effect of alkali ions on the thermal decomposition of cellulose is known at higher temperatures (DeGroot and Shafizadeh, 1984, Sekiguchi and Shafizadeh, 1984, Várhegyi et al., 1988). The results obtained for the cellulose content of the torrefied samples confirm that the alkali ions have a catalytic effect on cellulose decomposition, even at the low temperatures used in torrefaction. As Table 6 presents, increasing the torrefaction temperatures resulted in a significant increase in the measured Klason lignin content of the samples. Besides the acid-insoluble lignin, Klason lignin contains all acid-insoluble components of the sample, excluding ash. During the thermal treatment, some parts of the extractives, cellulose, hemicellulose, and acid soluble lignin were probably transformed into acid-insoluble carbonaceous products by cross-linking and charring reactions. The increasing torrefaction temperature favors these reactions, resulting in the increased Klason lignin value at higher temperatures.
Table 6 Composition of the untreated and torrefied samples. The percentage data are corrected with the mass loss values, thus the compositional data are referred to the original sample masses. Standard deviations are calculated from triplicates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Glucan (% m/m)</th>
<th>Xylan (% m/m)</th>
<th>Arabinan (% m/m)</th>
<th>Klason lignin (% m/m)</th>
<th>Other (% m/m)</th>
<th>Mass loss during torrefaction (% m/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Black locust wood (BL)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BL U</td>
<td>34.2 ± 0.7</td>
<td>15.8 ± 0.2</td>
<td>0.6 ± 0.0</td>
<td>25.8 ± 1.1</td>
<td>23.6</td>
<td>0</td>
</tr>
<tr>
<td>BL 200</td>
<td>31.2 ± 1.4</td>
<td>14.4 ± 0.4</td>
<td>0.8 ± 0.0</td>
<td>23.1 ± 0.1</td>
<td>21.5</td>
<td>9</td>
</tr>
<tr>
<td>BL 225</td>
<td>35.6 ± 1.1</td>
<td>12.5 ± 0.6</td>
<td>0.6 ± 0.0</td>
<td>24.4 ± 0.2</td>
<td>13.8</td>
<td>13</td>
</tr>
<tr>
<td>BL 250</td>
<td>31.3 ± 1.0</td>
<td>8.0 ± 0.5</td>
<td>0.1 ± 0.0</td>
<td>32.8 ± 2.4</td>
<td>6.7</td>
<td>21</td>
</tr>
<tr>
<td>BL 275</td>
<td>29.2 ± 1.1</td>
<td>4.1 ± 0.2</td>
<td>*N. D.</td>
<td>30.4 ± 0.8</td>
<td>4.4</td>
<td>32</td>
</tr>
<tr>
<td>BL 300</td>
<td>10.8 ± 1.1</td>
<td>0.3 ± 0.3</td>
<td>*N. D.</td>
<td>35.0 ± 0.2</td>
<td>3.0</td>
<td>51</td>
</tr>
<tr>
<td><strong>Rape straw (RS)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RS U</td>
<td>27.9 ± 0.6</td>
<td>15.3 ± 0.3</td>
<td>1.6 ± 0.0</td>
<td>21.1 ± 0.5</td>
<td>34.0</td>
<td>0</td>
</tr>
<tr>
<td>RS 200</td>
<td>26.2 ± 0.7</td>
<td>14.0 ± 0.5</td>
<td>1.3 ± 0.0</td>
<td>23.1 ± 0.1</td>
<td>26.4</td>
<td>9</td>
</tr>
<tr>
<td>RS 225</td>
<td>25.5 ± 0.7</td>
<td>11.2 ± 1.1</td>
<td>0.7 ± 0.1</td>
<td>24.3 ± 0.3</td>
<td>23.3</td>
<td>15</td>
</tr>
<tr>
<td>RS 250</td>
<td>24.3 ± 0.4</td>
<td>7.7 ± 0.1</td>
<td>0.3 ± 0.0</td>
<td>28.7 ± 0.2</td>
<td>15.0</td>
<td>24</td>
</tr>
<tr>
<td>RS 275</td>
<td>12.9 ± 0.2</td>
<td>2.3 ± 0.1</td>
<td>*N. D.</td>
<td>35.2 ± 0.1</td>
<td>10.6</td>
<td>39</td>
</tr>
<tr>
<td>RS 300</td>
<td>1.6 ± 0.0</td>
<td>*N. D.</td>
<td>*N. D.</td>
<td>37.9 ± 0.1</td>
<td>7.5</td>
<td>53</td>
</tr>
<tr>
<td><strong>Wheat straw (WS)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WS U</td>
<td>33.9 ± 0.6</td>
<td>21.2 ± 0.4</td>
<td>1.7 ± 0.1</td>
<td>19.1 ± 0.1</td>
<td>24.1</td>
<td>0</td>
</tr>
<tr>
<td>WS 200</td>
<td>33.0 ± 1.0</td>
<td>19.3 ± 0.7</td>
<td>2.3 ± 0.1</td>
<td>19.6 ± 0.2</td>
<td>18.7</td>
<td>7</td>
</tr>
<tr>
<td>WS 225</td>
<td>32.5 ± 0.2</td>
<td>17.7 ± 0.2</td>
<td>2.1 ± 0.1</td>
<td>20.2 ± 0.2</td>
<td>16.5</td>
<td>11</td>
</tr>
<tr>
<td>WS 250</td>
<td>28.6 ± 0.4</td>
<td>11.9 ± 0.3</td>
<td>0.6 ± 0.0</td>
<td>23.9 ± 0.1</td>
<td>15.0</td>
<td>20</td>
</tr>
<tr>
<td>WS 275</td>
<td>13.6 ± 0.2</td>
<td>2.3 ± 0.0</td>
<td>*N. D.</td>
<td>34.5 ± 0.3</td>
<td>9.6</td>
<td>40</td>
</tr>
<tr>
<td>WS 300</td>
<td>0.7 ± 0.0</td>
<td>0.2 ± 0.0</td>
<td>*N. D.</td>
<td>37.4 ± 0.3</td>
<td>5.7</td>
<td>56</td>
</tr>
</tbody>
</table>

*N. D.: not detected, below the detection limit
4.1.3 Thermogravimetry results of the samples

The thermal stability and formation of the volatile products of the untreated and torrefied samples were studied by the thermogravimetry/mass spectrometry method. The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves give information about the thermal stability of the untreated (Figure 23) and torrefied (Figure 24) samples. The comparison of the curves shows that the shape of the TG and DTG curves of the two straw samples are rather similar, while black locust wood behaves differently during thermal decomposition. As we discussed earlier, it is well-known from the literature (DeGroot and Shafizadeh, 1984, Sekiguchi and Shafizadeh, 1984, Várhegyi et al., 1988, Saleh et al., 2013, Shoulaifar et al., 2016) that the difference between the behavior of wood and herbaceous samples is partly due to the different alkali ion contents, which have a significant effect on the thermal properties of cellulose. The different thermal behaviors of the torrefied woody and herbaceous biomass materials can also be interpreted by their different inorganic ion contents. Furthermore, the relative amounts of alkali ions further increased in the torrefied samples.

The evaporation and decomposition of extractives in the raw samples are visible on the DTG curve as a broad shoulder starting at approximately 180 °C (Figure 23 b). The higher weight loss of raw rape straw compared to wheat straw and black locust (Figure 23 a) between 200 and 300 °C designates the highest extractive content of rape straw sample.

During torrefaction at 225 °C, the extractive content of the samples mostly evaporated; therefore, the above mentioned difference disappeared from the TG and DTG curves of rape straw (Figure 24 a and b) and the weight loss curves of the three torrefied materials overlap up to 300 °C. This observation is in accordance
with the results of chemical composition analysis, where a higher amount of
extractives and/or acid-soluble inorganics were determined in the untreated rape
straw sample (see “Other” component in Table 6) than in the other biomass
samples studied. The main DTG peak of the untreated samples (Figure 23 b) can be
explained by the decomposition of cellulose. The characteristic shoulder on the DTG
curve of the untreated black locust sample (Figure 23 b) up to 350 °C represents the
decomposition of hemicellulose. In the case of herbaceous samples, the
hemicellulose shoulder is not pronounced because the cellulose decomposition is
shifted to a lower temperature as a result of the catalytic effect of the high amounts
of alkali ions.

As the compositional analysis data demonstrate (Table 6), the
hemicellulose content of the samples did not degrade during torrefaction at 225 °C.
The DTG curve of black locust torrefied at 225 °C (Figure 24 b) has a significant
shoulder, representing the decomposition of hemicellulose. O-Acetyl-4-O-
methylglucuronoxylan is the main building block of hemicellulose in hardwood
species. In herbaceous biomass, arabinoxylans are the dominant hemicellulose
polysaccharides.

After torrefaction at 250 °C (Figure 24 c and d), the characteristic shoulder on the
DTG curve of black locust wood disappeared, indicating that hemicellulose
decomposed or its structure changed as a result of the torrefaction. The results of
the acidic hydrolysis revealed that about 40% of the hemicellulose content
decomposed during the torrefaction at 250 °C temperature. The significant residual
hemicellulose content of the samples torrefied at 250 °C contradicts the
disappearance of the hemicellulose shoulder from the DTG curve. These results can
be explained by the assumption that the thermally most labile functional groups
(e.g., acetyl groups) of hemicelluloses were split off under torrefaction; therefore,
the remaining hemicellulose chains became more stable and decomposed in a
temperature range similar to that of cellulose. With regard to the cellulose
component of the torrefied samples, the TG curves confirm the results of the
compositional analysis: Low-temperature torrefaction has only a small effect on the
amount of cellulose.

After torrefaction at 275 °C (Figure 24 e and f), the maximal rate of thermal
decomposition of wheat and rape straw samples decreased by about 50%,
indicating the high degree of cellulose decomposition during the torrefaction.
Torrefaction at 275 °C still did not significantly affect the cellulose content of black
locust sample. These observations also indicate the catalytic influence of alkali ions
on the decomposition of cellulose.
Figure 24  TG and DTG curves of black locust wood, rape straw and wheat straw after the various torrefaction treatmen.

(WS: wheat straw, RS: rape straw, BL: black locust)
After torrefaction at 300 °C, the DTG curve of black locust is significantly reduced but still with some cellulose content extant, while the DTG curves of wheat straw and rape straw have (Figure 24 h) a wide and flat shape, indicating the almost complete decomposition of cellulose. Lignin decomposes at a low rate in a wide temperature range from 250 to 600 °C; therefore, it does not have a separate DTG peak. Lignin is a complex cross-linked methoxyphenol-based polymer built of monolignol subunits: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. Lignin of the herbaceous materials is composed of all three types of monolignols, while the hardwood lignin is built of only coniferyl alcohol and sinapyl alcohol. The lignin and alkali ion contents of the samples have a considerable effect on the char yield of biomass. Lignin produces about 30% char (Jakab et al., 1995, 1997), whereas the decomposition of cellulose and hemicellulose leads to only about 5 and 5-10% solid residue, respectively. The inherent alkali ion content of lignocellulosic materials changes the thermal decomposition mechanism; a higher char yield and an increased amount of gaseous products are formed with increasing alkali ion content (Sekiguchi and Shafizadeh, 1984, Sebestyén et al., 2011).

4.1.4 Principal component analysis based on the HHV, TG parameters, and chemical composition data

The thermogravimetry parameters (\(T_{\text{peak}}\), \(\text{DTG}_{\text{max}}\), \(T_{\text{start}}\), \(T_{1\%}\), \(T_{\text{end}}\), and char yield), the chemical composition data (glucan, xylan, and lignin contents), and the higher heating values (HHV) of the samples have been used in the calculation as input data to illustrate the differences and similarities between the untreated and torrefied biomass samples (Tables 4 and 6, Figures 23 and 24). In the PCA calculation (Figure 25), the first principal component (Factor 1) characterizes 67.26%, while the second and third principal components (Factors 2 and 3) describe 14.67 and 9.86% of the total variance, respectively. These three factors describe adequately the main differences between the samples. The score plot for Factors 1 and 2 (Figure 25 a) shows that the black locust (BL), rape straw (RS), and wheat straw (WS) samples can be seen in different parts of the plot. The first principal component differentiates the untreated and mildly and severely torrefied samples. As a function of the second principal component (Factor 2), the herbaceous samples are found in the upper part of the score plot and the woody samples are found in the lower part of the score plot. This difference is apparently due to the different cellulose, hemicellulose, lignin, and extractive contents of the samples, which is reflected in the different thermal behaviors of woody and herbaceous materials.
Figure 25 PCA (a and c) score and (b and d) loading plots based on the calorific values, TG, and chemical composition data. The arrows show the direction of the variation of the samples with increasing torrefaction temperatures. (WS, wheat straw; RS, rape straw; and BL, black locust wood)
The loading plot for Factors 1 and 2 (Figure 25 b) shows that the values of glucan and xylan contents and DTGmax data correlate negatively with the HHV, Klason lignin content, char yield, T_{start}, and T_{1%} data. Factor 1 is composed of mainly these parameters and mostly separates the studied samples as a function of the torrefaction temperature. Figure 25 a shows that the herbaceous samples torrefied at 275 and 300 °C are separated, essentially indicating the severe decomposition. T_{peak} and T_{end} data contribute mainly to Factor 2; these parameters describe the cellulose decomposition.

Untreated black locust (hardwood) and wheat straw have similar cellulose contents (approximately 34%); however, straw samples have more than an order of magnitude higher K\(^+\) and Na\(^+\) contents than black locust (Table 5). As a result of the alkali catalysis, the characteristic temperatures of cellulose decomposition of the herbaceous samples shift to lower temperatures. Mainly this effect is reflected in Factor 2. Factor 3, describes almost 10% of the total variance.

The loading plot (Figure 25 d) shows that the values of T_{1%}, T_{start}, cellulose content, and DTG_{max} contribute to Factors 3 and 1 as well. T_{1%} and T_{start} can be attributed to the hemicellulose decomposition in untreated and mildly treated samples, while after severe torrefaction (i.e. after the decomposition of hemicellulose), these parameters belong to the cellulose decomposition. The samples formed two groups as a function of Factors 1 and 3, as shown in Figure 25 c. The severely torrefied samples are separated from the untreated and mildly torrefied biomass samples.

As mentioned above, the maximum rate of thermal decomposition (DTG_{max}) of straw samples decreased by half between the torrefied samples at 250 and 275 °C, while the DTG_{max} data of black locust wood only differ significantly between the samples treated at 275 and 300 °C. It was found that the hemicellulose and cellulose contents of the studied samples strongly decreased from 250 to 300 °C (see Table 6). At the severe torrefaction temperatures (275-300 °C), the chemical composition of the samples significantly changed during torrefaction; therefore, the thermal properties of the samples were altered to a greater extent in this temperature range.
4.1.5 Influence of inorganic ion contents on the thermal degradation process during torrefaction

To estimate the effect of the torrefaction pretreatment during thermochemical conversion, it is important to widen our knowledge on how the inorganic elements modify the thermal decomposition during torrefaction. The aim of this part is to clarify the influence of the inorganic ion contents on the thermal degradation process during torrefaction. For this purpose, we washed the raw samples with hot water to remove the majority of the water soluble inorganic components. The thermal degradation properties of raw and washed samples have been compared. The efficiency of the inorganic ion removal was verified by inductively coupled plasma optical emission spectrometry (ICP-OES) method. Table 7 shows the ash and potassium contents of the original and washed samples. As the data illustrate, ash contents of the two original straw samples are significantly higher in comparison to the original black locust sample; furthermore, the original wheat and rape straw samples have an order of magnitude higher $K^+$ content than the original wood sample. The ash content of the three studied samples is significantly decreased after the washing procedure; moreover, the potassium ion content of the samples was removed successfully.

Table 7 Ash and potassium contents of the original and washed samples (ICP-OES).

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Ash content (%)</th>
<th>$K^+$ content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original black locust wood</td>
<td>1.75</td>
<td>0.27</td>
</tr>
<tr>
<td>Washed black locust wood</td>
<td>1.48</td>
<td>0.01</td>
</tr>
<tr>
<td>Original wheat straw</td>
<td>5.68</td>
<td>1.69</td>
</tr>
<tr>
<td>Washed wheat straw</td>
<td>2.51</td>
<td>0.06</td>
</tr>
<tr>
<td>Original rape straw</td>
<td>6.04</td>
<td>1.86</td>
</tr>
<tr>
<td>Washed rape straw</td>
<td>1.93</td>
<td>0.03</td>
</tr>
</tbody>
</table>

The original and washed black locust wood, rape straw, and wheat straw were torrefied at five different temperatures (200, 225, 250, 275 and 300 °C) using 1 h isothermal period. The thermally untreated (original and washed) and treated samples were characterized and their thermal properties were compared. Chemical composition analysis (Figure 26), thermogravimetry measurements (Figures 27-30) and principal component analysis (Figure 31) were performed on untreated, hot water washed, and various torrefied black locust, rape straw, and wheat straw samples.
4.1.5.1 Comparison of the chemical composition of the original and washed samples

The compositional analysis of the original untreated and torrefied samples was discussed in detail in Section 4.1.2. The compositional analysis of the hot water washed samples was also carried out to monitor the effect of torrefaction on the thermal decomposition and compare the thermal behavior of these different samples (Table 8). Figure 26 shows the compositional analysis of the original and hot water washed samples, where the glucan content of the samples mainly characterizes the cellulose component of lignocellulose, while the sum of the xylan and arabinan contents represents the hemicellulose fraction. The Klason lignin is defined as the acid-insoluble residue of the samples without the acid-insoluble ash content. The fraction denoted “Other” represents the sum of the unquantified components. To compare the degradation degree of the components in the torrefied samples, one has to take into consideration the mass loss during the torrefaction experiment as well. As we discussed earlier, hemicellulose (measured as the sum of xylan and arabinan) is the thermally least stable component of the studied samples during torrefaction. The changes in the relative amount of hemicellulose show similar tendencies as a function of the torrefaction temperature for the original and hot water washed samples. After torrefaction at 275 °C the hemicellulose content of the original samples drastically decreases, while the washed samples torrefied at 275 °C still retain about 20-30% of the hemicellulose content of untreated sample. At 300 °C, only trace amounts of hemicellulose remained in the original samples, however the washed samples still have measurable amount of hemicellulose. Comparing the hemicellulose content of the original and washed samples, we can conclude that the effect of washing is more pronounced in the case of the straw samples. Studying the washed samples we may conclude that the thermal decomposition of hemicelluloses is influenced by the presence of alkaline ions in the low concentration range. As discussed above, the relative amount of hemicellulose changed similarly in the original wood and straw samples as a function of the torrefaction temperature indicating no measurable effect of the different alkali ion contents in the higher concentration range. The effect of alkali ion concentration was studied by Sebestyén et al. [2011] on the thermal decomposition of hemp and it was concluded that the TG/MS parameters of cellulose decomposition were changing very steeply in the low concentration range and they were levelling off in the high concentration range. It is possible that the concentration effect of the alkali ions is similar in case of hemicellulose decomposition, but the changes are much smaller.
Table 8 Composition of the washed untreated and torrefied samples. The percentage data are corrected with the mass loss values, thus the compositional data are referred to the original sample masses. Standard deviations are calculated from triplicates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Glucan (% m/m)</th>
<th>Xylan (% m/m)</th>
<th>Arabinan (% m/m)</th>
<th>Klason lignin (% m/m)</th>
<th>Other (% m/m)</th>
<th>Mass loss during torrefaction (% m/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Washed black locust (BL_W)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BL U W</td>
<td>38.6 ± 0.0</td>
<td>16.3 ± 0.0</td>
<td>2.0 ± 0.0</td>
<td>22.4 ± 0.2</td>
<td>20.7</td>
<td>0</td>
</tr>
<tr>
<td>BL 200 W</td>
<td>37.1 ± 0.4</td>
<td>15.5 ± 0.1</td>
<td>1.8 ± 0.1</td>
<td>22.7 ± 0.4</td>
<td>17.9</td>
<td>5</td>
</tr>
<tr>
<td>BL 225 W</td>
<td>37.6 ± 0.4</td>
<td>15.0 ± 0.2</td>
<td>1.5 ± 0.1</td>
<td>24.9 ± 0.6</td>
<td>14.7</td>
<td>6</td>
</tr>
<tr>
<td>BL 250 W</td>
<td>38.8 ± 0.5</td>
<td>10.5 ± 0.2</td>
<td>0.8 ± 0.2</td>
<td>26.8 ± 0.1</td>
<td>9.8</td>
<td>13</td>
</tr>
<tr>
<td>BL 275 W</td>
<td>34.54 ± 0.4</td>
<td>4.4 ± 0.2</td>
<td>0.3 ± 0.1</td>
<td>29.1 ± 0.5</td>
<td>6.6</td>
<td>25</td>
</tr>
<tr>
<td>BL 300 W</td>
<td>23.9 ± 2.5</td>
<td>1.0 ± 0.6</td>
<td>0.1 ± 0.2</td>
<td>29.7 ± 3.0</td>
<td>4.8</td>
<td>40</td>
</tr>
<tr>
<td><strong>Washed rape straw (RS_W)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RS U W</td>
<td>39.9 ± 0.2</td>
<td>23.0 ± 0.1</td>
<td>2.7 ± 0.0</td>
<td>18.1 ± 0.1</td>
<td>16.3</td>
<td>0</td>
</tr>
<tr>
<td>RS 200 W</td>
<td>39.3 ± 0.4</td>
<td>22.3 ± 0.2</td>
<td>2.6 ± 0.2</td>
<td>18.0 ± 0.1</td>
<td>14.4</td>
<td>4</td>
</tr>
<tr>
<td>RS 225 W</td>
<td>39.3 ± 0.3</td>
<td>21.2 ± 0.8</td>
<td>2.4 ± 0.0</td>
<td>18.5 ± 0.1</td>
<td>12.5</td>
<td>6</td>
</tr>
<tr>
<td>RS 250 W</td>
<td>38.1 ± 0.4</td>
<td>13.5 ± 0.6</td>
<td>1.2 ± 0.1</td>
<td>20.7 ± 0.9</td>
<td>11.7</td>
<td>15</td>
</tr>
<tr>
<td>RS 275 W</td>
<td>33.6 ± 0.5</td>
<td>4.0 ± 0.5</td>
<td>0.3 ± 0.0</td>
<td>24.8 ± 0.6</td>
<td>7.7</td>
<td>30</td>
</tr>
<tr>
<td>RS 300 W</td>
<td>28.3 ± 0.2</td>
<td>4.3 ± 1.6</td>
<td>0.3 ± 0.1</td>
<td>18.4 ± 1.4</td>
<td>6.8</td>
<td>42</td>
</tr>
<tr>
<td><strong>Washed wheat straw (WS_W)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WS U W</td>
<td>33.7 ± 0.3</td>
<td>17.9 ± 0.1</td>
<td>2.1 ± 0.1</td>
<td>21.0 ± 0.2</td>
<td>25.2</td>
<td>0</td>
</tr>
<tr>
<td>WS 200 W</td>
<td>32.0 ± 0.1</td>
<td>16.8 ± 0.1</td>
<td>1.9 ± 0.2</td>
<td>21.8 ± 0.3</td>
<td>21.4</td>
<td>6</td>
</tr>
<tr>
<td>WS 225 W</td>
<td>31.7 ± 0.2</td>
<td>15.3 ± 0.1</td>
<td>1.4 ± 0.2</td>
<td>23.0 ± 0.3</td>
<td>18.0</td>
<td>11</td>
</tr>
<tr>
<td>WS 250 W</td>
<td>31.9 ± 0.2</td>
<td>10.8 ± 0.4</td>
<td>0.7 ± 0.0</td>
<td>25.8 ± 0.6</td>
<td>14.0</td>
<td>17</td>
</tr>
<tr>
<td>WS 275 W</td>
<td>29.4 ± 0.2</td>
<td>5.0 ± 0.4</td>
<td>0.4 ± 0.2</td>
<td>28.0 ± 0.4</td>
<td>9.4</td>
<td>28</td>
</tr>
<tr>
<td>WS 300 W</td>
<td>21.6 ± 2.1</td>
<td>1.6 ± 1.4</td>
<td>0.2 ± 0.0</td>
<td>27.8 ± 4.5</td>
<td>7.2</td>
<td>42</td>
</tr>
</tbody>
</table>
The comparison of the original and washed samples of the same torrefaction temperature shows that the washed samples have significantly higher amount of cellulose than the original samples, even at the torrefaction temperature of 275-300 °C. As already mentioned, the presence of alkali ions modifies the thermal degradation of cellulose and lignin. The reason for the promoted decomposition rate of the original samples during torrefaction is most probably the alkali ion catalyzed decomposition of its cellulose content.

![Figure 26](image.png)

**Figure 26** Effect of torrefaction temperature on the composition of the original and washed black locust wood, wheat straw and rape straw (calculated on dry basis).
4.1.5.2 Effect of torrefaction temperature on the thermogravimetric properties of original and washed black locust wood, rape straw, and wheat straw

The TG and DTG curves of untreated and lightly (200 °C), mildly (225 and 250 °C) and severely (275 and 300 °C) torrefied samples can be seen in Figures 27-29, while Figure 30 presents the major thermogravimetric parameters (DTG\text{max}, T_{\text{peak}} and char obtained at 900 °C) of the original and washed biomass samples. $T_{\text{peak}}$ denotes the temperature of the maximal decomposition rate (DTG\text{max}). As Figure 27 a, c, and e shows, the shoulder of the extractives around 220 °C disappeared from the DTG curves of washed untreated samples, indicating the efficient removal of extractive content by hot water washing. It can be concluded, that the shape of the DTG curves of the untreated samples became rather similar after washing; the hemicellulose shoulder at around 300 °C shows a better separation from the cellulose peak (DTG\text{max}) in the three washed samples. As Figure 27-30 show, the maximal rate of cellulose decomposition of the untreated and torrefied samples is shifted to a higher temperature as a result of washing procedure due to the reduced alkali ion concentration. Furthermore, it can be concluded that the thermal stability of cellulose in the washed wood sample is raised by about 30 °C, while it is raised by about 50 °C in the hot water washed straw samples compared to the original samples (Figure 30 d, e, and f).

The char yield of the raw and torrefied hot water washed samples is significantly lower than for the unwashed samples (Figure 30 g, h, and i). The extent of lowering is higher than the decrease of the ash content as a result of washing. This result confirms the promoting effect of potassium on the char formation. The char yields are changed to a larger extent in case of washed straw samples than washed wood, due to greater reduction in the alkali ion concentration of straws as a result of washing. This observation is in agreement with the chemical composition results showing that the influence of washing is more pronounced in the case of the straw samples.

After torrefaction at 250 °C, the characteristic hemicellulose shoulder of the original samples disappeared, while the washed samples still have a shoulder (Figure 28 b, d, and f). Significant differences can be seen after severe torrefaction conditions (275 and 300 °C) between the original and hot water washed samples (Figure 29). After torrefaction at 275 °C, the maximal rate of thermal decomposition of the original straw samples are significantly reduced, while in case of the washed straw samples did not changed. This indicates that torrefaction at 275 °C still it did not affect considerably the cellulose content (Figure 29 c and e). After torrefaction at
300 °C, the DTG curves of the original straw samples have a wide and flat shape (Figure 29 d and f), indicating the almost complete decomposition of cellulose, while the same temperature only slightly affect the cellulose content of the washed straw samples. These observations also designate the catalytic effect of alkali ions on the decomposition of cellulose and are in agreement with the results of the compositional analysis. We can conclude, that the effect of washing is more pronounced at higher torrefaction temperatures.

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**Figure 27** TG and DTG curves of untreated and lightly (200 °C) torrefied black locust (BL), wheat straw (WS) and rape straw (RS) samples.
Figure 28 TG and DTG curves of the mildly (225 and 250 °C) torrefied black locust (BL), wheat straw (WS) and rape straw (RS) samples.
Figure 29 TG and DTG curves of the severely (275 and 300 °C) torrefied black locust (BL), wheat straw (WS) and rape straw (RS) samples.
Figure 30 The main thermogravimetric parameters of the samples as a function of the treatment temperatures. $T_{\text{peak}}$ cannot be defined in case of the original straw samples torrefied at 300 °C due to the wide and flat DTG curves.
4.1.5.3 Principal component analysis (PCA) based on TG parameters, and chemical composition data of the original and washed samples

The chemical composition data (Figure 26) and the thermogravimetry parameters (Figures 27-30) of the original and washed samples have been used in the PCA calculation as input data to illustrate the differences and similarities between the original, washed, and variously torrefied samples. The first principal component (Factor 1) describes 58.10% of the total variance of the data, while the second principal component (Factor 2) describes 18.79% of the total variance. As Figure 31 illustrates, the first principal component differentiates the untreated and mildly and severely torrefied samples, while as a function of the second principal component (Factor 2), the original herbaceous samples are found in the upper part of the score plot, and the washed samples are found in the lower part of the score plot. This difference is apparently due to the different inorganic content and chemical composition of the samples, which are reflected in the different thermal properties of original and washed materials. The PCA results illustrate that the difference between the thermal behaviors of the untreated and torrefied washed samples (represented by the changes of $T_{\text{start}}$, $T_{\text{peak}}$ and $\text{DTG}_{\text{max}}$) is much smaller than the difference between original and washed samples.

![Figure 31 Results of PCA: score (a) and loading (b) plots based on the compositional analysis and TG parameters. The arrows show the direction of the variation of the samples with the increasing torrefaction temperature. (WS, wheat straw; RS, rape straw; and BL, black locust, BL_225: black locust wood torrefied at 225 °C, BL_225_W: washed black locust wood torrefied at 225 °C)](image-url)
4.1.6 Thermogravimetry/mass-spectrometry results

The evolution profiles of the most characteristic decomposition products of the raw and torrefied black locust and wheat straw samples are presented in Figures 32-34. The pattern of the ion intensity curves of rape straw is very similar to that of wheat straw; hence, it is not presented here. As can be seen in Figures 32 and 33, relatively large amounts of water and carbon dioxide are produced during the thermal decomposition of the samples as a result of the various types of hydroxyl and other oxygen-containing functional groups in the natural polymers (cellulose, hemicellulose, and lignin). The higher temperature charring processes are characterized by the evolution of hydrogen (m/z 2) and methane (m/z 16). Figures 32 and 34 show the evolution of some characteristic organic volatile products and fragment ions from the raw and torrefied black locust wood and wheat straw samples. Formaldehyde (m/z 30) forms during the thermal decomposition of cellulose, hemicellulose, and lignin as well. The release of methanol can be monitored at m/z 31. Furthermore, m/z 31 is the main fragment ion of hydroxyacetaldehyde, which is an important product of cellulose decomposition.

![Graphs](image)

Figure 32 DTG curves and the evolution profiles (arbitrary units) of the main permanent gases, water and a few characteristic organic products and fragments from untreated black locust wood and wheat straw. (m/z 2, hydrogen; m/z 16, methane; m/z 18, water; m/z 44, CO₂; m/z 27, C₂H₃⁺; m/z 30, formaldehyde; m/z 31, CH₃O⁺; and m/z 60, acetic acid and hydroxyacetaldehyde)
The evolution curve at $m/z$ 60 ion may represent either acetic acid released mostly from the acetate groups of hemicellulose or hydroxyacetaldehyde formed mainly during cellulose decomposition. The $m/z$ 27 ion is a typical fragment ion of hydrocarbons.

The moisture content ($m/z$ 18 in Figure 32 and 33) releases from the samples up to 120 °C. During torrefaction, the moisture content of the sample was released; however, during sample handling, the torrefied samples can take up some water from the air depending upon the degree of hydrophilicity of the torrefied sample. The moisture content of the torrefied straw samples is higher than that of the torrefied wood samples, which may be explained by the higher inorganic ion content and, therefore, the more hydrophilic nature of the torrefied straw samples. The evolution of water, carbon dioxide, formaldehyde, and methanol (Figure 32) in the temperature range of 200-250 °C reveals the thermolysis of extractives and scission of lignin side groups from the untreated samples. These processes start at around 200 °C, and the significant shoulder at 230 °C on the DTG and ion curves of untreated black locust can be attributed to the decomposition of extractives (Mészáros et al., 2007). During 1 h thermal pretreatment at 225 °C, the extractive content of the sample decomposed; therefore, the shoulder at 230 °C disappeared from the torrefied samples (Figures 33 a and 34 a). The characteristic peaks or shoulders of formaldehyde, acetic acid, methanol, carbon dioxide, and water in the temperature range of 280–350 °C of the untreated wood sample (Figures 32 a and c) represent the decomposition of hemicellulose. In the case of the herbaceous samples, the shoulder is not pronounced (Figures 32 b and d) because the cellulose decomposition shifts to a lower temperature as a result of the higher alkali ion content. The evolution of acetic acid and carbon dioxide indicates the scission of the acidic groups from hemicellulose. The composition analysis (Table 6) revealed that the hemicellulose content of the samples does not decrease during thermal treatment at 225 °C. However, the ion intensities of the significant decomposition products of hemicellulose slightly decreased in the case of the wood sample (Figures 33 a and 34 a). This observation may point to the somewhat modified structure (e.g., scission of the most labile acidic groups) as a result of torrefaction at 225 °C.

The TG/MS curves of the samples torrefied at 250 °C (Figures 33 c and 34 c) verify our assumption based on the DTG curve that the decomposition of the remaining part of hemicellulose takes place in the temperature range of cellulose
decomposition. The main thermal decomposition product of cellulose is levoglucosan, which cannot be detected by TG/MS, but smaller decomposition products, such as hydroxyacetaldehyde ($m/z$ 60), formaldehyde ($m/z$ 30), and methanol ($m/z$ 31, which is also a fragment ion of hydroxyacetaldehyde), can be monitored (Figures 32 and 34). Significant amounts of water and carbon dioxide are released during cellulose decomposition as well (Figures 32 and 33). The ion intensities describing the decomposition of cellulose (in the temperature range of the main DTG peak) do not decrease as a result of the thermal treatment up to 250 °C torrefaction temperature. Increasing the temperature of the torrefaction to 275 °C, results in the reduced evolution of all cellulose decomposition products by about 40% in the wheat straw sample; while it does not decrease significantly in the case of the black locust sample. This observation shows the more developed degradation of cellulose in herbaceous wheat straw at 275 °C.

After torrefaction at 300 °C, the ion intensity curves of the black locust sample (Figures 33 g and 34 g) show significant but not complete degradation of cellulose, while in the case of the wheat straw sample (Figures 33 h and 34 h), the ion curves prove the almost complete degradation of cellulose and hemicellulose. These TG/MS results confirm the results of the chemical composition analysis (Table 6).

The evolution profile of methane ($m/z$ 16 in Figures 32 and 33) shows a wide bimodal shape. In the temperature range of 370-500 °C, methane forms during the thermal decomposition of lignin by the scission of the methoxy groups (Jakab et al., 1997). The slightly higher methane evolution from black locust wood in this temperature range is in accordance with the higher methoxy group content of hardwood lignin compared to herbaceous lignin. After torrefaction, the relative amount of Klason lignin increased in the samples as a result of the release of extractives as well as the degradation of hemicellulose and cellulose at higher torrefaction temperatures. The increased evolution of methane originating from the decomposition of lignin indicates this process. This effect is more pronounced in the case of the wood sample. In the temperature range of 400-600 °C, the evolution of small hydrocarbon molecules were observed, represented by the $m/z$ 27 ion curves in Figures 32 and 34. The relative intensity of the hydrocarbon evolution is increasing by the torrefaction temperature in the case of both the wood and straw samples. These hydrocarbon molecules may be produced by secondary reactions involving the decomposition products of cellulose, hemicellulose, and lignin. Methane formation above 500 °C and hydrogen evolution ($m/z$ 2 in Figure 33) above 600 °C occur during the charring reactions.
Figure 33 DTG curves and the evolution profiles (arbitrary units) of the main permanent gases and water from black locust wood and wheat straw torrefied at various temperatures. \((m/z\ 2, \text{hydrogen}; m/z\ 16, \text{methane}; m/z\ 18, \text{water}; m/z\ 44, \text{CO}_2)\)
Figure 34 DTG curves and the evolution (arbitrary units) of a few characteristic organic products and fragments from black locust wood and wheat straw torrefied at various temperatures. ($m/z$ 27, $C_3H_5^+$; $m/z$ 30, formaldehyde; $m/z$ 31, $CH_3O^+$; and $m/z$ 60, acetic acid and hydroxyacetaldehyde)
In comparison of the intensities of the selected ions as a function of the torrefaction temperature, it can be observed that the evolution of hydrogen and methane is increasing, while the intensities of the other presented lignocellulose decomposition products are decreasing with raising the torrefaction temperature. These changes indicate the progress of the thermal decomposition during the torrefaction. In the case of the black locust sample, the ion intensity curve of carbon dioxide has two small sharp peaks, at 530 and 670 °C, indicating the presence of calcium oxalate, which originates from the bark of black locust wood (Mészáros et al., 2004).

### 4.1.6 Principal component analysis based on the TG/MS data

PCA has been used to illustrate correlations between the ion intensity data of the main decomposition products obtained by the TG/MS technique. The integrated intensities of the characteristic mass spectrometric ion curves have been used in the PCA calculation (Figure 35). The first principal component (Factor 1) describes 79.67% of the total variance of the TG/MS data, while the second and third principal components (Factors 2 and 3) describe 11.56 and 3.19% of the total variance, respectively. The first principal component differentiates the untreated and lightly torrefied samples from the mildly and severely torrefied samples; therefore, Factor 1 correlates with the torrefaction temperature (Figure 35 a). The loading plot for Factors 1 and 2 (Figure 35 b) reveals that mainly organic molecules contribute to Factor 1.

The increasing torrefaction temperature correlates with the methane and hydrogen yields, which shows that the severely torrefied samples produced more gases during the charring reactions. On the other hand, the decreasing torrefaction temperature correlates mainly with the formaldehyde, acetone, and acetic acid formation because these compounds were released apparently during light and mild torrefaction; hence, their pyrolytic yield is decreasing with an increasing torrefaction temperature. The amounts of CO, CO₂, and water play the most important role in determining the second principal component (Factor 2). As seen earlier, more gaseous products and water vapor were released from the herbaceous plants than from the hardwood. These differences can be explained by the different alkali ion contents of the studied samples. The higher alkali ion content promotes the gas formation during torrefaction of wheat straw and rape straw via fragmentation. On the other hand, the depolymerization reactions are dominant during the torrefaction of black locust wood indicated by the higher yields of furfural (sum of m/z 95 and 96) and furanone (m/z 84), which also contribute to the
second principal component. On the other hand, the loading plots (Figure 35 d) suggest that the yields of furanone, furfural, and methanol (m/z 31) as well as acetic acid and hydroxyacetaldehyde (m/z 60) also play a role in determining the third principal component. At the given torrefaction temperatures, the yields of these compounds are higher during the decomposition of black locust wood than of that of wheat straw and rape straw. The second and third principal components (Factor 2 and 3) may be attributed to the effect of both the different chemical compositions and the inorganic contents of the studied samples.

Two sets of principal component analysis calculations (Figures 25 and 35) were undertaken using different types of data, which resulted in consistent results; the untreated and mildly torrefied samples were separated from the severely torrefied samples. The calculations revealed that the chemical composition and, therefore, the thermal properties have changed to a much greater extent in the temperature range of 275-300 °C than at lower torrefaction temperatures.
4.1.8 Formation of methyl chloride under torrefaction

In this part the effect of torrefaction on the lignocellulose chlorine content was studied. Evolution of methyl chloride (CH₃Cl) was detected among the decomposition products of untreated and torrefied wheat straw and rape straw samples by TG/MS experiments. In order to monitor the release of methyl chloride as a function of temperature, the evolution curves of the molecular ions at m/z 50 and 52 were selected. As Figures 36 and 37 show, the m/z 50 and 52 ion curves are similarly shaped in case of the untreated and torrefied wheat straw and rape straw samples and keep the intensity ratio of 3:1 in the whole temperature range. These facts confirm that the m/z 50 and 52 curves display the evolution of methyl chloride molecular ions correctly, since the intensity ratio of m/z 50 and 52 ions complies with that of natural isotope of chlorine atom at m/z 35 and 37 (3:1). As Figures 36 and 37 present, the amount of evolved methyl chloride was under the detection limit in case of the wood samples contrary to the straw samples. For the confirmation of the TG/MS observations, the chlorine content of the raw materials was measured by ISO 587:1997 in ISD DUNAFERR Zrt. Materials Testing and Calibrating Laboratories Directorate (Dunaújváros). The chlorine content of untreated black locust wood was 0.04%, while that of rape straw and wheat straw were 0.63% and 0.30% respectively, explaining the TG/MS results. The temperature range of methyl chloride evolution is quite wide, and corresponds to a wide temperature range of lignin decomposition. It starts already at around 200 °C, reaches its maximum at about 350 °C, and ends at around 450 °C in all cases.

Considering the relative intensity of the ion curves, the formation of methyl chloride was quite similar from the untreated and torrefied straw samples at 200, 225 and 250 °C. As Figures 37 shows, the relative intensity of the evolution curves of m/z 50 and 52 halved between torrefaction at 250 and at 275 °C, while after torrefaction at 300 °C the evolution curves of methyl chloride almost totally disappeared from the straw samples. As we discussed earlier, methyl chloride is the reaction product of the inorganic chlorine with methyl groups evolved from cellulose or lignin. Recent studies (Czégény et al., 2015, Wang et al. 2017) concluded that the methoxy groups of lignin are the methyl source of methyl chloride. Based on these papers we may conclude that methyl chloride forms analogously from straws, the wide temperature range of methyl chloride evolution also support this phenomenon. Our results revealed that most of the lignin methoxy groups of straw samples were probably cleaved during torrefaction at 275 and 300 °C, and the initial chlorine content of the straw samples decreased. Furthermore, we may conclude that TG/MS is an appropriate technique for the detection of methyl chloride from the variously torrefied samples.
Figure 36 DTG curves and the evolution profiles of methyl chloride (monitored at m/z 50 and 52) from untreated and torrefied (200 and 225 °C) black locust (BL), wheat straw (WS) and rape straw (RS) during TG/MS experiments in argon atmosphere.
Figure 37 DTG curves and the evolution profiles of methyl chloride (monitored at m/z 50 and 52) from mildly and severely torrefied black locust (BL), wheat straw (WS) and rape straw (RS) during TG/MS experiments in argon atmosphere.
4.2 Thermal behavior of untreated and various torrefied bark, stem wood, and stump of Norway spruce

In this study, Norway spruce stem wood, stump and bark were torrefied at 225, 275 and 300 °C with two residence times (30 and 60 min). 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 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 inorganic components of the samples were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) technique. Furthermore, the effect of torrefaction was also studied on the physiochemical properties of woody biomasses. Principal component analyses have been applied to identify the similarities and differences between the untreated and various torrefied stem wood, bark and stump samples. The changes in the chemical structure of the Norway spruce stem wood, stump, and bark were analyzed by Py-GC/MS method.

4.2.1 Characterization of untreated and torrefied parts of softwood

Table 9 shows a summary of solid yields, higher heating values and proximate and ultimate analyses of the biomass samples torrefied at various temperatures for 60 min in comparison with the untreated samples. The solid yields of stem wood, stump, and bark decreases with increase in torrefaction temperatures as shown in Table 9. As the torrefaction temperature increased to 275 °C, there are significant mass losses for the three studied biomass materials. The solid yields drop continuously with further increase of torrefaction temperature to 300 °C. Stump is the most sensitive to the increase of the torrefaction temperature. The yields of solid residue dramatically decrease from 90% to 46% as the torrefaction temperature increase from 225 °C to 300 °C.

Table 9 shows that higher heating values (HHV) of torrefied samples increased with the raise in torrefaction temperature. The HHV increased by about 20% from 19.51-20.14 MJ kg\(^{-1}\) for the untreated biomass to 23.49-24.35 MJ kg\(^{-1}\) for those torrefied at 300 °C. It should be noted that torrefaction under severe conditions produces torrefied biomass with higher HHV; however, a large amount of energy was lost due to the loss of sample mass upon torrefaction.
<table>
<thead>
<tr>
<th>Samples</th>
<th>Solid yield (%)</th>
<th>Proximate analysis (%)</th>
<th>Ultimate analysis (%, m/m, dry and ash free basis)</th>
<th>HHV (MJ kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>VM</td>
<td>Ash</td>
<td>FC</td>
</tr>
<tr>
<td>Stem wood (SW)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SW U</td>
<td>100</td>
<td>88.12</td>
<td>0.31</td>
<td>11.57</td>
</tr>
<tr>
<td>SW 225_60</td>
<td>91</td>
<td>85.42</td>
<td>0.39</td>
<td>14.19</td>
</tr>
<tr>
<td>SW 275_60</td>
<td>76</td>
<td>74.36</td>
<td>0.42</td>
<td>25.22</td>
</tr>
<tr>
<td>SW 300_60</td>
<td>58</td>
<td>58.65</td>
<td>0.49</td>
<td>40.86</td>
</tr>
<tr>
<td>Stump (ST)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ST U</td>
<td>100</td>
<td>86.69</td>
<td>0.41</td>
<td>12.90</td>
</tr>
<tr>
<td>ST 225_60</td>
<td>90</td>
<td>82.12</td>
<td>0.66</td>
<td>17.22</td>
</tr>
<tr>
<td>ST 275_60</td>
<td>69</td>
<td>73.34</td>
<td>0.66</td>
<td>26.60</td>
</tr>
<tr>
<td>ST 300_60</td>
<td>46</td>
<td>55.74</td>
<td>1.08</td>
<td>43.19</td>
</tr>
<tr>
<td>Bark (BA)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BA U</td>
<td>100</td>
<td>74.85</td>
<td>2.11</td>
<td>23.04</td>
</tr>
<tr>
<td>BA 225_60</td>
<td>82</td>
<td>68.10</td>
<td>2.87</td>
<td>29.02</td>
</tr>
<tr>
<td>BA 275_60</td>
<td>69</td>
<td>60.97</td>
<td>2.50</td>
<td>36.52</td>
</tr>
<tr>
<td>BA 300_60</td>
<td>61</td>
<td>47.94</td>
<td>4.13</td>
<td>47.93</td>
</tr>
</tbody>
</table>
The proximate analysis shows that the volatile matter (VM) content of the torrefied biomasses decreased with the increase of torrefaction temperature. At a temperature of 225 °C, the volatile matter content of all torrefied biomasses slightly decreased, while significant reduction was observed at temperatures of 275 °C and 300 °C. The ash content of the torrefied biomasses increased due to loss of organic matter during torrefaction.

As the ultimate analysis shows in Table 9, the elemental composition of the torrefied biomasses also changes as a function of torrefaction severity. As the torrefaction temperature increases from 225 °C to 300 °C, the carbon content of the stem wood increased from 50.46% to 64.21%, whereas the oxygen content decreased by more than 30%. Both atomic H/C and O/C ratios decrease with the increase of torrefaction severity. During torrefaction, conversion of biomass is mainly associated with dehydration, decarboxylation and depolymerisation of the organic portion of the biomass, resulting in loss of water and release of gases and light volatiles. Therefore, during torrefaction, the biomass loses relatively more oxygen and hydrogen compared to carbon, hence resulting in the increase of the heating value of the torrefied biomass, as shown in Table 9.

The alkali contents of the untreated samples have been determined using ICP-OES (Table 10). As the results illustrate, the raw stem wood and stump contain around 250-300 mg/kg potassium and around 1000 mg/kg calcium, while both the potassium and calcium content of the raw bark is about seven times higher than that of the stem wood and stump.

Table 10 The most important inorganic components of softwood parts (dry basis).

<table>
<thead>
<tr>
<th>Inorganic components (mg/kg)</th>
<th>Bark</th>
<th>Stem wood</th>
<th>Stump</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{2+}$</td>
<td>7803</td>
<td>1030</td>
<td>1235</td>
</tr>
<tr>
<td>K$^+$</td>
<td>2011</td>
<td>272</td>
<td>245</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>47</td>
<td>22</td>
<td>36</td>
</tr>
<tr>
<td>Si</td>
<td>3602</td>
<td>82</td>
<td>253</td>
</tr>
</tbody>
</table>

4.2.2 Chemical composition and thermal properties of the raw samples

Figure 38 a shows the chemical composition of the three untreated samples. The sum of the mannan and galactan contents represents the hemicellulose fraction, whereas the glucan content of the samples mainly characterizes the cellulose fraction of biomass. The Klason lignin content is defined as the acid insoluble residue of the samples without the acid insoluble ash.
The fraction denoted by “Other” represents the sum of unquantified components and includes extractives, acid soluble lignin and acid soluble minerals.

As Figure 38 a shows, untreated bark has the highest Klason lignin content (40.8%). The untreated stump has the highest hemicellulose content (23.4%), while the untreated stem wood has the highest cellulose content (42.5%). The lignocellulose content (sum of lignin, cellulose and hemicellulose) of the untreated stem wood is 89.9%, while that of the untreated stump and bark is 80.5% and 77.9%, respectively. The reason for the relatively lower lignocellulose content of stump and bark could be their higher extractives, acid soluble lignin and acid soluble mineral content.

The TG and DTG curves of the untreated samples are shown in Figure 38 b. The main DTG peak is dominated by the decomposition of cellulose, while the shoulder at lower temperature (around 320 °C) can be attributed mainly to hemicellulose decomposition. The lignin decomposes at a lower rate in a wide temperature range (200-600 °C).

The evaporation and decomposition reactions of extractives start at lower temperatures and it is visible as a shoulder on the main DTG peak from approximately 200 °C. The comparison of the three untreated samples shows that bark releases the most extractives, in the low temperature range. The untreated stump has the most characteristic hemicellulose shoulder, which is in agreement with the chemical composition results showing that stump has the highest hemicellulose content.

The decomposition of bark starts at the lowest temperature, the DTG peak maximum occurs at the lowest temperature, and the maximum rate of decomposition is considerably lower than in the case of the stem wood and stump. The high lignin content (40.8%) of bark results in the formation of a high yield of char during thermal decomposition. The different thermal behavior of the different untreated samples can be explained by their different composition as well as by the well-known fact that alkali ions have catalytic effects on the decomposition mechanism of cellulose (DeGroot and Shafizadeh, 1984, Jakab, 2015) and the charring reactions of lignin (Jakab et al., 1997).

Regarding the thermal behavior of the studied samples, further information is given by the mass spectrometry curves. The thermal decomposition of extractives, cellulose, hemicellulose and lignin results in a high yield of low molecular mass compounds at low heating rate, hence the evolution profiles of these products are characteristic to the decomposition of the different parts of the tree.
Figure 38 (a) Composition and (b) TG and DTG curves of untreated stem wood, stump, and bark.

Figure 39 a, c, and e presents the DTG curves as well as the evolution of water and the main permanent gases detected by the mass spectrometer during the thermal decomposition of the three untreated samples. Relatively large amounts of water ($m/z$ 18), carbon monoxide ($m/z$ 28) and carbon dioxide ($m/z$ 44) are formed during the thermal decomposition of the untreated materials due to the large number of hydroxyl and other oxygen containing functional groups in the natural polymers (cellulose, hemicellulose and lignin). In the temperature range of 300-430 °C besides carbon monoxide the ion current at $m/z$ 28 represents the CO$^+$ mass spectrometric fragment ion of organic oxygen containing volatile products as well (e.g., formaldehyde). In the temperature range of 500-900 °C, the charring processes are characterized by the evolution of carbon monoxide ($m/z$ 28), methane ($m/z$ 16) and hydrogen ($m/z$ 2).

Figure 39 b, d, and f shows the evolution of some characteristic organic volatile products and fragment ions from the untreated samples. Formaldehyde ($m/z$ 30) is released during the thermal decomposition of cellulose, hemicellulose and lignin, as well. The fragment ion at $m/z$ 31 represents mainly the evolution of methanol during the thermal decomposition. On the other hand, $m/z$ 31 is the main fragment ion of hydroxyacetaldehyde, which is a typical product of the cellulose decomposition. The evolution curve of the $m/z$ 45 ion represents mainly COOH$^+$, which is the main fragment ion of acidic products released from hemicellulose and cellulose. The $m/z$ 27 ion is a typical fragment ion of hydrocarbons.
As Figure 39 a, c, and e presents, the moisture content (m/z 18) is released from the untreated samples up to 200 °C. The higher intensity and broader shape of this water peak for the bark sample indicate a higher moisture content of the bark sample, which may be bonded mostly to the inorganic components (Table 9) of the bark sample.

As seen in Figure 39, considerably higher amounts of permanent gases and lower amounts of organic volatiles are released from raw bark than from raw stem wood and stump. The characteristic peaks or shoulders of carbon dioxide, water, formaldehyde and methanol in the temperature range of 200-300 °C can be attributed to the thermolysis of extractives and scission of lignin side groups from the untreated samples.

In case of stem wood and stump, the characteristic shoulder of formaldehyde, carboxyl group, carbon dioxide and water in the temperature range of 300-350 °C reveals the decomposition of hemicellulose (Figure 39 c-f). O-acetylgalactoglucomannans are the main hemicelluloses in softwoods. The evolution profile of COOH* and carbon dioxide indicates the scission of the acidic groups from hemicellulose. The untreated stump produces the highest amount of acid products as the m/z 45 fragment ion indicates, which can be explained by the highest hemicellulose content of the stump sample (Figure 38 a). The hemicellulose shoulder of the untreated bark is not pronounced which is in agreement with the chemical composition results showing that bark has the lowest hemicellulose content (Figure 38 a). The main thermal decomposition product of cellulose is levoglucosan, which cannot be detected by TG/MS, but smaller decomposition products like formaldehyde (m/z 30), hydroxyacetaldehyde (m/z 31) and methanol (m/z 31) originating from cellulose can be monitored at around 390 °C as shown in Figure 39 b, d, and f. Significant amounts of water vapor and carbon dioxide are released during cellulose decomposition, as well. Methane (m/z 16) is released in two main processes during the thermal decomposition of the untreated samples. In the first process at around 450 °C methane forms during the thermal decomposition of lignin by the scission of the methoxy groups (Jakab et al., 1997). The evolution of carbon monoxide, methane and hydrogen (Figure 39 a, c, and e) above 500 °C takes place during the charring processes. As a result of the higher lignin content of bark (Figure 38 a), the charring processes are more pronounced than in the stem wood and stump resulting in higher amount of methane, hydrogen, and char.
Figure 39 DTG curves and the evolution profiles of the molecular and fragment ions of the most characteristic decomposition products released from untreated bark (BA U), stem wood (SW U) and stump (ST U). (m/z 2, hydrogen; m/z 16, methane; m/z 18, water; m/z 28, CO; m/z 44, CO₂; m/z 27, C₂H₅⁺; m/z 30, formaldehyde; m/z 31, CH₂O⁺, m/z 45, COOH⁺).

4.2.3 Compositional analysis of torrefied samples

Compositional analysis of the torrefied biomass samples was carried out to monitor the decomposition of the lignocellulose polymeric components and understand the conversion behavior of the samples during torrefaction. The results are presented in Figure 40. In addition to the major biomass components, the weight loss of the
torrefied samples during torrefaction is also included to provide a comprehensive comparison of the raw and treated samples.

During torrefaction, lignocellulose materials decompose to different degrees depending on the torrefaction severity. The decrease of glucan and the sum of mannann and galactan reflects the decomposition of cellulose and hemicellulose, respectively. As Figure 40 shows, hemicellulose is the least thermally stable component of the studied biomass samples during torrefaction. About 20% of the hemicellulose content of the samples decompose up to 225 °C for each sample.

After torrefaction at 275 °C, the relative amount of the hemicellulose in the bark samples drastically decreases, while stem wood and stump have about one fifth of the hemicellulose content of the raw sample. The hemicellulose content of them further decreases and only a minor fraction was measured for samples torrefied at 300 °C. Figure 40 also shows that the content of cellulose (indicated by the content of glucan) does not decrease evidently even at the torrefaction temperature 275 °C for stem wood and stump, while a significant decrease (more than 80%) is observed for bark at this temperature.

At 300 °C torrefaction temperature, the residence time has a significant effect on the cellulose decomposition. After torrefaction at 300 °C for 30 and 60 min the cellulose content of the stump sample decreased to 48 and 21% of the cellulose content of the raw material, respectively, whereas that of stem wood decreased to only 20 and 11%, respectively. These observations may point to that the thermal stability of cellulose in the bark sample is lower compared to the stem wood and stump samples. The bark sample has more than an order of magnitude higher alkali content than stem wood and stump (Table 9). The alkali metals are known to exert a great influence on the thermal decomposition of cellulose. The change in the chemical compositions of the studied samples confirmed that the alkali metals have catalytic effects on the cellulose decomposition during thermal treatment in this temperature range.

As the bar diagram presents, the Klason lignin content of the torrefied samples increase considerably with increasing torrefaction temperatures. The Klason lignin contains all acid insoluble components of the sample, excluding ash. During torrefaction, certain fractions of the polysaccharides, acid soluble lignin and extractives were probably transformed into acid insoluble carbonaceous products by cross-linking and charring reactions. The increasing torrefaction temperature enhances these reactions, resulting in the greater amount of the calculated Klason lignin content at higher temperatures.
Figure 40 Changes in the chemical composition of stem wood, stump, and bark during torrefaction.

4.2.4 Thermogravimetry results of the torrefied samples

During torrefaction the lignocellulosic materials decompose to different degrees depending on the applied temperature and residence time. Figure 41 shows the TG and DTG curves of the various torrefied stem wood, stump and bark samples. The characteristic hemicellulose shoulder of the DTG curves decreased to some extent in case of the samples torrefied at 225 °C; however, it disappeared from the DTG curves of the samples torrefied at 275 and 300 °C. The cellulose content of stem wood and stump did not reduce considerably up to 275 °C, as the results show in Figures 40 and 41, while the degradation of cellulose in the bark sample was significant at this temperature. At 300 °C, only trace amounts of cellulose remained in bark, and the cellulose content of stem wood and stump strongly decreased. As already mentioned, the presence of alkali ions modifies the thermal degradation of cellulose and lignin. The reason for the promoted decomposition rate of bark during torrefaction is most probably the catalyzed decomposition of its cellulose content. As Figure 41 shows, the residence time did not have significant effect on the composition of the torrefied samples up to 275 °C; therefore, applying the longer residence time of 60 min in a real application is superfluous. At 300 °C, the torrefaction residence time had substantial effects on all parts of the spruce tree due to the severe decomposition reactions at this temperature.
4.2.5 Principal component analysis based on chemical composition and TG data

In the PCA calculation, the characteristic thermogravimetric parameters ($T_{\text{start}}$, $T_{\text{peak}}$, DTG$_{\text{max}}$, $T_{\text{end}}$, and char yield) and the chemical composition data (glucan, sum of mannan and galactan, as well as Klason lignin contents) have been used as input variables for the comparison of untreated and torrified stem wood, stump, and bark of spruce. In the PCA calculation, the first principal component (Factor 1) and the second principal component (Factor 2) account for 64% and 21% of the total variance, respectively. These two factors can adequately characterize the major
differences between the samples. The score plot (Figure 42 a) shows that the studied samples are located in four well separated groups. The untreated and mildly torrefied (at 225 °C) stem wood and stump samples belong to the same group, indicating that the torrefaction at 225 °C does not modify significantly the thermal properties of these samples compared to the untreated samples. The second group is formed from the stem wood and stump samples treated at 275 °C. The untreated and mildly torrefied (at 225 °C) bark samples are separated from the other samples, while all of the severely torrefied samples can be seen in the fourth group. These differences are mainly due to the different hemicellulose, cellulose and lignin content of the samples; which is reflected by the different thermal behavior of the studied samples, as well. The chemical composition and consequently the thermal behavior of the stem wood, stump, and bark samples have been changed to a greater extent at higher torrefaction temperature than at lower torrefaction temperature. The loading plot (Figure 42 b) shows that the values of glucan, sum of mannann and galactan, T\text{peak} and DTG\text{max} data correlate negatively with the lignin content and the char yield. Factor 1 is composed mainly of these parameters and primarily separates the samples as a function of the torrefaction temperature and residence time. As the PCA calculation shows (Figure 42 a), the effect of torrefaction temperature is greater than the effect of residence time. T_{\text{start}} and T_{\text{end}} data contribute mainly to Factor 2 and separates mostly the untreated and mildly torrefied bark samples from the others. The thermal decomposition of bark differs from the other samples due to the different composition (high lignin and alkali ion content).

Figure 42 PCA (a) score and (b) loading plots based on the TG parameters and the chemical composition data. (SW: stem wood, BA: bark, ST: stump, SW U: raw stem wood; SW 225_30: torrefied stem wood at 225°C for 30 min)
4.2.6 Thermogravimetry/mass spectrometry results of the torrefied samples

Figures 43-45 show the evolution of the most significant decomposition products from the torrefied bark, stem wood, and stump samples in order to get a better understanding of the above discussed differences in the decomposition during torrefaction. The curves for the individual species released from bark (Figure 43), stem wood (Figure 44) and stump (Figure 45) are plotted using the same scale in each of the figures. The pattern of the ion intensity curves of the samples torrefied at 225 and 275 °C for 30 min is very similar to that of the samples torrefied at 225 and 275 °C for 60 min; hence they are not presented here. As the water vapor evolution below 200 °C indicates, the moisture content of the torrefied bark samples is higher than that of the torrefied stem wood and stump samples. The reason could be the higher inorganic ion content, therefore the more hydrophilic nature of the torrefied bark samples.

The torrefaction removes the moisture content of the samples; however, during sample handling the torrefied sample can take up some water from the ambient air depending on the degree of hydrophilicity of the torrefied sample. The torrefied bark samples release higher amounts of permanent gases and lower amounts of organic volatiles than the torrefied stem wood and stump samples, prepared under the same torrefaction conditions. This observation indicates the catalytic effect of alkali ions on the decomposition of cellulose and is in agreement with the results of the compositional analysis, as well. The inherent alkali ion content of biomass materials changes through a catalytic effect the thermal decomposition mechanism, giving increased char yield and increased amount of water and permanent gases, at the expense of the yield of organic volatiles.

During torrefaction at 225 °C, the extractives content of the samples strongly decreased, therefore the shoulder of the DTG curves at 290 °C is less pronounced for the torrefied samples at 225 °C (Figures 43 a, 44 a and 45 a) than for the untreated samples (Figure 39). The main mass of the hemicellulose content of the bark, stem wood and stump samples was thermally stable during torrefaction at 225 °C; however, changes in the evolution pattern of COOH⁺ (Figures 43 b, 44 b and 45 b) point to the scission of the most labile acetate groups from the hemicellulose chains at this temperature.

The composition analysis revealed (Figure 40) that 8-26% hemicellulose remained in the samples after the thermal treatment at 275 °C; however, the shoulder of the DTG curve disappeared. The TG/MS results indicate that the decomposition of the remaining part of hemicellulose takes place in the temperature range of cellulose
decomposition. In case of stem wood and stump, the ion intensities describing the decomposition of cellulose (in the temperature range of the main DTG peak) do not decrease due to the thermal treatment up to 275 °C torrefaction temperature. This is in agreement with the chemical composition results showing that the cellulose content of the stem wood and stump samples only slightly decrease up to this temperature. The cellulose content of the bark sample decreased by half between the torrefied samples at 225 and 275 °C, resulting in a reduced evolution of all cellulose decomposition products. These observations show the more extensive degradation of the cellulose in bark at 275 °C.

As shown earlier, the evolution of methane shows a wide bimodal shape. In the temperature range of 350-500 °C, methane forms during the thermal decomposition of lignin by the scission of the methoxy groups. The reason for the different methane evolution profiles from the bark, stem wood and stump samples in this temperature range could be the different methoxy group content of the studied samples.

After severe torrefaction (275-300 °C), the relative amount of Klason lignin significantly increased in the samples due to the strong degradation of carbohydrates. It can be observed that the evolution of hydrogen, methane, and carbon monoxide above 430 °C are increasing, while the intensities of the hemicellulose and cellulose decomposition products are decreasing when raising the torrefaction temperature and residence time. The charring reactions are more pronounced in case of the bark sample. In the temperature range of 400-700 °C, the evolution of small hydrocarbon molecules were detected, denoted by the m/z 27 ion curves in Figures 43-45. The relative intensity of the hydrocarbon evolution is increasing with the torrefaction temperature for all the bark, stem wood and stump samples. These hydrocarbon molecules could be released by secondary reactions involving the decomposition products of cellulose, hemicellulose and lignin.

At 300 °C, the hemicellulose content of each studied sample almost completely decomposed during 30 min; the torrefaction residence time had a significant effect owing to the severe decomposition of cellulose. The torrefaction at 300 °C for 60 min resulted in reduced evolution of all cellulose decomposition products, decreasing by half in the stem wood and stump samples, while only traces of cellulose were measured in the bark sample. The severe decomposition of hemicellulose and cellulose resulted in the relatively low solid yield (43-70%) due to the significant dry matter loss during thermal degradation; therefore, this temperature is too high for most real applications.
Figure 43 DTG curves and the evolution profiles of molecular and fragment ions of the most characteristic decomposition products released from torrefied bark samples. \((\text{m/z} \; 2, \text{hydrogen}; \; \text{m/z} \; 16, \text{methane}; \; \text{m/z} \; 18, \text{water}; \; \text{m/z} \; 28, \text{CO}; \; \text{m/z} \; 44, \text{CO}_2; \; \text{m/z} \; 27, C_2H_3^+; \; \text{m/z} \; 30, \text{formaldehyde}; \; \text{m/z} \; 31, \text{CH}_3\text{O}^+; \; \text{m/z} \; 45, \text{COOH}^+)\)
Figure 44 DTG curves and the evolution profiles of molecular and fragment ions of the most characteristic decomposition products released from torrefied stem wood samples. (m/z 2, hydrogen; m/z 16, methane; m/z 18, water; m/z 28, CO; m/z 44, CO₂; m/z 27, C₂H₃⁺; m/z 30, formaldehyde; m/z 31, CH₃O⁺; m/z 45, COOH⁺)
Figure 45 DTG curves and the evolution profiles of molecular and fragment ions of the most characteristic decomposition products released from torrefied stump samples. (m/z 2, hydrogen; m/z 16, methane; m/z 18, water; m/z 28, CO; m/z 44, CO₂; m/z 27, C₂H₅⁺; m/z 30, formaldehyde; m/z 31, CH₃O⁺; m/z 45, COOH⁺)
4.2.7 Pyrolysis- gas chromatography/mass spectrometry results

The untreated and torrefied stem wood, stump, and bark samples were characterized by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). 550 °C pyrolysis temperature was selected on the basis of the TG/MS experiments, which indicated that this temperature is adequate for complete decomposition of the organic materials. Figure 46 shows the pyrograms of the untreated stem wood, stump and bark samples, while Table 11 lists the identification and the possible origin of the main decomposition products based on mass spectral libraries and literature data (Faix et. al., 1987; Genuit et al., 1987, Faix et al., 1990, Faix et al., 1991).

In Figure 46, the unresolved peaks at lower retention times (denoted by G) represent the evolution of gaseous and vapor products of low molecular weight, such as methane, carbon dioxide, and water, which may be formed by the scission of different functional groups of the numerous components. Comparing the pyrograms of untreated stump and bark, the composition of their pyrolysis products seems to be similar, while the pyrogram of the stem wood is different from them. The different thermal behavior of the untreated stem wood, stump, and bark samples during pyrolysis can be explained by their different composition as well as by the well-known fact that alkali ions have catalytic effect on the decomposition mechanism of cellulose (DeGroot and Shafizadeh, 1984, Jakab, 2015) and on the charring reactions of lignin (Jakab et al., 1997).

Acetic acid (2), 3-hydroxypropanal (4), and 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one (13) are the most typical decomposition products of hemicellulose under inert atmosphere. The comparison of the three pyrograms displays that untreated stump releases the highest amount of acetic acid and 3-hydroxypropanal, which is in agreement with the chemical composition results showing that stump has the highest hemicellulose content (Figure 38). The main decomposition product of cellulose during pyrolysis is levoglucosan (35), which is a dehydrated derivative of glucose and can be considered as the monomer of cellulose. Stem wood releases the highest yield of levoglucosan followed by stump and bark. The higher the cellulose content of the sample (Figure 38), the higher the levoglucosane yield during pyrolysis. Another characteristic thermal decomposition product of cellulose component is hydroxyacetaldehyde (1). Other carbohydrate products are also observed from the three untreated samples, which can be originated from both cellulose and hemicellulose. As Figure 46 and Table 11 illustrate several lignin
monomeric compounds were identified in the chromatograms of stem wood, stump and bark samples. The different distribution of the lignin products can be explained by the different chemical composition of the three studied parts of the spruce tree.

As we discussed above, the peaks at lower retention times in Figure 46, such as hydroxy acetaldehyde (1), acetic acid (2), and 1-hydroxy-2-propanone (3) correspond to the main smaller molecular mass products of hemicellulose and cellulose.

Figure 47 illustrates the beginning of the pyrograms of untreated and torrefied stem wood, stump, and bark samples. As Figure 47 shows the yield of hydroxyacetaldehyde (1), acetic acid (2), and 1-hydroxy-2-propanone (3) reduced after torrefaction at 225 °C in case of each studied samples, which is in agreement with the chemical composition (Figure 40) and TG (Figure 41) results. As can be seen in Figure 47 the yield of these acidic products further decreased after torrefaction at 275 °C, and almost totally disappeared at 300 °C.

Table 11 The main decomposition products released in the Py-GC/MS experiment of untreated stem wood, stump, and bark samples. Peak numbers refer to the peaks in Figures 46 and 47. Possible origin of the identified compounds: C: cellulose; H: hemicellulose; CH: carbohydrate, L: lignin

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret. time (min)</th>
<th>Compounds</th>
<th>Most abundant ions</th>
<th>Molar mass</th>
<th>Possible origin a</th>
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<td>4.2</td>
<td>Hydroxyacetaldehyde</td>
<td>31, 29, 32, 60</td>
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<td>2</td>
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<td>Acetic acid</td>
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<td>60</td>
<td>H, L</td>
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<td>5.7</td>
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<td>3-Hydroxypropanal</td>
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</tr>
<tr>
<td>5</td>
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<td>Carbohydrate</td>
<td>58, 57, 29</td>
<td></td>
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<td>2-Hydroxybutanal-3-one</td>
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<td>CH</td>
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<td>CH</td>
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<td>(5H)-Furan-2-one</td>
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<td>4-Hydroxy-5,6-dihydro-(2H)-pyran-2-one</td>
<td>114, 58, 29</td>
<td>114</td>
<td>H</td>
</tr>
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<td>15.8</td>
<td>2-Hydroxy-3-methyl-2-cyclopentene-1-one</td>
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<td>112</td>
<td>CH</td>
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<td>L, CH</td>
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<tr>
<td>No.</td>
<td>Ret. time (min)</td>
<td>Compounds</td>
<td>Most abundant ions</td>
<td>Molar mass</td>
<td>Possible origin</td>
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<td>2,4-Dimethylphenol</td>
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<td>4-Hydroxy-3-methyl-(5H)-furanone or 3-Methyl-2,4-furandione</td>
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<td>trans-Coniferyl alcohol</td>
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<td>L</td>
</tr>
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<td>43</td>
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<td>Coniferaldehyde</td>
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</tr>
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<td>35.6</td>
<td>cis-Synapyl alcohol</td>
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<td>46</td>
<td>37.0</td>
<td>trans-Synapyl alcohol</td>
<td>210, 167, 154, 182</td>
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<td>L</td>
</tr>
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<td>47</td>
<td>37.2</td>
<td>Synapaldehyde</td>
<td>208, 165, 137, 177</td>
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Figure 46 Pyrograms of untreated stem wood, stump, and bark samples. Numbered peak identities are given in Table 10.
Figure 47 The beginning of the pyrograms of untreated and torrefied stem wood, stump, and bark samples. Numbered peak identities are given in Table 10.
4.2.8 Particle size distribution of ground untreated and torrefied samples

The torrefaction of spruce stem wood, stump, and bark was carried out with chips, which need to be ground for various applications. The grindability of the untreated and torrefied samples was assessed by grinding them in a cutting mill (IKA MF 10.1) in Norway. The grinding of one sample included two stages: pre-grinding and fine grinding. In the pre-grinding stage, a known quantity of stem wood cubes, bark pieces, and stump chips with and without torrefaction treatment were fed into the cutting mill without a bottom sieve to reduce their sizes. The smaller pieces and grains produced from the pre-grinding stage were used for further fine grinding. Fine grinding of the products from the pre-grinding stage was carried out in the same cutting mill equipped with a 1mm bottom sieve. The particle size distribution of the samples after grinding was determined by passing the particles on sieves with different cut-sizes. Figure 48 shows the effect of torrefaction severity on the particle size distribution of stem wood, stump and bark.

![Particle size distributions for the stem wood, stump and bark as a function of torrefaction severity.](image)

**Figure 48** Particle size distributions for the stem wood, stump and bark as a function of torrefaction severity.
In general, the torrefaction temperature and residence time have considerable influences on percent of particles in the various size ranges. It can be seen that large particles in the size range of 0.5-1 mm of ground untreated stem wood and stump are 42% and 25%, respectively. After torrefaction at 225 °C, the amount of particles with such size significantly decreased to 18-20% and 10-12%, respectively. With further increase of torrefaction severity, the percent of particles in the same size range further decreased and only a small amount was obtained as the stem wood and stump were torrefied at 300 °C. In addition, the amount of particles with smaller sizes was also significantly increased for stem wood and stump torrefied at a higher temperature. In comparison, increasing the torrefaction residence time gave only a slight increase in the amount of particles with smaller sizes.

As shown in Figure 48, the particle size distribution of untreated and torrefied bark are quite different from those of stem wood and stump. For the untreated bark, the percentage of large particles (0.5 mm < d < 1 mm) is small, in comparison to stem wood and stump. It might be due to differences in content and nature of lignocellulose compositions (hemicellulose, cellulose and lignin) and the integrated structure of the compositions of the bark compared to the stem wood and stump. The major fraction of the untreated bark particles has a size in the range of 0.3 mm < d < 0.5 mm, which decreases evidently after torrefaction treatment. Moreover, the percentage of fine bark particles (d < 0.063 mm) increases considerably upon the increase of torrefaction temperature. The particle size distribution data show that the grindability of the torrified samples increases with the severity of the torrefaction.

Figure 49 shows cumulative particle size distribution curves of ground untreated and torrefied biomass samples. The particle size distribution curves clearly shift towards smaller particles. Similar changes of particle size distribution of ground biomass have been reported in other studies [Lehtikangas, 2001, Phanphanich and Mani, 2011]. As mentioned previously, torrefaction of biomass causes decomposition of hemicellulose and breakdown of the hemicellulose-cellulose interlinked matrix. It makes grinding of torrefied wood much easier with production of more small particles.
Figure 49 Cumulative particle size distributions for the stem wood, stump, and bark as a function of the torrefaction severity.
4.2.9 PCA calculation based on chemical composition and particle size distribution

Principal component analysis (PCA) has been used to illustrate statistical correlations between the chemical composition data (Figure 40) as well as the particle size distribution (Figure 48) of the ground raw and torrefied samples. In the PCA calculation, the first principal component (Factor 1) described 53.13% of the total variance and the second component (Factor 2) described 27.36% of the total variance, these two factors are adequate to characterize the major differences between the studied samples. It can be seen in the score plot (Figure 50 a) that the behavior of the bark samples during torrefaction clearly differs from that of the stem wood and stump samples. Factor 1 differentiates the raw, the mildly and the severely torrefied samples. As a function of Factor 2, the stem wood and stump samples are found in the upper, and the bark samples in the lower part of the score plot. This difference is probably due to the different chemical composition of the samples; which causes the different particle size distribution of the ground samples.

The loading plot (Figure 50 b) shows that the values of glucan, sum of mannan and galactan content and the “Other” part of the chemical composition (which contains extractives, acid soluble lignin and acid soluble minerals) correlate negatively with the Klason lignin content and the mass loss of the samples during torrefaction. Factor 1 is composed of mainly these parameters and mostly separates the samples as a function of the torrefaction severity. The particle size distribution data is reflected mainly in Factor 2. The raw bark has significantly higher extractives and Klason lignin content than the raw stem wood and stump, which may contribute to the different particle size distribution of the raw samples. For the raw bark, the percentage of fine particles (d < 0.1 mm) and large particles (0.5 mm < d < 1 mm) are quite small, however the percentage of medium size particles (0.2 mm < d < 0.5 mm) is rather large, in comparison to raw stem wood and stump. During torrefaction, the moisture content releases and the extractives and carbohydrate content of the samples degrade, therefore the torrefied samples become more brittle. Comparing the particle size distribution of the ground raw and torrefied samples we can conclude, that by applying more severe torrefaction before the grinding, the obtained particle size distribution of the stem wood, stump and bark sample become similar. The decreasing distance of bark samples from stem wood and stump samples on the score plot visualize this correlation.
Figure 50 Results of the principal component analysis based on the chemical composition and the particle size distribution data: (a) score plot and (b) loading plot. The arrows present the direction of the variation of the studied samples with increasing torrefaction temperature and residence time.

(SW, stem wood; ST, stump; B, bark; SW_U, untreated stem wood; SW_225_30, torrefied stem wood at 225 °C for 30 min)

5 Summary

The aim of my thesis was to study the thermal degradation process of torrefied hardwood, softwood, and herbaceous biomass materials with the goal of understanding deeper the structural changes of the main biomass components taking place during torrefaction. The results of the proximate and ultimate analyses, high heating values, compositional analysis data, TG/MS experiments and principal component analysis all clearly demonstrate the progress of the thermal decomposition during torrefaction in the temperature range of 200-300 °C. The joint evaluation of the results obtained by different analytical methods revealed new information about the thermal degradation of the investigated lignocellulose materials.
Compositional study of raw and torrefied hardwood and herbaceous materials
The purpose of this work was to compare the thermal behavior of black locust wood, rape straw, and wheat straw and reveal the chemical changes taking place during torrefaction at different temperatures. We found that the main mass of the hemicellulose content of each sample was thermally stable during 1 h of torrefaction at 225 °C; however, the acidic side groups of hemicellulose were partially split off at 225 °C torrefaction temperature. The thermal decomposition of hemicellulose after mild thermal treatment shifted to a higher temperature, indicating the modified structure of torrefied hemicellulose. Significant difference was not found in the thermal stability of the hemicellulose content of straw and wood samples, despite the large difference in the contents of inorganic materials. Therefore, we may conclude that the thermal decomposition of hemicelluloses does not depend measurably on the amount of alkaline ions in the given concentration range contrary to cellulose, where the significant catalytic effect of the alkali ions on the thermal decomposition is a well-known phenomenon. We found that after torrefaction at 275 °C, the hemicellulose content of each sample is strongly reduced. The degree of cellulose decomposition at 275 °C torrefaction temperature is significant only for straw samples, while cellulose is not degraded in the black locust wood sample at this temperature. The gradual increase in the amount of the acid insoluble materials indicates that the scission of the functional groups is accompanied by the enhanced formation of the crosslinked carbonaceous residues with an increasing torrefaction temperature. Two sets of PCA calculations were undertaken using different types of data, which resulted in consistent results; the untreated and mildly torrefied samples were separated from the severely torrefied samples. The calculations revealed that the chemical composition and, therefore, the thermal properties have changed to a much greater extent in the temperature range of 275−300 °C than at lower temperatures.

In order to study the effect of inorganic content during the low-temperature thermal treatment (torrefaction), we washed the raw samples with hot water to remove the majority of the water soluble inorganic components. We found that the thermal stability of cellulose in the hot water washed wood sample is raised by about 30 °C, while in case of the washed straw samples it is raised about 50 °C compared to the original samples. The char yield of the raw and torrefied hot water washed samples is significantly lower for the three studied samples than that of the original samples. We also concluded that the effect of washing is more pronounced at higher torrefaction temperatures. These observations confirm that alkali ions
have catalytic effects on the decomposition mechanism of cellulose and lignin even at mild thermal conditions.

The effect of torrefaction on the chlorine content of lignocelluloses was studied by thermogravimetry/mass-spectrometry method. The formation of methyl chloride was detected during thermal decomposition that we explained by the reaction of chlorine with the methyl groups of lignin. We concluded that most of the methoxy groups of straw lignins were probably cleaved during torrefaction at 275 and 300 °C, and at the same time the initial chlorine content of the straw samples decreased. Therefore, the severely torrified straw samples produced only small amount of methyl chloride during thermal decomposition.

**Comparative study of torrefied bark, stem wood and stump of Norway spruce**

The aim of this work was to gain information about the thermal behaviors and physicochemical properties of stem wood, stump and bark of Norway spruce. The main differences between the thermal decomposition of the studied samples are interpreted in terms of the chemical composition with the goal of understanding the mechanisms of the decomposition of biomass components during torrefaction. We found that the decomposition of hemicellulose starts with the cleavage of the functional groups at 225 °C. We concluded that the thermally less stable acidic side groups are cleaved at this temperature, increasing the hydrophobicity of the product in this way, which is an important goal during the practical application of torrefaction. Significant decomposition of cellulose started as low as at 275 °C torrefaction temperature for the bark sample, while it was found to be stable for stem wood and stump, which can be explained by the high alkali ion content of bark. Therefore, we concluded that lower torrefaction temperature should be applied for bark, than for stem wood and stump to obtain products degraded to a similar degree. The torrefaction residence time did not have significant influence up to 275 °C on the thermal behavior of the samples. However, at 300 °C the composition of the torrefied samples changed substantially with the torrefaction residence time due to the intensive decomposition of cellulose. Torrefaction at 300 °C temperature induced severe changes in all biomass components, resulting in significant mass and energy losses; hence this temperature is too high for most of the applications. We found that the treated stem wood and stump behaved similarly during torrefaction; therefore they can be utilized together during thermochemical conversion. From the results of this work, it can be concluded that a mild torrefaction can considerably improve physicochemical properties of spruce stem wood and stump as solid fuel. Therefore, the utilization and conversion of them for energy production can be improved markedly.
5.1 Novel scientific findings

1. I demonstrated that the combined application of carbohydrate and lignin content determination and thermal decomposition techniques (e.g. TG/MS) provides complementary information on the structural changes in the complex biomass samples during torrefaction. The acidic hydrolysis followed by HPLC analysis of the sugars gives quantitative data on the composition of the carbohydrate backbone; while pyrolytic methods are suitable for the characterization of the functional groups, as well. (Paper I. and Paper II.)

2. Although the chemical composition of hemicelluloses and alkali ion content of herbaceous plants, deciduous and coniferous trees are different, the stabilities of these hemicelluloses do not differ during thermal treatments. (Paper I. and Paper II.)

3. I established by chemical analysis that the hemicellulose backbone of woody and herbaceous plants do not alter essentially during torrefaction at 225 °C; however, the acidic side groups of hemicelluloses are split off as detected by thermal decomposition methods. (Paper I. and Paper II.)

4. I observed that the thermal stability of cellulose in the washed black locust wood sample is raised by about 30 °C, while it is raised about 50 °C in the hot water washed rape and wheat straw samples compared to the original samples. I found that the effect of washing is more pronounced at 275 and 300 °C torrefaction temperatures. (Paper VI.)

5. Lower torrefaction temperature is suggested to be applied for the samples of high potassium content (wheat straw, rape straw and wood bark) because the high alkali ion content of the herbaceous plants and bark significantly catalyzes the thermal decomposition of cellulose and lignin even at low (200-300 °C) temperatures. Furthermore, I observed that the thermal decomposition of hemicelluloses depended on the amounts of alkaline ions in the low concentration range, but differences were not measurable at higher concentrations. (Paper I.-V.)

6. I established that during thermal decomposition, the relative intensity of methyl chloride decreased by half between the straw samples torrefied at 250 and 275 °C, while after torrefaction at 300 °C, methyl chloride almost totally ceased to be released from the straw samples. The reduced methyl chloride formation was explained by the demethylation of the methoxy groups of straw lignin and the decreased chloride ion content of the torrefied straw samples. (Paper VI.)
7. The low temperature thermal treatment of various parts of Norway spruce (bark, stem wood, stump) was compared. I proved that the treated stem wood and stump behaved similarly during torrefaction; therefore, they can be utilized together during thermochemical conversion. However, torrefaction of bark require about 25 °C lower temperature than stem wood and stump. (Paper II., Paper III. and Paper V.)

8. Performing principal component analyses, I proved that the thermal treatment of higher temperature (275-300 °C) resulted in significant changes in the composition and the thermal behavior of the samples. In the cases of torrefaction at 225 and 275 °C, the duration of the thermal treatment does not affect the composition of the samples significantly, whereas at 300 °C the residence time has a major effect on the composition manifested in the strong decomposition of cellulose. I concluded that this temperature is too high for most of the applications (Paper II., Paper III. and Paper V.)
6 References


FAO-Food and Agriculture Organization of the United Nations.


STATEMENT

I the undersigned, hereby declare, that this PhD thesis was written by me, and I only used the sources listed in the reference list.

NYILATKOZAT

Alulírott Barta-Rajnai Eszter kijelentem, hogy ezt a doktori értekezést magam készítettem és abban csak a megadott forrásokat használtam fel. Minden olyan részt, amelyet szó szerint, vagy azonos tartalomban, de átfogalmazva más forrásból átvettem, egyértelműen, a forrás megadásával megjelöltem.

I.
Comprehensive Compositional Study of Torrefied Wood and Herbaceous Materials by Chemical Analysis and Thermoanalytical Methods

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ABSTRACT: In this work, the torrefaction of three biomass materials, black locust wood, wheat, and rape straw, was studied at various temperatures: 200, 225, 250, 275, and 300 °C. The thermal stability and formation of the decomposition products of the untreated and treated samples were measured by the thermogravimetry/mass spectrometry method. The degree of hemicellulose and cellulose decomposition during torrefaction at different temperatures was characterized by compositional analysis of the torrefied and untreated samples. The cellulose, hemicellulose, and Klasson lignin contents of the raw and torrefied biomass samples were determined by acidic hydrolysis and subsequent high-performance liquid chromatography analysis. The inorganic ion contents of the untreated samples were measured by the inductively coupled plasma optical emission spectrometry method. The joint evaluation of the results obtained by various analytical methods revealed that the acidic side groups of hemicellulose were partially split off, while the main mass of hemicellulose did not degrade at 225 °C torrefaction temperature. About 40% of hemicellulose degrades at 250 °C torrefaction temperature and the remainder decomposes at a higher temperature. Although hemicellulose has a different chemical structure in the hardwood and straws, no significant differences were observed in the thermal stability of hemicelluloses in the three studied samples. When the significantly higher alkali ion content of the straw samples is taken into consideration, it was concluded that the alkali ion content of the samples did not modify the thermal stability of hemicellulose. Statistical analysis [principal component analysis (PCA)] has been used to present correlations between the torrefaction temperature, chemical composition, and thermal parameters of the samples. The PCA calculations revealed substantial changes in the chemical composition and thermal properties of biomass materials as a result of torrefaction at 275–300 °C temperatures.

1. INTRODUCTION
Biomass is a primary type of renewable energy source, which is one of the most abundant energy sources on the Earth. In energetic utilization, the unfavorable properties of the untreated biomass are the following: high moisture content, low calorific value, low energy density, high oxygen content, and hydrophilic nature. The transportation and storage are costly as a result of the low density of biomass materials, especially for those derived from the agricultural sector. The unfavorable properties of raw biomass can be improved by torrefaction, which is a thermal treatment between 200 and 300 °C in an inert atmosphere for the partial conversion of biomass.1–3 The torrefaction process can be classified into light, mild, and severe torrefaction, where the temperatures are approximately 200–235, 235–270, and 270–300 °C, respectively. During torrefaction, the moisture content of biomass is removed and the acidic functional groups of the hemicellulose component are cleaved.4,5 These reactions result in the increase of the calorific value and the higher stability against biodegradation of the torrefied biomass, leading to reduced transportation and storage costs.6–8

Several types of biomass materials have been torrefied, including agricultural9–15 and forestry16–20 byproducts. Torrefied wood and straw in the form of pellets can be directly cofired with coal in a relatively high ratio, hereby using the processing infrastructures at existing coal power plants. As a consequence of the difference in the relative amount of cellulose, hemicellulose, lignin, and extractives, the woody and herbaceous materials behave differently during thermal decomposition.21,22 Several factors may affect the thermal decomposition of lignocellulosic materials. The alkali ions have
a significant impact on the thermal degradation mechanisms of cellulose; \(^\text{123-30}\) the depolymerization reaction is hindered; and the fragmentation reactions are promoted, leading to the decreased decomposition temperature and the increased char yield. Sebestyén et al.\(^\text{3}\) concluded that the concentration of the potassium and sodium ions in the hemp sample determines the effect of alkali ions to a great extent. The largest alteration of the thermogravimetry/mass spectrometry (TG/MS) parameters was detected in the 0–0.2 mmol g\(^{-1}\) concentration range of the alkali ions. Of all of the inorganic components of biomass, potassium has the biggest influence on the thermal behavior.\(^\text{25–23}\) The inorganic ions also modify the decomposition of lignin.\(^\text{1,2,3}\) although to a lesser extent than in the case of cellulose.

Thermal analysis and pyrolysis are useful methods to reveal differences in the composition of biomass samples without separating the components.\(^\text{35,36}\) The coupled techniques, such as TG/MS\(^\text{37–39}\) and thermogravimetry/Fourier transform infrared spectrometry (TG/FTIR),\(^\text{40,41}\) can provide detailed information about the volatile decomposition products of the samples.

In this work, the torrefaction of black locust wood (\textit{Robinia pseudoacacia}), wheat straw (\textit{Triticum aestivum}), and rape straw (\textit{Brassica napus}) was studied, which are typical biomass products or by-products in Hungary. Black locust wood is native to the southeastern United States, but it is widespread in Europe as well. It can be a promising biomass for future energy production because of its high growth rate and favorable fuel characteristics, such as low ash content and high heating value. Straw is a low-value by-product of the agricultural industry, and it is available in large quantities.

The purpose of this work is to study the thermal behavior of torrefied woody and herbaceous biomass materials and understand the chemical changes that take place during torrefaction at different temperatures. The thermal stability and formation of the volatile products of the untreated and treated samples were studied by TG/MS. The chemical composition (cellulose, hemi-cellulose, and lignin contents) of the untreated and torrefied samples was determined by a two-step acid hydrolysis. The obtained thermoanalytical and compositional data were evaluated by statistical analysis with the goal to present correlations between the temperature of the torrefaction pretreatment, thermal behavior of the wood and herbaceous samples, and chemical composition of the samples.

2. EXPERIMENTAL SECTION

2.1. Materials. A black locust wood and two herbaceous biomass materials (rape straw and wheat straw) were selected for the torrefaction study. The raw samples were dried in an oven at 105 °C for 8 h to obtain samples of similar moisture content for the experiments and to avoid biodegradation during storage. Despite the thorough drying, the samples had about 6% moisture content prior to the torrefaction experiments (on the basis of the TG measurement), which can be explained apparently by the moisture uptake during sample handling. The untreated samples were ground to <1 mm particle size by a cutting mill.

2.2. Torrefaction. The torrefaction experiments were performed in a nitrogen atmosphere in a horizontal tube furnace. About 12 g samples were treated in a glass boat of 200 mm long. The flow rate of the nitrogen gas was set to a relatively low value of 20 mL min\(^{-1}\) to avoid the removal of the smaller particles from the boat. The torrefaction experiments were performed at 200, 225, 250, 275, and 300 °C temperatures using an isothermal period of 1 h.

2.3. Proximate and Ultimate Analyses. The samples were characterized before and after torrefaction, using proximate and elemental (ultimate) analyses. The moisture and volatile contents of the untreated and torrefied biomass samples were determined by TG, heating the samples from room temperature up to 950 °C. The amount of ash was measured using the standard method proposed by the National Renewable Energy Laboratory (NREL/TP-510-42622), applying 550 °C ashing temperature. The fixed carbon content was determined by difference. The carbon and hydrogen contents of the untreated and torrefied biomass samples were measured by an elemental analyzer. The oxygen content was determined by difference. Three parallel proximate and ultimate analyses were performed to validate repeatability of the results, which was found to be quite satisfactory with a maximum ±1% standard deviation.

2.4. Higher Heating Value (HHV) Determination. The HHV was determined using an automatic IKA C 5000 bomb calorimeter. The combustion of about 0.5 g of dried sample in a pure oxygen atmosphere was performed under 30 bar pressure. Benzoic acid calibration was applied to determine the heat capacity of the calorimeter. All heating values were calculated from the averages of three replicates.

2.5. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The ashing of 2 g of biomass samples was carried out in a furnace at 550 °C according to the CEN/TS 14775:2004 European Union (EU) standard method. The ashes were fused with a fusion blend (2:1 Li2B4O7/LiBO\(_2\)) at 920 °C and digested by 25 mL of 33% nitric acid. The sodium, potassium, calcium, and silicon contents of the untreated samples were measured by a Spectro Genesis ICP-OES (Spectro Analytical Instruments) with air plasma observation.

2.6. Carbohydrate and Klason Lignin Content Determination. The contents of carbohydrates were determined according to the method of Sluiter et al.,\(^\text{42}\) applying slight modifications. The milled samples were dried at 40 °C for 1 day. The untreated and torrefied biomass samples were treated in a two-step acid hydrolysis with 72% H\(_2\)SO\(_4\) for 2 h at room temperature and then with 4% H\(_2\)SO\(_4\) for 1 h at 121 °C. The obtained suspensions were filtered and washed with distilled water through G4 glass filter crucibles. The sugar concentrations (glucose, xylose, and arabinose) of the acid-insoluble ash contents were analyzed with high-performance liquid chromatography (HPLC) using an Agilent 1260 system with a Hi-Plex H column (Agilent, Santa Clara, CA) at 65 °C. An eluent of 5 mM H\(_2\)SO\(_4\) was used at a flow rate of 0.5 mL min\(^{-1}\). The solid residues obtained after washing were dried at 105 °C until a constant weight. The dried residues consisted of acid-insoluble organics and acid-insoluble ash. The amounts of total ash and acid-insoluble ash were determined by ashing the sample at 550 °C for 5 h until the sample weight was constant.\(^\text{3}\) The Klason lignin content was calculated by subtracting the acid-insoluble ash content from the acid-insoluble residue content. All experimental data were determined using three replicates.

2.7. TG/MS. The TG/MS experiments were carried out using a modified PerkinElmer TGS-2 thermobalance connected to a Hiden HAL quadrupole mass spectrometer. About 5 mg samples were heated from 25 to 950 °C at a rate of 20 °C min\(^{-1}\) in a platinum sample pan. The evolved products were led through a glass-lined metal capillary heated at 300 °C using argon carrier gas at a flow rate of 140 mL min\(^{-1}\). The high flow rate minimizes the time delay between the measurements of the mass in the thermobalance and the ion intensities in the mass spectrometer. The ion source of the mass spectrometer was operated at 70 eV electron energy. The mass range of 2–150 Da was scanned. The ion intensities were normalized to the sample mass and to the intensity of the \(^{3}\)Ar isotope of the carrier gas.

2.8. Principal Component Analysis (PCA). As a result of the large number of samples and experimental data, a chemometric tool, PCA, using Statistica 12 software (StatSoft, Inc., Tulsa, OK), was employed. PCA has been applied to find correlations between TG data, energy content, and chemical composition of the samples as well as to reveal further correlations between the TG/MS data of the untreated and torrefied samples. PCA is a technique that decreases the data dimensionality and makes pattern visualization by converting the original measured data into new uncorrelated variables (principal components).\(^\text{44}\) The principal components (factors) are the linear combinations of the original measured variables. The principal
components (factors) explain different percentages of the total variance; generally two or three factors are enough to describe the differences and similarities between the samples. The results can be presented in the score plots, which place the samples in the space of two factors. Factor loadings show the correlation between the original data and the principal components.

3. RESULTS AND DISCUSSION

3.1. Characterization of Untreated and Torrefied Biomass Samples. The solid yield, proximate and ultimate analysis data, and energy content of the untreated and torrefied samples are shown in Table 1. During torrefaction, the moisture content and volatiles release from the sample, resulting in a decrease of the sample mass. Up to the temperature of 250 °C, the yield of the solid residue was quite similar for the three investigated samples. In comparison of the results obtained at 250 and 275 °C, it can be established that a significant decrease of the solid yield occurred in rape and wheat straw samples (15 and 20%, respectively), while the solid yield was reduced to a lesser extent in black locust wood (11%). This observation indicates a higher degree of decomposition of herbaceous samples at about 275 °C.

The proximate analysis data of the torrefied samples show that the moisture content and volatile matter decreased, while the ash and fixed carbon contents increased in the samples prepared at a higher torrefaction temperature as a result of the progress of the thermal decomposition. Black locust wood had a higher volatile matter content and a lower fixed carbon yield than wheat and rape straw samples, prepared under the same torrefaction conditions.

The ultimate analysis shows that the increasing torrefaction temperature increased the carbon content and reduced the oxygen and hydrogen contents of the torrefied materials. The calorific value of the torrefied samples increased with the increasing temperature. Torrefaction at 225 °C increased the HHV of the samples by at least 3.5% in comparison to the value of the untreated samples (17.6–18.2 MJ kg⁻¹). Torrefaction at 275 °C resulted in an increase of 19–27% of the HHV. All of the proximate and ultimate analysis data as well as the calorific values verify the gradual thermal decomposition of the biomass samples by an increasing temperature.

PCA has been performed to obtain statistical correlations between the solid yields, energy contents, and proximate and ultimate analysis data (Table 1). The PCA results can be found in Figure S1 of the Supporting Information.

The alkali ion contents of the untreated samples have been determined using the ICP–OES technique. Table 2 shows the most important data of the ICP−OES technique of each studied biomass was performed to understand better the thermal conversion process during torrefaction. The results are presented in Figure 1. The glucan content of the samples mainly characterizes the cellulose component of biomass, while the sum of the xylan and arabinan contents represents the hemicellulose fraction. The Klassen lignin is defined as the acid-insoluble residue content of the samples without the acid-insoluble ash content. The fraction denoted “other” in Figure 1 represents the sum of the unquantified components and includes extractives, acid-soluble lignin, and acid-soluble minerals. To compare the degradation degree of cellulose, hemicellulose, and lignin in the torrefied samples, one has to take into consideration the mass loss during

### Table 1. Characterization of the Studied Samples

<table>
<thead>
<tr>
<th>sample</th>
<th>solid yield (%)</th>
<th>MC (%)</th>
<th>VM (%)</th>
<th>ash (%)</th>
<th>FC (%)</th>
<th>H (%)</th>
<th>O (%)</th>
<th>HHV (MJ kg⁻¹)</th>
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</thead>
<tbody>
<tr>
<td>BL U</td>
<td>100</td>
<td>6.08</td>
<td>77.85</td>
<td>1.75</td>
<td>14.32</td>
<td>48.10</td>
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<td>87</td>
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<td>50.59</td>
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<td>60.65</td>
<td>8.30</td>
<td>26.85</td>
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<td>RS U</td>
<td>100</td>
<td>7.16</td>
<td>71.16</td>
<td>6.04</td>
<td>15.64</td>
<td>46.3</td>
<td>5.46</td>
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<td>85</td>
<td>4.62</td>
<td>68.99</td>
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<td>48.86</td>
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<td>49.38</td>
<td>4.23</td>
<td>41.04</td>
</tr>
<tr>
<td>WS 225</td>
<td>89</td>
<td>3.68</td>
<td>69.69</td>
<td>5.80</td>
<td>20.83</td>
<td>47.68</td>
<td>4.10</td>
<td>42.42</td>
</tr>
<tr>
<td>WS 250</td>
<td>80</td>
<td>3.48</td>
<td>66.20</td>
<td>6.92</td>
<td>23.40</td>
<td>48.49</td>
<td>6.62</td>
<td>38.11</td>
</tr>
<tr>
<td>WS 275</td>
<td>89</td>
<td>3.68</td>
<td>69.69</td>
<td>5.80</td>
<td>20.83</td>
<td>47.68</td>
<td>4.10</td>
<td>42.42</td>
</tr>
<tr>
<td>WS 300</td>
<td>44</td>
<td>2.37</td>
<td>38.12</td>
<td>12.52</td>
<td>46.98</td>
<td>62.28</td>
<td>4.83</td>
<td>20.37</td>
</tr>
</tbody>
</table>

### Table 2. Most Important Inorganic Components of the Studied Samples

<table>
<thead>
<tr>
<th>sample</th>
<th>Si (%)</th>
<th>K⁺ (%)</th>
<th>Na⁺ (%)</th>
<th>Ca²⁺ (%)</th>
<th>Mg²⁺ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>black locust</td>
<td>ND</td>
<td>0.12</td>
<td>ND</td>
<td>0.085</td>
<td>0.017</td>
</tr>
<tr>
<td>rape straw</td>
<td>0.03</td>
<td>1.86</td>
<td>0.072</td>
<td>0.503</td>
<td>0.158</td>
</tr>
<tr>
<td>wheat straw</td>
<td>1.07</td>
<td>1.69</td>
<td>0.008</td>
<td>0.137</td>
<td>0.077</td>
</tr>
</tbody>
</table>

**ND** = not determined, below the detection limit.
the torrefaction experiment as well. Therefore, Figure 1 also shows the mass loss during the torrefaction at the different temperatures.

The comparison of the chemical composition of the three untreated samples shows that black locust has the highest Klason lignin content (25.7%), while wheat straw has the highest hemicellulose content (23%) of the three samples. The lignocellulose content (sum of cellulose, hemicellulose, and lignin) of black locust wood is around 76%, while that of the untreated rape straw is only 66%. The reason could be the higher amount of extractive compounds and the higher acid-soluble mineral content of the rape straw sample. The later assumption is supported by the highest alkaline earth ion content of the rape straw sample, as shown in Table 2.

During torrefaction, the lignocellulose materials decompose to different degrees depending upon the applied temperature. The variation of the amount of gluca, xylan, and arabinoxylan in the torrefied samples (see Figure 1) reflects the changes in the proportion of cellulose and hemicellulose in the samples. The decreasing carbohydrate yields indicate the progress of the thermal decomposition of hemicellulose and cellulose during torrefaction at various temperatures.

As the results present, hemicellulose (measured as the sum of arabinoxylan and xylan) is the thermally least stable component of the lignocellulose fraction during torrefaction. The hemicellulose content of the torrefied samples is slightly decreased up to 225 °C for each studied sample. The samples torrefied at 250 °C have about half of the hemicellulose content of the untreated sample for each biomass. At higher torrefaction temperatures, the relative amount of hemicellulose drastically decreases and only traces of hemicellulose were measured in the samples torrefied at 300 °C. The changes in the relative amount of hemicellulose show a similar tendency as a function of the torrefaction temperature for each sample, indicating that the thermal stability of hemicellulose is similar in the studied wood and herbaceous samples. Hence, it can be concluded that the alkali ion content of the samples does not significantly modify the thermal stability of hemicellulose.

The variation of the cellulose content in the untreated and torrefied samples is demonstrated by the amount of gluca (Figure 1). As the bar diagram shows, the cellulose content of black locust wood does not decrease considerably up to 275 °C torrefaction temperature. In the case of the two herbaceous samples, the degradation of cellulose is significant at this temperature; the relative decrease is almost 50% in both cases. At 300 °C torrefaction temperature, about 60% of the cellulose content of black locust decomposes, while cellulose almost disappears from rape and wheat straw samples. On the basis of this observation, it can be concluded that the thermal stability of cellulose in the herbaceous samples is lowered by about 25 °C compared to wood. The herbaceous samples have more than an order of magnitude higher alkali ion content than wood. The catalytic effect of alkali ions on the thermal decomposition of cellulose is known. The results obtained for the cellulose content of the torrefied samples confirm that the alkali ions have a catalytic effect on cellulose decomposition, even at the low temperatures used in torrefaction.

As Figure 1 presents, increasing the torrefaction temperatures resulted in a significant increase in the measured Klason lignin content of the samples. Besides the acid-insoluble lignin, Klason lignin contains all acid-insoluble components of the sample, excluding ash. During the thermal treatment, some parts of the extractives, cellulose, hemicellulose, and acid-soluble lignin were probably transformed into acid-insoluble carbonaceous products by cross-linking and charring reactions. The increasing torrefaction temperature favors these reactions, resulting in the increased Klason lignin value at higher temperatures.

3.3. TG Results. The TG and derivative thermogravimetric (DTG) curves of the samples are shown in Figure 2. A comparison of the curves shows that the shape of the TG and DTG curves of rape straw and wheat straw samples are rather similar, while black locust wood behaves differently during thermal decomposition. It is described in the literature that the difference between the behavior of wood and herbaceous samples is partly due to the different alkali ion contents, which have a significant effect on the thermal properties of cellulose. The different thermal behaviors of the torrefied woody and herbaceous biomass materials can also be interpreted by their different inorganic contents. In addition, the relative amounts of alkali ions further increased in the samples during the torrefaction.

The evaporation and decomposition of extractives in the untreated samples are visible on the DTG curve as a broad shoulder starting at approximately 180 °C. The higher weight loss of untreated rape straw compared to wheat straw and black locust (panels a and b of Figure 2) between 200 and 300 °C indicates the higher extractive content of this sample. During torrefaction at 225 °C, the extractive content of the samples mostly evaporated; therefore, the above-mentioned difference disappeared from the TG and DTG curves of rape straw (panels c and d of Figure 2) and the weight loss curves of the three torrefied biomass overlap up to 300 °C. This observation is in accordance with the results of compositional analysis, where a higher amount of extractives and/or acid-soluble inorganics was determined in the untreated rape straw sample (see “other” component in Figure 1) than in the other biomass samples studied.

The main DTG peak of the untreated samples (Figure 2b) can be explained by the decomposition of cellulose. The characteristic shoulder on the DTG curve of the untreated black locust sample (Figure 2b) up to 350 °C represents the decomposition of hemicellulose. In the case of herbaceous samples, the hemicellulose shoulder is not pronounced because the cellulose decomposition shifted to a lower temperature as a result of the catalytic effect of the high amounts of alkali ions. O-Acetyl-4-O-methylglucuronoxylan is the main building block of hemicellulose in hardwood species. In herbaceous biomass, arabinoxylans are the dominant hemicellulose polysaccharides. As the compositional analysis data demonstrate (Figure 1), the
hemicellulose content of the samples did not degrade during torrefaction at 225 °C. Accordingly, the obtained DTG curve of black locust torrefied at 225 °C (Figure 2d) has a significant shoulder, representing the decomposition of hemicellulose. After torrefaction at 250 °C (panels e and f of Figure 2), the characteristic shoulder on the DTG curve of the wood sample disappeared, indicating that hemicellulose decomposed or its structure changed as a result of the torrefaction. The results of the acidic hydrolysis revealed that about 40% of the hemicellulose content decomposed during the torrefaction at 250 °C temperature. The significant hemicellulose content of the samples torrefied at 250 °C contradicts the disappearance of the hemicellulose shoulder from the DTG curve. These results can be explained by the assumption that the thermally most labile functional groups (e.g., acetyl groups) of hemicelluloses were split off under torrefaction; therefore, the
remaining hemicellulose chains became more stable and decomposed in a temperature range similar to that of cellulose. With regard to the cellulose component of the torrefied biomass samples, the TG curves confirm the results of the compositional analysis. Low-temperature torrefaction has only a small effect on the amount of cellulose. After torrefaction at 275 °C (panels g and h of Figure 2), the maximal rate of thermal decomposition of both straw samples decreased by about 50%, indicating the high degree of cellulose decomposition during the torrefaction. In the case of the black locust sample, torrefaction at 275 °C still did not significantly affect the cellulose content. These observations also indicate the catalytic effect of alkali ions on the decomposition of cellulose and are in agreement with the results of the compositional analysis. After torrefaction at 300 °C, the DTG curve of black locust is significantly reduced but still with some cellulose content extant, while the DTG curves of wheat straw and rape straw have (Figure 2j) a wide and flat shape, indicating the almost complete decomposition of cellulose. Lignin decomposes at a low rate in a wide temperature range from 250 to 600 °C; hence, it does not have a separate DTG peak. Lignin is a complex cross-linked methoxyphenol-based polymer built of so-called monolignol subunits: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. Lignin of the herbaceous plants is composed of all three types of monolignols, while the hardwood lignin is built of only coniferyl alcohol and sinapyl alcohol. The lignin and alkali ion contents of the samples have a considerable effect on the char yield of biomass. Lignin produces about 30% char, whereas the decomposition of cellulose and hemicellulose leads to only about 5 and 5−10% solid residue, respectively. The inherent alkali ion content of biomass changes the thermal decomposition mechanism; a higher char yield and an increased amount of gaseous products are formed with an increasing alkali ion content.31

3.4. PCA Based on the Calorific Values, TG, and Chemical Composition Data. The TG parameters (T_peak, DTG_max, T_start, T_end, and char yield), glucan, xylan, and lignin contents, and HHVs have been used in the calculation as input data to illustrate the differences and similarities between the untreated and torrefied biomass samples (Table 1 and Figures 1 and 2). Besides the extrapolated T_start value, T_1% was also used for the description of the beginning of the decomposition, which represents the temperature of 1% mass loss after the release of the adsorbed water. T_start denotes the
start of hemicellulose decomposition, while \( T_{\text{end}} \) shows the end of cellulose decomposition. In the PCA calculation, the first principal component (factor 1) characterizes 67.26%, while the second and third principal components (factors 2 and 3) describe 14.67 and 9.86% of the total variance, respectively. These three factors describe adequately the main differences between the samples. The score plot for factors 1 and 2 (Figure 3a) shows that the black locust (BL), rape straw (RS), and wheat straw (WS) samples can be seen in different parts of the plot. The first principal component differentiates the untreated and mildly and severely torrefied samples. As a function of the second principal component, the herbaceous samples are found in the upper part of the score plot and the woody samples are found in the lower part of the score plot. This difference is apparently due to the different cellulose, hemicellulose, lignin, and extractive contents of the samples, which is reflected in the different thermal behaviors of woody and herbaceous materials.

The loading plot for factors 1 and 2 (Figure 3b) shows that the values of glucan and xylan contents and DTG\(_{\text{max}}\) data correlate negatively with the HHV, lignin content, char yield,
T_{start} and T_{1%} data. Factor 1 is composed of mainly these parameters and mostly separates the samples as a function of the torrefaction temperature. Figure 3a shows that the herbaceous samples torrefied at 275 and 300 °C are separated, essentially indicating the severe decomposition. T_{peak} and T_{end} data contribute mainly to factor 2; these parameters describe the cellulose decomposition. Untreated black locust (hardwood) and wheat straw have similar cellulose contents (approximately 34%); however, straw samples have more than an order of magnitude higher K\(^+\) and Na\(^+\) contents than those of black locust (Table 2). As a result of the alkali catalysis, the characteristic temperatures of cellulose decomposition of the herbaceous samples shift to lower temperatures. Mainly this effect is reflected in factor 2.

Factor 3 describes almost 10% of the total variance. The loading plot (Figure 3d) shows that the values of T_{1%}, T_{start}, cellulose content, and DTG_{max} contribute to factors 3 and 1 as well. T_{1%} and T_{start} can be attributed to the hemicellulose decomposition in untreated and mildly treated samples, while after severe torrefaction, i.e., after the decomposition of
hemicellulose, these parameters belong to the cellulose decomposition. The samples formed two groups as a function of factors 1 and 3, as shown in Figure 3c. The severely torrefied samples are separated from the untreated and mildly torrefied biomass samples. As mentioned above, the maximum rate of thermal decomposition (DTGmax) of straw samples decreased by half between the torrefied samples at 250 and 275 °C, while the DTGmax data of black locust wood only differ significantly between the samples treated at 275 and 300 °C. It was found that the hemicellulose and cellulose contents of the studied samples strongly decreased from 250 to 300 °C (see Figure 1). At the severe torrefaction temperatures (275–300 °C), the chemical composition of the samples significantly changed during torrefaction; therefore, the thermal properties of the samples were altered to a greater extent in this temperature range.

3.5. TG/MS Results. The evolution profiles of the most characteristic decomposition products of the untreated and torrefied black locust and wheat straw samples are presented in Figures 4 and 5. The curves for the individual species released from black locust wood and wheat straw are plotted in the same scale in each of the figures. The pattern of the ion intensity curves of rape straw is very similar to that of wheat straw; hence, it is not presented here.

Figure 4 shows the evolution of the main permanent gases and water from black locust wood and wheat straw. Relatively large amounts of water and carbon dioxide are produced during the thermal decomposition of the samples as a result of the various types of hydroxyl and other oxygen-containing functional groups in the natural polymers (cellulose, hemicellulose, and lignin). The higher temperature charring processes are characterized by the evolution of hydrogen (m/z 2) and methane (m/z 16). Figure 5 shows the evolution of some characteristic organic volatile products and fragment ions from the black locust wood and wheat straw samples. Formaldehyde (m/z 30) forms during the thermal decomposition of cellulose, hemicellulose, and lignin as well. The release of methanol can be monitored at m/z 31. Furthermore, m/z 31 is the main fragment ion of hydroxyacetalddehyde, which is an important product of cellulose decomposition. The evolution curve at m/z 60 ion may represent either acetic acid released mostly from the acetate groups of hemicellulose or hydroxyacetalddehyde formed mainly during cellulose decomposition. The m/z 27 ion is a typical fragment ion of hydrocarbons.

The moisture content (m/z 18 in Figure 4) releases from the samples up to 120 °C. During torrefaction, the moisture content of the sample was released; however, during sample handling, the torrefied sample can take up some water from the air depending upon the degree of hydrophilicity of the torrefied sample. The moisture content of the torrefied straw samples is higher than that of the torrefied wood samples, which may be explained by the higher inorganic content and, therefore, the more hydrophilic nature of the torrefied straw samples.

The evolution of water, carbon dioxide, formaldehyde, and methanol (panels a and b of Figures 4 and 5) in the temperature range of 200–250 °C reveals the thermolysis of extractives and scission of lignin side groups from the untreated samples. These processes start at around 200 °C, and the significant shoulder at 230 °C on the DTG and ion curves of untreated black locust can be attributed to the decomposition of extractives. During 1 h thermal pretreatment at 225 °C, the extractive content of the sample decomposed; therefore, the shoulder at 230 °C disappeared from the torrefied samples (Figures 4c and 5c).

The characteristic peaks or shoulders of formaldehyde, acetic acid, methanol, carbon dioxide, and water in the temperature range of 280–350 °C of the untreated wood sample (Figures 4a and 5a) represent the decomposition of hemicellulose. In the case of the herbaceous samples, the shoulder is not pronounced because the cellulose decomposition shifts to a lower temperature as a result of the higher alkali ion content. The evolution of acetic acid and carbon dioxide indicates the scission of the acidic groups from hemicellulose. The composition analysis revealed that the hemicellulose content of the samples does not decrease during thermal treatment at 225 °C. However, the ion intensities of the significant decomposition products of hemicellulose slightly decreased in the case of the wood sample (Figures 4c and 5c). This observation may point to the somewhat modified structure (e.g., scission of the most labile acidic groups) as a result of torrefaction at 225 °C. The TG/MS curves of the samples torrefied at 250 °C (Figures 4e and 5e) verify our assumption based on the DTG curve that the decomposition of the remaining part of hemicellulose takes place in the temperature range of cellulose decomposition.

The main thermal decomposition product of cellulose is levoglucosan, which cannot be detected by TG/MS, but smaller decomposition products, such as hydroxyacetalddehyde (m/z 60), formaldehyde (m/z 30), and methanol (m/z 31, which is also a fragment ion of hydroxyacetalddehyde), can be monitored (Figure 5). Significant amounts of water and carbon dioxide are released during cellulose decomposition as well (Figure 4). The ion intensities describing the decomposition of cellulose (in the temperature range of the main DTG peak) do not decrease as a result of the thermal treatment up to 250 °C torrefaction temperature. Increasing the temperature of the torrefaction to 275 °C results in the reduced evolution of all cellulose decomposition products by about 40% in the wheat straw sample, while it does not decrease significantly in the case of the black locust sample. This observation shows the more developed degradation of cellulose in herbaceous wheat straw at 275 °C. After torrefaction at 300 °C, the ion intensity curves of the black locust sample (Figures 4i and 5i) show significant but not complete degradation of cellulose, while in the case of the wheat straw sample (Figures 4j and 5j), the ion curves prove the almost complete degradation of cellulose and hemicellulose. These TG/MS results confirm the results of the compositional analysis (Figure 1).

The evolution profile of methane (m/z 16 in Figure 4) shows a wide bimodal shape. In the temperature range of 370–500 °C, methane forms during the thermal decomposition of lignin by the scission of the methoxy groups.33 The slightly higher methane evolution from black locust in this temperature range is in accordance with the higher methoxy group content of hardwood lignin compared to herbaceous lignin. After torrefaction, the relative amount of lignin increased in the samples as a result of the release of extractives as well as the degradation of hemicellulose and cellulose at higher torrefaction temperatures. The increased evolution of methane originating from the decomposition of lignin indicates this process. This effect is more pronounced in the case of the wood sample. In the temperature range of 400–600 °C, the evolution of small hydrocarbon molecules were observed, represented by the m/z 27 ion curves in Figure 5. The relative intensity of the hydrocarbon evolution is increasing by the torrefaction
temperature in the case of both the wood and straw samples. These hydrocarbon molecules may be produced by secondary reactions involving the decomposition products of cellulose, hemicellulose, and lignin.

Methane formation above 500 °C and hydrogen evolution (m/z 2 in Figure 4) above 600 °C occur during the charring reactions. In comparison of the intensities of the selected ions as a function of the torrefaction temperature, it can be observed that the evolution of hydrogen and methane is increasing, while the intensities of the other presented lignocellulose decomposition products are decreasing with raising the torrefaction temperature. These changes indicate the progress of the thermal decomposition during the torrefaction. In the case of the black locust sample, the ion intensity curve of carbon dioxide has two small sharp peaks, at 530 and 670 °C, indicating the presence of calcium oxalate, which originates from the bark of black locust wood.

3.6. PCA Based on the TG/MS Data. PCA has been applied to find further correlations between the ion intensity data of the main decomposition products obtained by the TG/MS technique. The integrated intensities of the characteristic mass spectrometric ion curves have been used in the PCA calculation (Figure 6). The first principal component (factor 1) describes 79.67% of the total variance of the TG/MS data, while the second and third principal components (factors 2 and 3) describe 11.56 and 3.19% of the total variance, respectively. The first principal component differentiates the untreated and lightly torrefied samples from the mildly and severely torrefied samples; therefore, factor 1 correlates with the torrefaction temperature (Figure 6a). The loading plot for factors 1 and 2 (Figure 6b) reveals that mainly organic molecules contribute to factor 1. The increasing torrefaction temperature correlates with the methane and hydrogen yields, which shows that the severely torrefied samples produced more gases during the charring reactions. On the other hand, the decreasing torrefaction temperature correlates mainly with the formaldehyde, acetone, and acetic acid formation because these compounds were released apparently during light and mild torrefaction; hence, their pyrolytic yield is decreasing with an increasing torrefaction temperature. The amounts of CO, CO₂, and water play the most important role in determining the second principal component. As seen earlier, more gaseous products and water vapor were released from the herbaceous plants than from the hardwood. These differences can be explained by the different alkali ion contents of the studied samples. The higher alkali ion content promotes the gas formation during torrefaction of wheat straw and rape straw via fragmentation. On the other hand, the depolymerization reactions are dominant during the torrefaction of black locust wood indicated by the higher yields of furfural (sum of m/z 95 and 96) and furanone (m/z 84), which also contribute to the second principal component. On the other hand, the loading plots (Figure 6d) suggest that the yields of furanone, furfural, and methanol (m/z 31) as well as acetic acid and hydroxyacetaldehyde (m/z 60) also play a role in determining the third principal component. At the given torrefaction temperatures, the yields of these compounds are higher during the decomposition of black locust wood than of that of wheat.
straw and rape straw. The second and third principal components may be attributed to the effect of both the different chemical compositions and the inorganic contents of the studied samples.

4. CONCLUSION

Comprehensive compositional analysis of untreated and torrefied wood and herbaceous samples has been performed with the goal of understanding deeper the thermal degradation processes taking place during torrefaction. The hemicellulose, cellulose, and Klason lignin contents of native and torrefied samples were determined after acidic hydrolysis. TG/MS was applied to provide further information about the composition of the samples by breaking down the macromolecules into smaller building blocks. The joint interpretation of the changes in the chemical composition, thermal stability, and evolution profiles of typical lignocellulose decomposition products as a result of the thermal treatment revealed new information about the thermal degradation of the lignocellulose materials.

The extractable compounds evaporate at the beginning of the torrefaction; the volatile extractives disappeared from the samples torrefied at 225 °C. The main mass of the hemicellulose content of each wood and herbaceous sample was thermally stable during 1 h of torrefaction at 225 °C; however, changes in the evolution pattern of acetic acid indicate the scission of the most labile acetate groups from the hemicellulose chains at this temperature. About 40% of the hemicellulose content decomposes at 250 °C in the case of black locust wood and rape and wheat straw samples as well. The thermal decomposition of hemicellulose after mild thermal treatment shifted to a higher temperature, indicating the modified structure of torrefied hemicellulose. No significant difference was found in the thermal stability of straw and wood samples, despite the large difference in the contents of inorganic materials. Therefore, it can be concluded that the thermal stability of hemicellulose is not influenced by the inorganic content of the sample contrary to cellulose, where the significant catalytic effect of the alkali ions on the thermal decomposition is a well-known phenomenon. The hemicellulose content of each sample torrefied at 275 °C is strongly reduced.

The degree of cellulose decomposition at 275 °C torrefaction temperature is significant only for herbaceous samples, while cellulose is not degraded in the wood sample at this temperature. The gradual increase in the amount of the acid-insoluble materials indicates that the scission of the functional groups is accompanied by the enhanced formation of the cross-linked carbonaceous residues with an increasing torrefaction temperature. The results of the proximate and ultimate analyses, HHVs, compositional analysis data, and TG/MS experiments all clearly demonstrate the progress of the thermal decomposition during torrefaction in the temperature range of 200–300 °C. Statistical correlations have been found between the torrefaction temperature, chemical composition, and TG/MS data of the untreated and torrefied samples using PCA. Three sets of PCA calculations were undertaken using different types of data, which resulted in consistent results; the untreated and mildly torrefied samples were separated from the severely torrefied samples. The calculations revealed that the chemical composition and, therefore, the thermal properties have changed to a much greater extent in the temperature range of 275–300 °C than at lower torrefaction temperatures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.6b01030.

PCA performed to find statistical correlations between the solid yields, energy contents, and proximate and ultimate analysis data (Table 1) and PCA results (Figure S1) (PDF).

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Notes

The authors declare no competing financial interest.

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NOMENCLATURE

BL = black locust
RS = rape straw
WS = wheat straw
BL U = untreated black locust
BL 200 = torrefied black locust obtained from torrefaction at 200 °C
HHV = higher heating value
MC = moisture content
VM = volatile matter
FC = fixed carbon
DTG = maximum value of the derivative thermogravimetric curves
T_peak = temperature of the maximum of the derivative thermogravimetric curves
T_1% = temperature belonging to the 1% mass loss of the dried samples
T_start = extrapolated temperature of the beginning of decomposition (on the derivative thermogravimetric curve)
T_end = extrapolated temperature of the end of cellulose decomposition (on the derivative thermogravimetric curve)
char = char residue at 950 °C temperature
PCA = principal component analysis

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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.

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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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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 Klasson 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.

Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA</td>
<td>bark</td>
</tr>
<tr>
<td>ST</td>
<td>stump</td>
</tr>
<tr>
<td>SW</td>
<td>stem wood</td>
</tr>
<tr>
<td>SW U</td>
<td>untreated stem wood</td>
</tr>
<tr>
<td>SW 225_60</td>
<td>torrefied stem wood obtained by torrefaction at 225 °C for 60 min isothermal period</td>
</tr>
<tr>
<td>DTG\text{max}</td>
<td>maximum value of the $-\frac{\text{dm}}{\text{dt}}$ curves</td>
</tr>
<tr>
<td>T\text{start}</td>
<td>extrapolated temperature of the beginning of decomposition (on the DTG curve)</td>
</tr>
<tr>
<td>T\text{peak}</td>
<td>temperature belonging to the DTG\text{max}</td>
</tr>
<tr>
<td>T\text{end}</td>
<td>extrapolated temperature of the end of cellulose decomposition (on the DTG curve)</td>
</tr>
<tr>
<td>Char</td>
<td>char residue at 900 °C temperature</td>
</tr>
<tr>
<td>% m/m</td>
<td>mass percent</td>
</tr>
<tr>
<td>PCA</td>
<td>principal component analysis</td>
</tr>
<tr>
<td>TG/MS</td>
<td>thermogravimetry/mass spectrometry</td>
</tr>
</tbody>
</table>
2. Materials and methods

2.1. Materials

Different parts of a representative single Norway spruce (*Picea abies*) tree were selected for the torrefaction study: bark, stem wood and stump. The samples originated from a Norway spruce forest in South Norway. The trees in the forest site have high ages, more than one hundred years old on average. After harvested, the trees were divided into three parts: trunk, stump, and forest residues. The trunk was further debarked to obtain stem wood and bark. The stem wood was first cut to strips, and then further chopped into cubes with sides of 1 cm. The bark was chopped into pieces and those with length of around 5–7 cm were used for the torrefaction experiments. The stump was shredded into pieces and the pieces with length of 3–5 cm were torrefied.

2.2. Methods

2.2.1. Torrefaction experiments

The torrefaction experiments were carried out in a batch tube reactor placed in an electrical furnace in nitrogen atmosphere using flow rates of 1 L/min. Approximately 80 g samples were heated up at a heating rate of 15 °C/min to temperatures of 225, 275 and 300 °C in the tube reactor followed by 30 and 60 min isothermal periods, whereafter the reactor was cooled down to room temperature. For further experiments the untreated and torrefied samples were ground by a cutting mill to <1 mm particle size.

2.2.2. Higher heating value determination

The higher heating value (HHV) was determined using an automatic IKA C 5000 bomb calorimeter. The combustion of approximately 0.5 g dried sample in pure oxygen atmosphere was performed under 30 bar pressure. The heat capacity of the calorimeter system was determined by benzoic acid calibration. All heating values were calculated using the average of three replicates.

2.2.3. Inductively coupled plasma-optical emission spectroscopy (ICP-OES)

Approximately 2 g biomass samples were ashed at 550 °C in a furnace according to CEN/TS 14775:2004 standard method. The ashes were fused at 920 °C with a fusion blend (**Li**2**B**2**O**3:**Li**BO**2**, 2:1) and digested by 25 mL 33% nitric acid. The calcium, potassium, sodium, and magnesium contents of the samples were determined by a Spectro Genesis ICP-OES (Spectro Analytical Instruments) with axial plasma observation. The amounts of the ashes have been determined according to the CEN/TS 14775 EU standard method.

2.2.4. Carbohydrate and Klason lignin content determination

The contents of carbohydrates were determined according to the method of Sluiter et al. [28] applying slight modifications. The milled samples (<1 mm) were dried at 40 °C for 1 day. The raw and torrefied biomass samples were treated in a two-step acid hydrolysis with 72% H2SO4 for 2 h at room temperature, and then with 4% H2SO4 for 1 h at 121 °C. The gained suspensions were filtered and washed with distilled water through G4 glass filter crucibles. The sugar concentrations (glucose, mannose and galactose) of the filtered supernatants were analyzed by high performance liquid chromatography (HPLC) using an Agilent 1260 system with a Hi-Plex H column (Agilent, CA, USA) at 65 °C. An eluent of 5 mM H2SO4 was used at a flow rate of 0.5 mL min⁻¹. The solid residues obtained after washing were dried at 105 °C until constant weight. The dried residues consisted of acid-insoluble organics and acid-insoluble ash. The total ash and acid-insoluble ash contents were measured by ashing the sample at 550 °C for 5 h until the sample weight was constant [29]. The Klason lignin content was calculated by subtracting the acid insoluble ash content from the acid insoluble residue content. All experimental data were determined using three replicates.

2.2.5. Thermogravimetry/mass spectrometry (TG/MS)

The TG/MS system consists of a modified Perkin-Elmer TGS-2 thermobalance and a Hiden HAL quadrupole mass spectrometer. About 5 mg samples were analyzed in argon atmosphere. The samples were heated at a rate of 20 °C min⁻¹ from 25 to 900 °C in a platinum sample pan. The evolved products were flushed through a glass lined metal capillary heated at 300 °C by argon gas using a flow rate of 140 mL min⁻¹. The ion source of the mass spectrometer was operated at 70 eV electron energy. The mass range of 2–150 Da was scanned. The ion intensities were normalized to the sample mass and to the intensity of the 38Ar isotope of the carrier gas (used as an internal standard). Since the MS intensities of various products have different magnitudes, they have been scaled to gain comparable peak heights in the plots. The curves of the individual species developed from bark, stem wood and stump are plotted using the same scale in each of the TG/MS figures.

2.2.6. Principal component analysis (PCA)

Due to the large number of samples and experimental data, principal component analysis (PCA) using the Statistica 12 software (StatSoft, Inc. Tulsa, Oklahoma, USA), was employed. PCA has been used to reveal correlations between the TG data and the chemical composition of the studied samples. PCA is a technique for reduction of data dimensionality, which allows detecting patterns and visualization of patterns retaining as much important information present in the original data as possible [30,31]. The values that represent the samples in the space defined by the principal components (Factors) are the component scores. Factor loadings show the correlation between the original variables and the Factors, and it may help understand the underlying nature of a particular Factor.

3. Results and discussion

3.1. Comparison of the three untreated samples

Table 1 summarizes the higher heating value, the ash content and selected data of the ICP-OES characterization of the untreated samples. As the results illustrate, the heating values are rather similar, while the bark has significantly higher ash content than stem wood and stump. The bark has an order of magnitude higher K⁺ and Si contents than stem wood and stump. Furthermore, the Na⁺ and Ca²⁺ contents of the bark are also higher compared to stem wood and stump.

<table>
<thead>
<tr>
<th>Inorganic components (mg/kg, db)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca²⁺</td>
</tr>
<tr>
<td>Na⁺</td>
</tr>
<tr>
<td>K⁺</td>
</tr>
<tr>
<td>Si</td>
</tr>
</tbody>
</table>

Table 1 Characterization of the untreated samples.

<table>
<thead>
<tr>
<th></th>
<th>Bark</th>
<th>Stem wood</th>
<th>Stump</th>
</tr>
</thead>
<tbody>
<tr>
<td>Higher heating value (MJ/kg, db)</td>
<td>20.14</td>
<td>19.78</td>
<td>19.51</td>
</tr>
<tr>
<td>Ash content (% m/m, db)</td>
<td>2.43</td>
<td>0.31</td>
<td>0.43</td>
</tr>
<tr>
<td>Inorganic components (mg/kg, db)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>7803</td>
<td>1030</td>
<td>1235</td>
</tr>
<tr>
<td>Na⁺</td>
<td>47</td>
<td>22</td>
<td>36</td>
</tr>
<tr>
<td>K⁺</td>
<td>2011</td>
<td>272</td>
<td>245</td>
</tr>
<tr>
<td>Si</td>
<td>3602</td>
<td>82</td>
<td>253</td>
</tr>
</tbody>
</table>

*a* Dry basis.  
*b* As received.
Fig. 1a shows the chemical composition of the three untreated samples. The sum of the mannan and galactan contents represents the hemicellulose fraction, whereas the glucan content of the samples mainly characterizes the cellulose fraction of biomass. The Klason lignin content is defined as the acid insoluble residue of the samples without the acid insoluble ash. Besides the acid insoluble lignin, the Klason lignin contains all acid insoluble components of the sample, excluding ash. The fraction denoted by “Other” represents the sum of unquantified components and includes extractives, acid soluble lignin and acid soluble minerals. As Fig. 1a shows, the bark sample has the highest Klason lignin content, stem wood has the highest cellulose content and stump has the highest hemicellulose content. The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the untreated samples are shown in Fig. 1b. The main DTG peak is dominated by the decomposition of cellulose, while the shoulder at lower temperature (around 320 °C) can be attributed mainly to hemicellulose decomposition. The lignin decomposes at a lower rate in a wide temperature range (200–600 °C). The evaporation and decomposition reactions of extractives start at lower temperatures and it is visible as a shoulder on the main DTG peak from approximately 160 °C. The comparison of the three untreated samples shows that bark releases the most extractives, in the low temperature range. The untreated stump has the most characteristic hemicellulose shoulder, which is in agreement with the chemical composition results showing that stump has the highest hemicellulose content. The decomposition of bark starts at the lowest temperature, the DTG peak maximum occurs at the lowest temperature, and the maximum rate of decomposition is considerably lower than in the case of the stem wood and stump. The high lignin content (41%) of bark results in the formation of a high yield of char during thermal decomposition. The different thermal behavior of the different untreated samples can be explained by their different composition as well as by the fact that alkali ions have catalytic effects on the decomposition mechanism of cellulose [23–25] and the charring reactions of lignin [23,26,27].

Regarding the thermal behavior of the studied samples, further information is given by the mass spectrometry curves. The thermal decomposition of extractives, cellulose, hemicellulose and lignin results in a high yield of low molecular mass compounds at low heating rate, hence the evolution profiles of these products are characteristic to the decomposition of the different parts of the tree. Fig. 2a, c and e presents the DTG curves as well as the evolution of water and the main permanent gases, while Fig. 2b, d and f presents the evolution of some typical organic products measured by the mass spectrometer during the thermal decomposition of the three untreated samples.

Relatively large amounts of water (m/z 18), carbon monoxide (m/z 28) and carbon dioxide (m/z 44) are formed during the thermal decomposition of the untreated materials (Fig. 2a, c and e) due to the large number of hydroxyl and other oxygen-containing functional groups in the natural polymers (cellulose, hemicellulose and lignin). In the temperature range of 300–430 °C besides carbon monoxide the ion current m/z 28 represents the CO mass spectrometric fragment ion of organic oxygen-containing volatile products as well (e.g., formaldehyde). In the temperature range of 500–900 °C, the charring processes are characterized by the evolution of carbon monoxide (m/z 28), methane (m/z 16) and hydrogen (m/z 2). Formaldehyde (m/z 30) is released during the thermal decomposition of cellulose, hemicellulose and lignin, as well. The fragment ion m/z 31 represents mainly the evolution of methanol during the thermal decomposition. On the other hand, m/z 31 is the main fragment ion of hydroxyacetaldehyde, which is a typical product of the cellulose decomposition. The evolution curve of the m/z 45 ion represents mainly COOH*, which is the main fragment ion of acidic products released from hemicellulose and cellulose. The m/z 27 ion is a typical fragment ion of hydrocarbons.

The moisture content (m/z 18 in Fig. 2a, c and e) is released from the untreated samples up to 200 °C. The higher intensity and broader shape of this water peak for the bark sample indicate a higher moisture content of the bark sample, which may be bonded mostly to the inorganic content (Table 1) of the bark sample. As seen in Fig. 2, considerably higher amounts of permanent gases and lower amounts of organic volatiles are released from raw bark than from raw stem wood and stump. The characteristic peaks of shoulders of carbon dioxide, water, formaldehyde and methanol in the temperature range of 200–300 °C can be attributed to the thermolysis of extractives and scission of lignin side groups from the untreated samples. In case of stem wood and stump, the characteristic shoulder of formaldehyde, carboxyl group, carbon dioxide and water in the temperature range of 300–350 °C reveals the decomposition of hemicellulose (Fig. 2c and e). O-acetyl-galactoglucomannans are the main hemicelluloses in softwoods.
The evolution profile of COOH⁺ and carbon dioxide indicates the scission of the acidic groups from hemicellulose. As seen in Fig. 2, the untreated stump produces the highest amount of acid products as the m/z 45 fragment ion indicates, which can be explained by the highest hemicellulose content of the stump sample (Fig. 1). The hemicellulose shoulder of the untreated bark is not pronounced which is in agreement with the chemical composition results showing that bark has the lowest hemicellulose content (Fig. 1). The main thermal decomposition product of cellulose is levoglucosan, which cannot be detected by TG/MS, but smaller decomposition products like formaldehyde (m/z 30), hydroxyacetaldehyde (m/z 31) and methanol (m/z 31) originating from cellulose can be monitored at around 390 °C as shown in Fig. 2b, d and f. Significant amounts of water vapor and carbon dioxide are released during cellulose decomposition, as well. Methane (m/z 16) is released in two main processes during the thermal decomposition of the untreated samples. In the first process at around 450 °C methane forms during the thermal decomposition of lignin by the scission of the methoxy groups [27]. The evolution of carbon monoxide, methane and hydrogen (Fig. 2a, c and e) above 500 °C takes place during the charring processes. As a result of the higher lignin content of bark (Fig. 1), the charring processes are more pronounced than in the stem wood and stump resulting in higher amount of methane, hydrogen, and char.
3.2. Effect of torrefaction temperature and residence time

During torrefaction the lignocellulosic materials decompose to different degrees depending on the applied temperature and residence time. Fig. 3 shows the TG and DTG curves of the various torrefied bark, stem wood, and stump samples. The carbohydrate and lignin contents of the untreated and torrefied biomass samples (Table 2) were also determined in order to understand better the thermochemical conversion process during torrefaction.

As the mannan and galactan contents demonstrate in Table 2, the sugar units of hemicellulose did not degrade during torrefaction at 225 °C. However, the characteristic hemicellulose shoulder of the DTG curves decreased revealing the structural modification as a result of the torrefaction (Figs. 2 and 3a and b). These results can be explained by the hypothesis that the acidic side groups of hemicellulose were partially split off, while the main hemicellulose content did not degrade at 225 °C. As the result of the partial scission of acidic side groups, the hydrophilicity of the biomass decreases, and therefore it takes up less moisture during storage [7]. The biomass with less moisture has higher energetic value, giving lower transportation cost, and moreover it can be stored stably with a low risk of biological deterioration. The cellulose content of stem wood and stump did not reduce considerably up to 275 °C, as the results show in Table 2, and Fig. 3, while the degradation of cellulose in the bark sample was significant at this temperature. At 300 °C, only trace amounts of cellulose were found in bark, and the cellulose content of stem wood and stump strongly decreased.

As already mentioned, the presence of alkali ions modifies the ther-
nal degradation of cellulose [23–25] and lignin [23,26,27]. The reason for the promoted decomposition rate of bark during torrefaction is most probably the catalyzed decomposition of its cellulose content. As Fig. 3 shows, the residence time had no significant effect on the composition of the torrefied samples up to 275 °C; therefore applying the longer residence time of 60 min in a real application is superfluous. At 300 °C, the torrefaction residence time had substantial effects on all parts of the spruce tree due to the severe decomposition reactions at this temperature.

Figs. 4–6 show the evolution of the most significant products from the torrefied bark, stem wood, and stump samples, respectively, in order to get a better understanding of the above discussed differences in the decomposition during torrefaction. The curves for the individual species released from bark (Fig. 4), stem wood (Fig. 5) and stump (Fig. 6) are plotted using the same scale in each of the figures. The pattern of the ion intensity curves of the samples torrefied at 225 and 275 °C for 30 min is very similar to that of the samples torrefied at 225 and 275 °C for 60 min; hence they are not presented here. As the water vapor evolution below 200 °C indicates, the moisture content of the torrefied bark samples is higher than that of the torrefied stem wood and stump samples. The reason could be the higher inorganic ion content, therefore the more hydrophilic nature of the torrefied bark samples. The torrefaction removes the moisture content of the samples; however, during sample handling the torrefied sample can take up some water from the ambient air depending on the degree of hydrophilicity of the torrefied sample. The torrefied bark samples release higher amounts of permanent gases and lower amounts of organic volatiles than torrefied stem wood and stump samples, prepared under the same torrefaction conditions. This observation indicates the catalytic effect of alkali ions on the decomposition of cellulose and is in agreement with the results of the compositional analysis, as well. The inherent alkali ion content of lignocellulosic biomass changes through a catalytic effect the thermal decomposition mechanism, giving increased char yield and increased amount of water and permanent gases, at the expense of the yield of organic volatiles [26]. During torrefaction at 225 °C, the extractives content of the samples strongly decreased, therefore the shoulder of the DTG curves at 290 °C is less pronounced for the torrefied samples at 225 °C (Figs. 4a, 5a and 6a) than for the untreated samples (Fig. 2). The main mass of the hemicellulose content of the bark, stem wood and stump samples was thermally stable during torrefaction at 225 °C; however, changes in the evolution pattern of COOH* (Figs. 4b, 5b and 6b) point to the scission of the most labile acetate groups from the hemicellulose chains at this temperature. The composition analysis revealed (Table 2) that 8–26% hemicellulose remained in the samples after the thermal treatment at 275 °C; however, the shoulder of the DTG curve disappeared. The TG/MS results indicate that the decomposition of the remaining part of hemicellulose takes place in the temperature range of cellulose decomposition.

In case of stem wood and stump, the ion intensities describing the decomposition of cellulose (in the temperature range of the main DTG peak) do not decrease due to the thermal treatment up to 275 °C torrefaction temperature. This is in agreement with the chemical composition results showing that the cellulose content of the stem wood and stump samples only slightly decrease up to this temperature. The cellulose content of the bark sample decreased by half between the torrefied samples at 225 and 275 °C, resulting in a reduced evolution of all cellulose decomposition products. These observations show the more extensive degradation of the cellulose in bark at 275 °C. As shown earlier, the evolution of methane shows a wide bimodal shape. In the temperature range of 350–500 °C, methane forms during the thermal decomposition of lignin by the scission of the methoxy groups [27]. The reason for the different methane evolution profiles from the bark, stem wood and stump samples in this temperature range could be the different methoxy group content of the studied samples. After severe torrefaction (275–300 °C), the relative amount of Klasson lignin significantly increased in the samples due to the strong degradation of carbohydrates. It can be observed that the evolution of hydrogen, methane, and carbon monoxide above 430 °C are increasing, while the intensities of the hemicellulose and cellulose decomposition products are decreasing when raising the torrefaction temperature and residence time. The charring reactions are more pronounced in case of the bark sample. In the temperature range of 400–700 °C, the evolution of small hydrocarbon molecules were detected, denoted by the m/27 ion curves in Figs. 4–6. The relative intensity of the hydrocarbon evolution is increasing with the torrefaction temperature for all the bark, stem

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solid yield (% m/m)</th>
<th>Glucan (% m/m)</th>
<th>Mannan + galactan (% m/m)</th>
<th>Klason lignin (% m/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bark</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BA U</td>
<td>100</td>
<td>27.5 ± 0.7</td>
<td>9.7 ± 0.2</td>
<td>40.8 ± 0.3</td>
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<tr>
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<td>24.4 ± 0.6</td>
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<td>0.3 ± 0.0</td>
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<td>61</td>
<td>1.5 ± 0.1</td>
<td>0.1 ± 0.0</td>
<td>92.0 ± 0.4</td>
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<td></td>
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<tr>
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<td>18.3 ± 0.5</td>
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<td>17.1 ± 0.4</td>
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<td>8.3 ± 0.3</td>
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<td>87.3 ± 1.4</td>
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<td>Stump</td>
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<tr>
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<td>23.0 ± 0.3</td>
<td>27.7 ± 0.7</td>
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<td>28.2 ± 1.8</td>
<td>21.5 ± 0.4</td>
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<td>ST 275_30</td>
<td>72</td>
<td>29.7 ± 0.4</td>
<td>4.9 ± 0.2</td>
<td>57.2 ± 0.4</td>
</tr>
<tr>
<td>ST 275_60</td>
<td>70</td>
<td>29.0 ± 0.4</td>
<td>4.6 ± 0.2</td>
<td>59.6 ± 1.0</td>
</tr>
<tr>
<td>ST 300_30</td>
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<td>25.6 ± 0.6</td>
<td>1.1 ± 0.0</td>
<td>68.6 ± 0.3</td>
</tr>
<tr>
<td>ST 300_60</td>
<td>46</td>
<td>13.7 ± 0.5</td>
<td>0.4 ± 0.0</td>
<td>82.3 ± 0.5</td>
</tr>
</tbody>
</table>
Fig. 4. The DTG curves and the evolution profiles of the most characteristic decomposition products and fragment ions released from torrefied bark samples (m/z 2, hydrogen; m/z 16, methane; m/z 18, water; m/z 28, carbon monoxide; m/z 44, carbon dioxide; m/z 27, C$_2$H$_3$; m/z 30, formaldehyde; m/z 31, CH$_3$O$^+$; m/z 45, COOH$^+$).
Fig. 5. The DTG curves and the evolution profiles of the most characteristic decomposition products and fragment ions released from torrefied stem wood samples ($m/z$ 2, hydrogen; $m/z$ 16, methane; $m/z$ 18, water; $m/z$ 28, carbon monoxide; $m/z$ 44, carbon dioxide; $m/z$ 27, $C_2H_2$; $m/z$ 30, formaldehyde; $m/z$ 31, $CH_3O^+$; $m/z$ 45, COOH$^+$).
Fig. 6. The DTG curves and the evolution profiles of the most characteristic decomposition products and fragment ions released from torrefied stump samples (m/z 2, hydrogen; m/z 16, methane; m/z 18, water; m/z 28, carbon monoxide; m/z 44, carbon dioxide; m/z 27, C\(_2\)H\(_3\)+; m/z 30, formaldehyde; m/z 31, CH\(_3\)O+; m/z 45, COOH\(^+\)).
wood and stump samples. These hydrocarbon molecules could be released by secondary reactions involving the decomposition products of cellulose, hemicellulose and lignin. At 300 °C, the hemicellulose content of each studied sample almost completely decomposes during 30 min; the torrefaction residence time has a significant effect owing to the severe decomposition of cellulose. The torrefaction at 300 °C for 60 min results in reduced evolution of all cellulose decomposition products, decreasing by half in the stem wood and stump samples, while only traces of cellulose were measured in the bark sample. The severe decomposition of hemicellulose and cellulose results in the relatively low solid yield (43–70%) due to the significant dry matter loss during thermal degradation, therefore this temperature is too high for most real applications.

3.3. PCA calculation based on chemical composition and TG data

Principal component analysis has been applied to identify the similarities and differences between the untreated and various torrefied stem wood, bark and stump samples. In the PCA calculation, the characteristic thermogravimetric parameters (Tstart, Tpeak, DTGmax, Tend, and char yield) and the chemical composition data (glucan, sum of mannan and galactan, as well as Klason lignin contents) have been used as input variables. Tstart denotes the start of hemicellulose decomposition in the untreated and mildly torrefied samples, while after severe torrefaction, this parameter belongs to the cellulose decomposition. Tend reflects the end of the cellulose decomposition. The Tstart and Tend values have been determined by extrapolation of the DTG curve. In the PCA calculation the first principal component (Factor 1) and the second principal component (Factor 2) account for 64% and 21% of the total variance, respectively. These two factors can adequately characterize the major differences between the untreated and torrefied samples. The score plot (Fig. 7a) shows that the studied samples are located in four well separated groups. The untreated and mildly torrefied (at 225 °C) stem wood and stump samples belong to the same group, indicating that the torrefaction at 225 °C does not modify significantly the thermal properties of these samples compared to the untreated samples. The second group is formed from the stem wood and stump samples treated at 275 °C. The untreated and mildly torrefied (at 225 °C) bark samples are separated from the other samples, while all of the severely torrefied samples can be seen in the fourth group. These differences are mainly due to the different hemicellulose, cellulose and lignin content of the samples; which is reflected by the different thermal behavior of the studied samples, as well. The chemical composition and consequently the thermal behavior of the stem wood, stump, and bark samples have been changed to a greater extent at higher torrefaction temperature than at lower torrefaction temperature. The loading plot (Fig. 7b) shows that the values of glucan, sum of mannan and galactan, Tpeak and DTGmax data correlate negatively with the lignin content and the char yield. Factor 1 is composed mainly of these parameters and primarily separates the samples as a function of the torrefaction temperature and residence time. As the PCA calculation shows (Fig. 7a), the effect of torrefaction temperature is greater than the effect of residence time. Tstart and Tend data contribute mainly to Factor 2, and separates mostly the untreated and mildly torrefied bark samples from the others. The thermal decomposition of bark differs from the other samples due to the different composition (high lignin and alkali ion content).

4. Conclusion

A comparative study on the thermal behavior of untreated and various torrefied bark, stem wood, and stump of Norway spruce has been performed to better understand the thermal degradation process taking place during torrefaction. TG/MS and chemical composition analysis were applied to provide information about the structural changes of the main components and to compare the effects of different torrefaction conditions. Depending on the biomass feedstock properties and the needs of product applications, different torrefaction conditions will be optimal. The moisture content and the extractable compounds evaporate at first during torrefaction; the volatile extractive content strongly decreased in the samples torrefied at 225 °C. The comparison of the mannan and galactan content with the TG/MS results shows that the decomposition of hemicellulose starts with the cleavage of the functional groups, while the scission of the polysaccharide chains occurs at higher temperature. The thermally less stable acidic side groups are cleaved at this temperature, increasing the hydrophobicity of the product in this way, which is an important goal during the practical application of torrefaction. The hemicellulose chain of each sample was thermally stable during torrefaction at 225 °C; however, it degraded to a great extent at 275 °C as indicated by the chemical analysis. Significant decomposition of cellulose started as low as at 275 °C torrefaction temperature for the bark sample, while it was found to be stable for stem wood and stump, which can be explained by the high alkali ion content of bark. Therefore, lower torrefaction temperature should be applied for bark, than for stem wood and stump to obtain products degraded.
to a similar degree. The torrefaction residence time (30 vs. 60 min) did not have significant influence up to 275 °C on the thermal behavior of the samples. However, at 300 °C the composition of the torrefied samples changed substantially with the torrefaction residence time due to the intensive decomposition of cellulose. Torrefaction at 300 °C temperature induces severe changes in all biomass components, resulting in significant mass and energy losses; hence this temperature is too high for most of the applications.

Acknowledgements

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The short version of the paper was presented at ICAE2016 on Oct 8–11, Beijing, China. This paper is a substantial extension of the short version of the conference paper.

References

Effect of torrefaction on physiochemical characteristics and grindability of stem wood, stump and bark

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HIGHLIGHTS

• Changes in chemical composition and grindability of torrefied samples.
• Principal component analyses reveal statistical correlations between grindability and chemical compositions.
• SEM analyses show torrefied sample particles having lower length-to-diameter ratios.

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ABSTRACT

In this work, Norway spruce stem wood, stump and bark were torrefied in a bench scale tubular reactor at 225, 275 and 300 °C with two residence times (30 and 60 min). Effect of torrefaction on general properties, chemical composition, grindability and microstructure and morphology of biomass samples were studied. An increase in heating value and fixed carbon content of the torrefied biomass was observed for increasing torrefaction temperature and residence time. Chemical compositions of torrefied biomass samples considerably changed with increase of torrefaction severity. For the stem wood and stump, the relative hemicellulose content significantly decreased from respectively 42.3% and 29.8% to less than 1% after torrefaction at 300 °C for 60 min. The hemicellulose content of untreated bark decreased from 27.5% to 0.14% after torrefaction at the same conditions. Additionally, the cellulose content of the torrefied bark drastically decreased already to half the initial value at a torrefaction temperature of 275 °C, with only trace amounts left in the 300 °C torrefied products. The grindability of stem wood and stump were substantially improved after torrefaction treatment. The energy required for grinding stem wood and stump torrefied at 225 °C decreased to respectively 87 and 70 kWh/ton, which are less than 50% of the energy needed for grinding the untreated samples. For raw bark, much less grinding energy is required compared to those for raw stem wood and stump, and torrefaction has minor effects on the grindability of bark. The ground torrefied biomass samples have much smaller particles than those of the untreated ones. SEM analysis results show that particles from ground torrefied samples lose their fibrous structure with decrease of length-to-diameter ratios, compared to untreated biomass samples. It explains the shift in particle size distribution curves towards smaller particles as obtained from the sieving tests.

1. Introduction

Adoption and utilization of renewable energy sources are important for the modern society, considering the ever increasing energy demands and severe global warming due to use of fossil fuels. In future energy scenarios, biomass will play an important role in the energy supply [1]. A wide range of energy products can be produced from biomass via thermochemical conversion and biological conversion routes, which can be in the form of solid (bio-solid), liquid (bio-oil) or gas (bio-gas or syngas) [2]. Therefore, biomass is a flexible energy source that can be converted into various energy products to meet different demands. Norway has abundant forest resources and more than 40% of the land is covered by forest [3]. Biomass materials from the forest has a great potential to provide suitable feedstocks for bioenergy.

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However, further development of bioenergy and utilization of biomass in a large scale have been hindered by limitations of the biomass as solid fuel. These limitations are mainly related to physical and chemical properties of the biomass [4,5]. Compared to coal, biomass materials normally have low bulk density, poor grindability, low calorific value, high moisture content and hydropscopicity [6]. These limitations greatly affect the conversion efficiency of biomass materials into energy. In addition, the whole biomass-to-energy value chain is considerably impacted by these limitations due to costly storage, handling and transportation of biomass [7,8]. Among many pretreatment technologies, torrefaction of biomass has gained continuous interests in the past decade [1,5,6,9,10]. Torrefaction is usually conducted in inert atmosphere at a temperature range from 200 to 300 °C, driving out the moisture, and parts of the volatile organic compounds in the biomass [1,11]. Torrefied biomass retains most of the chemical energy in the raw biomass materials. Upon torrefaction, biomass can be ground easily into small particles with higher shape uniformity and sphericity [12–14]. This is mainly due to reduction of moisture content and change of chemical compositions of the raw biomass during torrefaction [10,15,16]. Torrefied biomass with unique properties are more suitable for logistics and further conversion to energy. Key torrefaction process parameters include temperature, residence time, pressure, gas atmosphere and heating rate [1]. These parameters have critical effects on torrefaction behaviour, distribution and properties of torrefaction products and the overall energy and mass conversion efficiency [17]. On the other hand, the characteristics of biomass materials will also play an important role in the torrefaction process.

During harvesting and thinning of forest, stem wood is a main product with residues such as tops and branches as well as the stumps left behind in the forest. It has been reported that stump constitute 22–24% of the stem volume of a mature conifer tree, representing a very significant bioenergy potential [18,19]. A vast amount of bark is generated as the stem wood is debarked before further utilization for pulp and paper and timber products production [20]. Both stump wood and bark are still underutilized resources and have a great potential for energy production. Compared to stem wood, the stump and bark have additional drawbacks as solid fuel, related to their physical properties and appearance, as well as to higher ash/inorganic contents [21,22]. Torrefaction is a promising technology to upgrade bark and stump into high quality solid fuels with more uniform properties. Until now, the biomasses subjected to torrefaction studies have mainly been stem wood from different wood species, agricultural wastes, short rotation coppice and algae [1,13,14,16,23–29]. In comparison to previous work, very little is known about torrefaction behaviours of bark and stump from trees and the properties of their torrefied solid counterparts [22,27]. In addition, previous studies have focused on the effect of process conditions on the mass yield and energy yield of biomass upon torrefaction treatment and general properties of torrefied biomass [10,14,17,28,30]. In the literature, there are detailed studies on chemical composition analyses of untreated wood materials. However, presently, discussion of the effect of torrefaction on chemical compositions of bark and stump wood are rarely found in public available literatures.

The main objective of the present work is to study effects of torrefaction on the physiochemical properties, grinding energy consumption and chemical composition of woody biomasses including stem wood, stump and bark from Norway spruce. The results from this work will contribute to further utilization of torrefied spruce stem and stump wood as upgraded feedstocks suitable for cofiring in power plant or gasification for energy production purpose.

2. Materials and methods

2.1. Biomass materials

In the present work stem wood, stump and bark from Norway spruce (Picea abies) were investigated. The Norway spruce trees harvested in South Norway were divided into three parts including trunk (with bark), stump and tops and branches. The trunk wood was debarked to get stem wood and bark. The stem wood was cut into strips and further into cubes with sides of 1 cm. The stump was shredded into chips and those with size of 3–5 cm were subjected to further experiments. The bark was chipped into pieces and the pieces with size of 5–7 cm were used. The stem wood cubes, bark and stump chips were dried at 105 °C for 24 h for further analysis and torrefaction experiments.

As can be seen from Table 1, the stump has similar properties as those of the stem wood. The fixed carbon content of the stump is 1.3% higher than that of the stem wood. On the other hand, the bark contains as much as 23.0% fixed carbon, but also 2.1% ash. Compared to stem wood and stump, contents of inorganic elements in bark are significantly higher as shown in Table 1, the stump has similar properties as those of the stem wood.

2.2. Torrefaction experiments

The torrefaction experiments were conducted in a bench-scale tubular reactor. It includes a tubular vessel, an electrical gas preheater with a temperature controller, a condensate receiver and a gas supply system. For one torrefaction experiment, around 80 g of untreated biomass sample was first loaded into the vessel. After sample loading, the tubular vessel was closed tightly and connected with the gas supply system and the condenser. The tubular vessel was then placed inside an electrically heated furnace and the temperature in the furnace is monitored by three thermocouples located on the top, middle and bottom of the furnace. The tubular vessel is continuously purged with 1 L min⁻¹ nitrogen to eliminate presence of oxygen, thereby avoiding possible oxidation and ignition of the sample inside. The sample was heated up at a heating rate of 15 °C/min to three final temperatures (225, 275 and 300 °C). The residence time for one sample at each final temperature was 30 and 60 min, respectively. After each torrefaction experiment, the reactor was cooled down to room temperature with continuous purge of the nitrogen. The cooled torrefied biomass materials were discharged and weighted to determine the solid yield. The mass yield of one torrefaction experiment was calculated as the percentage of initially loaded pre-dried biomass sample, as follows:

\[
\text{Mass yield} = \left( \frac{m_{\text{torrefied}}}{m_{\text{un-treated}}} \right) \times 100
\]

Then the torrefied biomasses were loaded in airtight plastic bags and stored in a desiccator for further studies [10].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stem wood</th>
<th>Stump</th>
<th>Bark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile matter content (wt%, db)</td>
<td>88.12</td>
<td>86.69</td>
<td>74.85</td>
</tr>
<tr>
<td>Ash content (wt%, db)</td>
<td>0.31</td>
<td>0.41</td>
<td>2.11</td>
</tr>
<tr>
<td>Fixed carbon content (wt%, db)</td>
<td>11.57</td>
<td>12.90</td>
<td>23.04</td>
</tr>
<tr>
<td>K (mg/kg, db)</td>
<td>272</td>
<td>245</td>
<td>201</td>
</tr>
<tr>
<td>Ca (mg/kg, db)</td>
<td>1030</td>
<td>1235</td>
<td>7803</td>
</tr>
<tr>
<td>Na (mg/kg, db)</td>
<td>22</td>
<td>36</td>
<td>47</td>
</tr>
<tr>
<td>Si (mg/kg, db)</td>
<td>82</td>
<td>253</td>
<td>3602</td>
</tr>
</tbody>
</table>
2.3. Fuel characterization

The untreated and torrefied biomass were subjected to proximate analysis. The volatile matter and ash content were determined according to procedures described in ASTM Standard E872 and D1102. The fixed carbon content is calculated by difference from one hundred and the sum of volatile matter and ash content. The C, H, N and S contents were measured by employing an elemental analyzer (Eurovector EA 3000 CHNS-O Elemental Analyser). The oxygen content is calculated by difference. For each sample, the proximate and elemental analysis was repeated 3–5 times respectively and average values of these measurements are presented. The gross calorific value of ground untreated and torrefied biomasses was measured by using an adiabatic oxygen bomb calorimeter (IKA C2000 calorimeter) based on ASTM Standard D5865–03. For each measurement, around 1 g of sample was loaded in a glass crucible and combusted inside the bomb calorimeter surrounded by a water jacket. After ignition by a pure cotton thread in pure oxygen, the sample start to burn and released heat that is transferred to the water jacket causing the temperature to increase. The higher heating value of one sample was calculated based on the increase in temperature and expressed in MJ/kg. Based on the mass yields and higher heating values, relative energy density (on mass basis) and energy yield (in %) for a sample torrefied at different conditions can be calculated as follows:

\[
\text{Relative energy density} = \frac{\text{HHV}_{\text{torrefied}}}{\text{HHV}_{\text{untreated}}} \tag{2}
\]

\[
\text{Energy yield} = \text{mass yield} \times \left(\frac{\text{HHV}_{\text{torrefied}}}{\text{HHV}_{\text{untreated}}} \right) \tag{3}
\]

2.4. Chemical composition analysis

Chemical composition analysis is an efficient way to study chemical composition changes of biomass during thermal treatment. Additionally, chemical composition analysis results contribute to explain properties changes (i.e., grindability) of biomass subject to torrefaction. For untreated and torrefied biomass samples, the contents of carbohydrates were analysed according to the slightly modified method reported by Sluiter et al. [31]. The untreated and torrefied biomass samples were milled to particles smaller than 1 mm and digested by a two-step acid hydrolysis. The samples were treated with 72% H₂SO₄ for 2 h at room temperature, and then with 4% H₂SO₄ for 1 h at 121 °C. The suspensions of each digestion product were filtered and washed by distilled water through glass filter crucibles. The sugar concentrations (glucan, mannan and galactan) of the filtered supernatants were analysed with high performance liquid chromatography (HPLC) using an Agilent 1260 system with a Hi-Plex H column (Agilent, CA, USA) at 65 °C. An eluent of 5 mM H₂SO₄ was used at a flow rate of 0.5 mL min⁻¹. The solid residues remaining after washing were dried at 105 °C until reaching a constant weight. This fraction contains the acid-insoluble organics and ash. The dry solid residues were heated at 550 °C for 5 h in air to determine the content of acid-insoluble ash. The Klason lignin content was calculated by deducting the acid-insoluble ash content from the dried acid-insoluble residue content. All experimental data were determined using three replicates [10].

2.5. Grindability test

The grindability of the raw and torrefied biomass samples was assessed by grinding them in a cutting mill (IKA MF 10.1). The grinding of one sample included two stages: pre-grinding and fine grinding. In the pre-grinding stage, a known quantity of stem wood cubes and bark and stump chips with and without torrefaction treatment were fed into the cutting mill without a bottom sieve to reduce their sizes. The smaller pieces and grains produced from the pre-grinding stage were used for further fine grinding. Fine grinding of the products from the pre-grinding stage was carried out in the same cutting mill equipped with a 1 mm bottom sieve. The cutting mill motor was equipped with a circuit breaker to avoid possible motor overloading. The electricity consumed during the pre- and fine grinding stages was monitored by a digital wattmeter (Paladin 256-TWKW from Crompton Instruments), which was connected to computer for recording instantaneous power consumption every 2 s. The power consumption for an empty load was also recorded before each grinding stage with sample loaded into the mill. The empty load was subtracted from each grinding test in order to obtain the energy requirements for grinding the biomass. The specific energy consumption required for grinding was calculated by integrating the area below the instantaneous power consumption curve (watt-seconds) with respect to time required for grinding the given amount of sample. For one sample, the integrated values from both the pre-grinding and fine grinding stage were summed to obtain the total power consumption. The energy consumption required for grinding one sample is expressed per unit mass for comparison purpose. The powder samples produced in the fine grinding stage were sieved by a vibrating sieving machine (Fritsch Analysette 3 Pro) with the following mesh sizes: 1 mm, 0.5 mm, 0.3 mm, 0.2 mm, 0.1 mm and 0.063 mm. The sample particles collected from the different sieves were weighed and presented as a percentage of the initial sample mass.

2.6. PCA analysis

Principal component analysis (PCA) using Statistica 12 software (StatSoft, Inc. Tulsa, Oklahoma, USA) was employed due to the large number of samples and experimental data [32]. The main purposes of a PCA analysis are to identify patterns in data and finding patterns to decrease the data dimensionality with minimal loss of information. PCA finds a new coordinate system: it transforms the original measured variables into new uncorrelated variables called principal components (Factors). Each principal component (Factor) is a linear combination of the original measured variables. Factor 1 accounts for the maximum of total variance. Factor 2 is uncorrelated with Factor 1 and accounts for the maximum of the residual variance, and so on for additional factors. Usually two or three Factors can satisfactorily reveal the major similarities and differences between the samples. For the PCA technique, the singular vectors and singular values are calculated from the covariance (or correlation) matrix. The axis corresponding to the principal singular vector is the one along which the variance of the data is maximized. The singular vector with the highest singular value is the first principle component of the data. The axis corresponding to the second singular vector (the singular vector corresponding to the second largest singular value) is the axis along which the variance of distances from the first axis is greatest, and so on. The outcomes can be presented in score plots, which shows the samples’ location in the space of Factor 1 and Factor 2 (the two principal components). Factor loadings show the correlation between the original measured data and the Factors (principal components). In this work, PCA has been used to reveal correlations between the chemical composition data and the particle size distribution of the untreated and torrefied samples. Factor 1 and Factor 2 described 53.13% and 27.36% of the total variance respectively, and these two factors are then adequate to describe the two main differences between the studied samples.
2.7. SEM analysis

Scanning electron microscopy analysis was carried out to investigate microstructure and morphology of untreated and torrefied biomass materials. The ground untreated and torrefied biomass particles with size in the range of 0.6–1 mm and smaller than 0.063 mm were examined by scanning electron microscopy (Zessia Ultra, 55 Limited Edition). The sample particles were spread on an adhesive carbon tape fastened on a sample tab and sent into the SEM for scanning. The SEM was operated with the same parameters for particles in the same size range, which are from untreated and torrefied biomasses. Therefore, the SEM images are comparable for the sample particles in terms of size, shape and morphology.

3. Results and discussion

3.1. Torrefied biomass mass and energy yields

Table 2 shows the mass yield, energy yield, relative energy density and HHV of the torrefied samples as a function of the final temperature and residence time. Mass yields of stem wood, stump and bark decrease with increase in torrefaction temperatures as shown in Table 2. As the torrefaction temperature increased to 275 °C, there are significant mass losses for the three studied biomass materials. The mass yields of all three studied biomass materials drop continuously with further increase of torrefaction temperature to 300 °C. Compared to stem wood and bark, the stump is more sensitive to increase of the torrefaction temperature. The yields of solid dramatically declines from above 90% to 46–55% as the torrefaction temperature increase from 225 °C to 300 °C. The mass yields decrease with increase of residence time as shown in Table 2. However, torrefaction time gave less significant effect than temperature on mass yields for all experiments conducted at 225 and 275 °C. On the other hand, at the torrefaction temperature 300 °C, the mass yields of stem wood and stump were considerably affected by the increase in torrefaction time, which was reduced by about 11.1% and 9.4%, respectively, when the torrefaction time was increased from 30 to 60 min. Table 2 shows that HHV of torrefied biomass materials increased with raise in torrefaction temperature and time. The HHV values increased from 19.51–19.89 MJ kg$^{-1}$ for the untreated biomass to 23.38–24.35 MJ kg$^{-1}$ for those torrefied at 300 °C. The highest increase of HHV was observed for bark, which increase from 19.51 MJ kg$^{-1}$ to 24.35 MJ kg$^{-1}$. With increase of torrefaction temperature from 225 to 300 °C, the energy yield of the torrefied samples decreased from 93.05% to 55.63% as shown in Table 2. Although torrefaction under severe conditions produces torrefied biomass with higher HHV, a large amount of energy was lost due to loss of sample mass upon torrefaction, explaining the decrease of the energy yield shown in Table 2. The relative energy density of torrefied stem wood, bark and stump was enhanced with increase of torrefaction temperature and time.

3.2. Characterization of untreated and torrefied biomass as solid fuel

Table 3 shows a summary of proximate and ultimate analyses of the untreated and torrefied biomass samples. The volatile matter content of the torrefied biomasses decrease with increase of torrefaction temperature and residence time. At a temperature of 225 °C, the volatile matter content of all torrefied biomasses slightly decreased, while significant reduction was observed at temperatures of 275 °C and 300 °C. The ash content of the torrefied biomasses increased due to loss of organic matter during torrefaction. Similar changes of proximate analysis results were also found in studies on torrefied pine, birch, logging residues and other woody biomass species [10,27–30,33].

As shown in Table 3 the elemental composition of the torrefied biomasses also change as a function of torrefaction severity. As the torrefaction temperature increases from 225 °C to 300 °C, the elemental carbon content of the stem wood increased from 50.1% to 64.2%, whereas the elemental hydrogen content decreased from 6.1% to 5.5%. Moreover, more pronounced increases of elemental carbon and reduction of elemental hydrogen content were observed from the torrefied bark. Changes in elemental composition of the torrefied biomass are illustrated in a Van Krevelen diagram in Fig. 1. Both atomic H/C and O/C ratios decrease with increase of torrefaction severity. The torrefied bark had generally smaller H/C and O/C ratios compared to those of torrefied stem wood and stump. A similar decreasing of atomic H/C and O/C ratios of torrefied biomasses have been reported in previous studies [17,23,28,33]. During torrefaction, conversion of biomass is mainly associated with dehydration, decarboxylation and depolymerisation of the organic portion of the biomass, resulting in loss of water and release of gases and light volatiles [5]. Therefore, during
torrefaction, the biomass loses relatively more oxygen and hydrogen compared to carbon. Due to change of content of elemental carbon, hydrogen, and oxygen, the heating value of the torrefied biomass increase consequently, as shown in Table 2.

3.3. Compositional analysis of raw and torrefied samples

Compositional analysis of raw and torrefied biomass samples was carried out to follow the decomposition of the lignocellulose polymeric components and understand the conversion behaviour of the samples during torrefaction. The results are presented in Fig. 2. The Klason lignin contains the acid insoluble residue of the samples without the acid insoluble ash. The glucan content of the samples mostly characterizes the cellulose fraction of the biomass, whereas the sum of the mannan and galactan content represents the hemicellulose fraction of the samples. The fraction named “Other” represents all undetermined components such as extractives, acid soluble lignin and acid soluble minerals. To provide a comprehensive comparison of the raw and treated samples, the weight loss of the torrefied samples during torrefaction is presented in Fig. 2. As shown in Fig. 2, untreated bark has the highest Klason lignin content (40.8%). The untreated stump has the highest hemicellulose content (23.4%), while the untreated stem wood has the highest cellulose content (42.5%). The lignocellulose content (sum of lignin, cellulose and hemicellulose) of the untreated stem wood is 89.9%, while that of the untreated stump and bark is 80.5% and 77.9%, respectively. The reason for the relatively lower lignocellulose content of stump and bark could be their higher extractives, acid soluble lignin and acid soluble mineral content.

The alkali contents of the raw samples have been determined using ICP-OES (Table 1). The raw stem wood and stump contain around 250–300 mg/kg potassium and around 1000 mg/kg calcium, while both the potassium and calcium content of the raw bark is about seven times higher than that of the stem wood and stump. During torrefaction, lignocellulosic materials decompose to different degrees upon torrefaction severity [34,35]. The decrease of both glucan and the sum of mannan and galactan reflects decomposition of cellulose and hemicellulose in the

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>VM (%, db)</th>
<th>Ash (%, db)</th>
<th>FC (%, db)</th>
<th>C (% daf)</th>
<th>H (% daf)</th>
<th>N (% daf)</th>
<th>S (% daf)</th>
<th>O (% daf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated stem wood</td>
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<td>11.57</td>
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<td>225 °C-30 min</td>
<td>87.90</td>
<td>0.33</td>
<td>11.77</td>
<td>50.06</td>
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<td>225 °C-60 min</td>
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<td>14.19</td>
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<td>21.07</td>
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<td>5.98</td>
<td>0.07</td>
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<tr>
<td>275 °C-60 min</td>
<td>74.36</td>
<td>0.42</td>
<td>25.22</td>
<td>55.14</td>
<td>5.87</td>
<td>0.08</td>
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<tr>
<td>300 °C-30 min</td>
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<td>36.65</td>
<td>62.17</td>
<td>5.72</td>
<td>0.14</td>
<td>0.01</td>
<td>31.96</td>
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<td>300 °C-60 min</td>
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<td>0.16</td>
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<td>86.69</td>
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<td>2.38</td>
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<tr>
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<td>4.13</td>
<td>47.93</td>
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<td>3.25</td>
<td>0.71</td>
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As Fig. 2 shows, hemicellulose (measured as the sum of mannose and galactose) is the least thermally stable component of the studied biomass samples during torrefaction. About 20% of the hemicellulose content of the samples decompose up to 225 °C for each of the studied samples. After torrefaction at 275 °C, the relative amount of the hemicellulose in the bark samples drastically decreases, while stem wood and stump have about one fifth of the hemicellulose content of the raw sample. The hemicellulose content of them further decrease and only a minor fraction was measured for samples torrefied at 300 °C. The bar diagram also shows that the content of cellulose - indicated by the content of glucan - does not decrease evidently at the torrefaction temperature 275 °C for stem wood and stump, while a significant decrease (more than 80%) is observed for bark at this temperature. At 300 °C torrefaction temperature, the residence time has a significant effect on the cellulose decomposition. After torrefaction at 300 °C for 30 and 60 min the cellulose content of the stump sample decreased to 48 and 21% of the cellulose content of the raw material, respectively, whereas that of steam wood decreased to only 20 and 11%, respectively. These observations may point to that the thermal stability of cellulose in the bark sample is lower compared to the stem wood and stump samples. The bark sample has more than an order of magnitude higher alkali content than stem wood and stump (Table 1). The alkali metals are known to exert a great influence on the thermal decomposition of cellulose [22,35–37]. The change in the chemical compositions of the studied samples confirmed that the alkali metals have catalytic effects on the cellulose decomposition during thermal treatment in this temperature range. As the bar diagram presents, the Klason lignin content of the torrefied samples increase considerably with increasing torrefaction temperatures. The Klason lignin contains all acid insoluble components of the sample, excluding ash. During torrefaction, certain fractions of the polysaccharides, acid soluble lignin and extractives were probably transformed into acid insoluble carbonateous products by cross-linking and charring reactions [12,22]. The increasing torrefaction temperature support these reactions, resulting in the greater amount of Klason lignin content at higher temperatures.

**3.4. Effect of torrefaction on grindability**

Fig. 3 shows the total energy required for grinding the raw and torrefied biomass samples, which includes energy consumed for both the pre-grinding and fine grinding steps. For stem wood and stump, the energy required for grinding the samples was reduced significantly as a result of torrefaction treatment. Compared to raw stem wood and stump, only about half of the energy is needed for grinding the stem wood and stump torrefied at 225 °C. This trend is in good agreement with those reported in literatures for the grinding of stem wood and stump wood [14,19,28]. It indicates that significant energy savings associated with size reduction can be achieved by torrefying stem wood and stump, even at a mild torrefaction condition. In the present work, the same amount, 25 g, of raw and torrefied biomass samples were subjected to grinding tests. The time used for grinding torrefied biomass samples were evidently reduced compared to those for raw biomasses. The time used for finishing pre and fine grinding of stem wood cubes were 389 s in total, which decreased to 146 and 58 s for grinding the same weight of stem wood cubes torrefied at 225 and 300 °C degrees with 60 min holding time, respectively. Reduced grinding times for torrefied stump wood and bark were also observed. The change of energy and time required for grinding untreated and torrefied biomasses can be linked to decomposition of polymeric components of the studied biomasses during torrefaction. For a woody plant, the plant cell wall is a tough layer protecting the plant structure against mechanical stress [12]. In the cell wall, the cellulose microfibers and macrofibrils are linked or embedded in a matrix of disoriented hemicellulose to form a cellulose-hemicellulose network [5,38]. The cell wall with such a microstructure provides high strength and tenacity, making the plant mechanically strong [1]. Therefore, the wood has anisotropic and fibrous nature, which makes grinding of wood energy intensive and makes it difficult to obtain fine particles. During torrefaction, continuous decomposition of hemicellulose causes weakening and destruction of the highly interlinked cellulose-hemicellulose matrix which no longer is capable to support the cellulose fibres [12]. At a high enough torrefaction temperature, both hemicellulose and cellulose decompose more intensively into volatiles and char-like brittle solid [37]. This results in loss of tenacity and mechanical strength of cell walls and wood structure consequently. Hence, the energy requirement for grinding torrefied wood into small particles is significantly reduced. As shown in Fig. 2, both the hemicellulose and cellulose content in the stem and stump wood considerably decreases with increase of torrefaction severity. It partially explains the reduction of the energy requirements for grinding the torrefied stem wood and stump.

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Compared to stem wood and stump, much less energy is needed for grinding the untreated bark. In addition, the torrefaction treatment has minor effects on the energy consumption for grinding bark, although that of the hemicellulose and cellulose were considerably reduced. It might be due to differences in content and nature of lignocellulose compositions (hemicellulose, cellulose and lignin) and the integrated structure of the compositions of the bark compared to the stem wood and stump. Similar differences in grindability have been observed for coniferous and deciduous wood [12]. Torrefied coniferous wood predominately consisting of mannan-based hemicellulose has poorer grindability compared to deciduous wood mainly consisting of xylan-based hemicellulose [33].

Fig. 4 shows the effect of torrefaction severity on size distribution of particles passing varying sieves with different cut-sizes. In general, torrefaction temperature and residence time have considerable influences on percent of particles in the various size ranges. It can be seen that 42 wt% and 25 wt% of respectively ground untreated stem wood and stump are large particles in the size range of 0.5–1 mm. After torrefaction at 225 °C, the amount of particles with such size significantly decreased to 18–20 wt% and 10–12 wt%, respectively. With further increase of torrefaction severity, the percent of particles in same size range further decrease and only a small amount was obtained as the stem wood and stump were torrefied at 300 °C. In addition, the amount of particles with smaller sizes was also significantly increased for stem wood and stump torrefied at a higher temperature. In comparison, increasing the torrefaction residence time gave only a slight increase in the amount of particles with smaller sizes. As shown in Fig. 4, the particle size distribution of untreated and torrefied bark are quite different from those of stem wood and stump. For the untreated bark, the percentage of large particles (0.5 mm < d < 1 mm) is small, in comparison to stem wood and stump. The major fraction of the untreated bark particles has a size in the range of 0.3 mm < d < 0.5 mm, which decreases evidently after torrefaction treatment. Moreover, the percentage of fine bark particles
(d < 0.063 mm) increases considerably upon the increase of torrefaction temperature. Fig. 5 shows cumulative particle size distribution curves of ground untreated and torrefied biomass samples. The particle size distribution curves clearly shift towards smaller particles. Similar changes of particle size distribution of ground biomass have been reported in other studies [10,21]. As mentioned already, torrefaction of biomass causes decomposition of hemicellulose and breakdown of the hemicellulose-cellulose interlinked matrix. It makes grinding of torrefied wood much easier with production of more small particles.

3.5. PCA calculation based on chemical composition and particle size distribution as a function of torrefaction severity

Principal component analysis (PCA) has been applied to illustrate statistical correlations between the chemical composition data (Fig. 2) as well as the particle size distribution (Fig. 4) of the ground raw and torrefied samples. In the PCA calculation, the first principal component (Factor 1) described 53.13% of the total variance and the second component (Factor 2) described 27.36% of the total variance, these two factors are adequate to characterize the major differences between the studied samples. In the score plot (Fig. 6a) it can be seen that the behaviour of the bark samples during torrefaction clearly differ from the stem wood and stump samples. Factor 1 differentiates the raw, the mildly and the severely torrefied samples. As a function of the Factor 2, the stem wood and stump samples are found in the upper, and the bark samples in the lower part of the score plot. This difference is probably due to the different cellulose, hemicellulose, lignin, and extractive content of the samples; which is reflected in the different particle size distribution of the ground samples.

The loading plot (Fig. 6b) shows that the values of glucan, sum of mannans and galactans content and the “Other” part of the chemical composition (which contains extractives, acid soluble lignin and acid soluble minerals) correlate negatively with the mass loss and the Klason lignin content of the samples. Factor 1 is composed of mainly these parameters and mostly separates the samples as a function of the torrefaction severity. Particle size distribution data is reflected mainly in Factor 2. The raw bark has significantly higher extractives and Klason lignin content than that of the raw stem wood and stump, which may contribute to the different particle size distribution of the raw samples. For the raw bark, the percentage of fine particles (d < 0.1 mm) and large particles (0.5 mm < d < 1 mm) are quite small, however the percentage of medium size particles (0.2 mm < d < 0.5 mm) is rather large, in comparison to raw stem wood and stump. During torrefaction, the moisture content releases and the extractives and carbohydrate content of the samples degrade, therefore the torrefied samples become more brittle. Comparing the particle size distribution of the ground raw and torrefied samples we can conclude, that by applying more severe torrefaction before the grinding, the obtained particle size distribution of the stem wood, stump and bark sample become similar. The decreasing distance of bark samples from stem wood and stump samples on the score plot visualize this correlation.

3.6. SEM analysis

Scanning electron microscopy was used to investigate microstructure and morphology of untreated and torrefied stem wood, stump and bark. As shown in Fig. 4, the amount of ground stem wood and stump particles with size in the range 0.5 mm < d < 1 mm and d < 0.063 mm were changed substantially at torrefaction temperatures of 225 and 300 °C. Therefore, ground stem wood and stump particles in the two size ranges were examined by SEM. For comparison purpose, the ground bark particles in the same size range were studied.

Figs. 7–9 show SEM images of untreated and torrefied stem wood, stump and bark particles in the size range of
Fig. 6. Result of the principal component analysis based on the chemical composition and the particle size distribution data: (a) score plot and (b) loading plot. Score plot shows the studied samples in the space defined by the Factors. Factor loading denotes the correlation between original variables and the Factors. The arrows present the direction of the variation of the studied samples with increasing torrefaction temperature and residence time. SW, stem wood; ST, stump; B, bark; SW_U, untreated stem wood; SW_225_30, torrefied stem wood at 225 °C for 30 min.

Fig. 7. SEM images of the ground particles (0.5 mm < d < 1 mm) from stem wood (a) untreated, (b) torrefied at 225 °C with 60 min and (c) torrefied at 300 °C with 60 min.

Fig. 8. SEM images of the ground particles (0.5 mm < d < 1 mm) from stump (a) untreated, (b) torrefied at 225 °C with 60 min and (c) torrefied at 300 °C with 60 min.

Fig. 9. SEM images of the ground particles (0.5 mm < d < 1 mm) from bark (a) untreated, (b) torrefied at 225 °C with 60 min and (c) torrefied at 300 °C with 60 min.

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0.5 mm < d < 1 mm. For the untreated stem wood, it contains a mixture of large and long particles and thin fibres as shown in Fig. 7a. One should note that it is the particle diameter (shortest dimension) that determines whether a particle can pass through a sieve with a certain cut-size. Fig. 7b displays that there is no evident change of particle diameters at a torrefaction temperature of 225 °C, but the particle lengths are reduced significantly compared to untreated stem wood particles shown in Fig. 7a. It means that more particles with smaller length-to-diameter ratios can pass through a sieve, explaining the percentage reduction of large particles displayed in Fig. 4. Additionally, with reduction of the length-to-diameter ratio, torrefied stem wood particles become more spherical, which can consequently improve fluidisation behaviours and conversion efficiency [12]. In the plant cell wall, the oriented cellulose fibres are interlinked and bond by disoriented hemicellulose chains to form a hemicellulose-cellulose matrix [12]. The combination of orientation of cellulose fibres and their length is a main cause why the major fraction of ground woody biomass are particles with needle shape and high length-to-diameter ratio. During torrefaction, decomposition and depolymerisation of cellulose in the stem wood resulted in decrease of cellulose fibres and length of ground particles consequently. Fig. 6c shows that, after torrefaction at 300 °C, the ground stem wood particles are more porous with massive pores and some open tubular structure. The later one is mainly due to decarbonisation and destruction of lignin. The porous structure of the stem wood torrefied at 300 °C (Figs. 3 and 4) allows for the better grindability and lower energy consumption. Figs. 8 and 9 show that untreated stump and bark have different microstructure and morphology than stem wood. Almost no thin fibres can be observed from Fig. 8a and Fig. 9a. In addition, it can be seen that the length-to-diameter ratios of the particles shown in the images are not large. It explains why rather small amounts of particles in this size range (0.5 mm < d < 1 mm) were obtained from sieving tests, in comparison to results from stem wood. Fig. 8c displays that stump has porous structure with many pores and tubular openings. For the bark, increasing torrefaction severity caused a number of openings and fissures on the surface, which can be explained by the decomposition of polymeric compositions and volatilisation of gas products. The porosity is most visible for the torrefied bark at 300 °C and 60 min holding time, i.e. the most severe torrefaction condition.

Figs. 10–12 show SEM images of untreated and torrefied stem wood, stump and bark particles in the size range of d < 0.063 mm. It is clearly seen that untreated wood has a fibrous structure with large length-to-diameter ratios. After torrefaction, more isolated particles are observed and no fibres can be seen. As reported in other studies, presence of the fibres can cause linking and agglomeration of fine wood particles, which are also more difficult to pass through the sieve openings [14]. It partially explains that only a small amount of particles with size less than 0.063 mm were obtained from the sieving test. On the other hand, particles from torrefied stem wood have much more smooth and clean surfaces, compared to those from untreated stem wood. Additionally, more particles with smaller length-to-diameter ratios can be observed in Fig. 10b and 10c. Hence, the evident increase of fine particles shown in Fig. 4 can be explained by reduction of fibres and particle length-to-diameter ratios. Fig. 11 shows that small untreated stump particles have similar structure as the stem wood, but with less fibres. With increase of torrefaction severity, more particles with shorter length were produced as shown in Fig. 11c. The small untreated bark particles have considerably smaller sizes and more spherical shape compared to stem wood and stump. Compared to ground particles from bark torrefied at 225 °C (Fig. 12b), much more smaller particles can be observed (Fig. 12c). It agrees well with the significant increase of the amount of the small particles obtained from the sieving test (Fig. 4). In brief, SEM analysis revealed that ground raw stem wood and stump contain a particles mixture of bulky particles with xylem tissues and thin fibres. Upon torrefaction, stem wood and stump...
particles lose their characteristic fibrous structure and become more spherical. Particles with the appearance of thin fibres were hardly found in the ground torrefied stem wood and stump.

4. Conclusions

Torrefaction of Norway spruce stem wood, bark and stump significantly improve heating value compared to that of untreated biomasses. The hemicellulose and cellulose contents of the torrefied biomass samples decreased with increase of torrefaction temperature and residence time, with increase of the lignin content accordingly. For the stem wood and stump torrefied at 225 °C, only approximately half of the grinding energy was needed compared to grinding the dried raw feedstocks. In addition, the coarse particles with sizes in the range of 0.5–1 mm were completely removed after grinding when the stem wood and stump were torrefied at 275 °C. Much less energy was required for grinding bark, and torrefaction did not affect the grinding energy requirement significantly. The SEM analyses revealed changes of morphological structures of the studied biomass samples before and after torrefaction. For the stem wood and stump, fibres and particles with large length-to-diameter ratios were substantially reduced after torrefaction at increasing temperatures. For the particles from biomass samples torrefied at 300 °C, they generally have more porous structure with observation of pores and tubular openings on the surface. From the results of this work, it can be concluded that a mild torrefaction can considerably improve physiochemical properties and grindability of spruce stem wood and stump as solid fuel. Therefore, the utilization and conversion of them for energy production can be improved markedly.

Acknowledgements

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IV.
Effect of Temperature and Duration of Torrefaction on the Thermal Behavior of Stem Wood, Bark, and Stump of Spruce

E. Barta-Rajnai, L. Wang, Z. Sebestyén, Zs. Bartá, R. Khalil, Ø. Skreiberg, M. Grønli, E. Jakab, Z. Czégény*

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 minutes isothermal periods. The untreated and torrefied biomass materials were characterized by thermogravimetric analysis (TGA). The TGA results are interpreted in terms of the chemical composition determined by the cellulose, hemicellulose and Kason lignin content. The alkali ion contents of the samples were measured by 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.

Keywords: torrefaction; thermogravimetry, spruce, cellulose, hemicellulose, lignin

1. Introduction

Lignocellulosic biomass is one of the most important renewable energy resources; however, in energetic applications the raw material has several disadvantages, such as the high oxygen content, low calorific value, low energy density, hydrophilic nature and high moisture content.

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Torrefaction is a promising mild thermal pretreatment method between 200 and 300 °C in an inert atmosphere for improving the mentioned disadvantages of lignocellulosic biomass [1]. The purpose of the pretreatment from a chemical point of view is the removal of water and the acidic groups of hemicelluloses or the whole hemicellulose fraction with minor degradation of cellulose and lignin in the biomass [2]. In order to maximize the effectiveness of the energy extraction, we need to characterize the biomass materials as much as possible.

The Norwegian national energy strategy has a goal of reducing Norway’s greenhouse gas emissions by 30% before 2020 and by nearly 100% before 2050 [3]. This strategy indicates that the bioenergy utilization is going to increase over the next few years. Norway has considerable forest resources (more than 40% of the land is covered by forest) and the standing forest volume is increasing. Stem wood is the main harvesting product while the other parts of the tree (including bark and stump) are considered as by-products. These forest residues represent an abundant and underutilized source of renewable energy. Norway spruce is the most abundant wood species in Norway and in the Northern hemisphere. Many studies have been carried out on the thermal characteristics of Norway spruce stem wood [4-5], however only a few articles are available on the thermal decomposition of its bark and stump [6-7]. As a consequence of the difference in the relative amounts of cellulose, hemicellulose, lignin, extractives, and inorganic materials, the different parts of the tree are expected to behave differently during thermal decomposition. In this work, thermogravimetric (TGA) measurements and compositional analyses have been carried out to compare the thermal behavior of untreated and torrefied Norway spruce stem wood, bark, and stump.

2. Materials and Methods

Different parts of a representative single Norway spruce (Picea abies) tree were selected for the torrefaction study, namely: stem wood, bark, and stump. The samples originated from a Norway spruce forest in South Norway. After harvested, the trees were divided into three parts including trunk, stump, and forest residues. The trunk was further debarked to obtain stem wood and bark. The stem wood was first cut to strips, then further chopped into cubes with size of 1 x 1cm. The bark was chipped into pieces and those with length of around 5-7 cm were used for the torrefaction experiments. The stump was shredded into pieces and the pieces with size of 3-5 cm were torrefied.

The torrefaction experiments were carried out in a tube reactor placed in an electrical furnace in nitrogen atmosphere using flow rates of 1 l min⁻¹. About 80 g samples were treated in the tube reactor at 225 °C, 275 °C and 300 °C temperatures using 30 and 60 minutes isothermal periods. For further experiments the untreated and torrefied samples were ground by a cutting mill to <1 mm particle size.

The higher heating value was determined using an automatic IKA C 5000 bomb calorimeter. The combustion of about 0.5 g dried sample was performed in pure oxygen atmosphere under 30 bar pressure. The heat capacity of the calorimeter system was determined by benzoic acid calibration.

The amounts of the ashes have been determined using a CEN/TS 14775 EU standard method. The calcium, potassium, sodium and silicon contents of the ashes were determined by a Spectro Genesis ICP-OES (Spectro Analytical Instruments) with axial plasma observation.
The contents of carbohydrates were determined according to the method of Sluiter et al. [8] applying slight modifications. The untreated and torrefied biomass samples were treated in a two-step acid hydrolysis. The obtained suspensions were filtered and washed, then the sugar concentrations (glucose, mannose and galactose) of the filtered supernatants were analyzed with high performance liquid chromatography (HPLC). All experimental data were determined using three replicates.

The thermogravimetric analyses were performed using a modified Perkin-Elmer TGS-2 thermobalance. About 5 mg samples were measured in argon atmosphere at a flow rate of 140 mL min\(^{-1}\). The samples were flushed for 45 minutes by the carrier gas before the experiments to achieve an inert atmosphere. The samples were heated in a platinum sample pan at a rate of 20 °C min\(^{-1}\) from 25 to 950 °C.

3. Results and Discussion

3.1 Comparison of the three untreated samples

Table 1 summarizes the higher heating value, the ash content and selected data of the ICP-OES characterization of the untreated samples. As the results illustrate, the energy contents of the samples are rather similar, while the bark sample has significantly higher ash content than the two other samples. The bark sample has an order of magnitude higher K\(^+\) and Si content than stem wood and stump. Furthermore, the Na\(^+\) and Ca\(^{2+}\) contents of the bark sample are also higher compared to the other two samples.

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<tbody>
<tr>
<td>Higher heating value (MJ/kg, db(^{\text{a}}))</td>
<td>19.78</td>
<td>20.14</td>
<td>18.57</td>
</tr>
<tr>
<td>Ash content (% m/m, ar(^{\text{b}}))</td>
<td>0.31</td>
<td>2.43</td>
<td>0.43</td>
</tr>
<tr>
<td>Ca(^{2+}) (ppm, db(^{\text{a}}))</td>
<td>1030</td>
<td>7803</td>
<td>1235</td>
</tr>
<tr>
<td>K(^+) (ppm, db(^{\text{a}}))</td>
<td>272</td>
<td>2011</td>
<td>245</td>
</tr>
<tr>
<td>Na(^+) (ppm, db(^{\text{a}}))</td>
<td>22</td>
<td>47</td>
<td>36</td>
</tr>
<tr>
<td>Si (ppm, db(^{\text{a}}))</td>
<td>82</td>
<td>3602</td>
<td>253</td>
</tr>
</tbody>
</table>

\(^{\text{a}}\)dry basis, \(^{\text{b}}\)as received

Fig. 1a shows the chemical composition of the three untreated samples. The sum of the mannan and galactan content represents the hemicellulose fraction, whereas the glucan content of the samples mainly characterizes the cellulose fraction of biomass. The Klasen lignin content is defined as the acid insoluble residue of the samples without the acid insoluble ash. Besides the acid insoluble lignin, the Klasen lignin contains all acid insoluble components of the sample excluding ash. The fraction denoted by Other represents the sum of unquantified components and includes extractives, acid soluble lignin and acid soluble minerals. As Fig. 1a shows, the bark sample has the highest amount of Klasen lignin, stem wood has the highest cellulose and stump has the highest hemicellulose content. The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the untreated samples are shown in Fig. 1b. The main DTG peak is dominated by the decomposition of cellulose, while the shoulder at lower temperature (around 320 °C) can be attributed mainly to hemicellulose decomposition. The lignin decomposes at a lower rate in a wide temperature range (200–600 °C). The evaporation and decomposition reactions of extractives start at lower temperatures and it is visible as a shoulder on the main DTG peak from approximately 160 °C.
The comparison of the three untreated samples shows that bark releases the most extracts at the low temperature range. The untreated stump has the most characteristic hemicellulose shoulder which is in agreement with the chemical composition results showing that stump has the highest hemicellulose content. The decomposition of bark starts at a lower temperature, the DTG peak maximum occurs at a lower temperature, and the maximum rate of decomposition is considerably smaller than in case of the stem wood and stump. The high lignin content (41%) of bark results in the formation of a high amount of char during thermal decomposition. The different thermal behavior of the different untreated samples can be explained by their different composition as well as by the fact that alkali ions have catalytic effect on the decomposition mechanism of cellulose [9-10] and the charring reactions of lignin [11].

Fig. 1. (a) Composition of untreated bark, stem wood, and stump. (b) TG and DTG curves of untreated bark, stem wood, and stump.

3.2 Effect of torrefaction temperature and residence time

During torrefaction the lignocellulose materials decompose to different degrees depending on the applied temperature and residence time. Fig. 2 shows the TG and DTG curves of the various torrefied bark, stem wood, and stump. The compositional analysis of the torrefied biomass samples (Table 2) was also performed in order to understand better the thermochemical conversion process during torrefaction. As the mannan and galactan content demonstrates in Table 2, the sugar units of hemicellulose did not degrade during torrefaction at 225 °C. However, the characteristic hemicellulose shoulder of the DTG curves decreased revealing the structural change as a result of the torrefaction. These results indicate that the side groups of hemicellulose were partially split off, while the main hemicellulose content did not degrade at 225 °C. As the results (Table 2, Fig. 2) show, the cellulose content of stem wood and stump did not reduce considerably up to 275°C, while the degradation of cellulose in the bark sample was significant at this temperature. At 300 °C, only trace amounts of cellulose were found, and the cellulose content of stem wood and stump strongly decreased. As it was mentioned above, the presence of alkali ions modified the thermal degradation of cellulose [9-10] and lignin [11]. The reason of the promoted decomposition rate of bark during torrefaction is most probably the catalyzed decomposition of its cellulose content. As Fig. 2 shows, the residence time had no significant effect on the composition of the torrefied samples up to 275°C, while at 300 °C the duration of torrefaction had substantial effect due to the severe decomposition of cellulose at this temperature.
Table 2. Solid yields of torrefaction and composition of the untreated and torrefied bark, stem wood, and stump (dry basis). Standard deviations are calculated from triplicates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>Solid yield (%)</th>
<th>Glucan (%)</th>
<th>Mannan + Galactan (%)</th>
<th>Klason lignin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bark</td>
<td>Untreated</td>
<td>100</td>
<td>27.47 ± 0.7</td>
<td>9.68 ± 0.2</td>
<td>40.79 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>225°C, 30 min</td>
<td>90</td>
<td>28.38 ± 0.2</td>
<td>9.77 ± 0.2</td>
<td>49.61 ± 1.3</td>
</tr>
<tr>
<td></td>
<td>225°C, 60 min</td>
<td>82</td>
<td>24.35 ± 0.6</td>
<td>8.75 ± 0.1</td>
<td>56.69 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>275°C, 30 min</td>
<td>73</td>
<td>12.26 ± 0.7</td>
<td>1.80 ± 0.1</td>
<td>78.84 ± 1.4</td>
</tr>
<tr>
<td></td>
<td>275°C, 60 min</td>
<td>69</td>
<td>7.69 ± 0.3</td>
<td>0.81 ± 0.0</td>
<td>85.99 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>300°C, 30 min</td>
<td>63</td>
<td>2.68 ± 0.1</td>
<td>0.26 ± 0.0</td>
<td>90.04 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>300°C, 60 min</td>
<td>61</td>
<td>1.52 ± 0.1</td>
<td>0.14 ± 0.0</td>
<td>91.98 ± 0.4</td>
</tr>
<tr>
<td>Stem wood</td>
<td>Untreated</td>
<td>100</td>
<td>42.54 ± 0.9</td>
<td>18.26 ± 0.5</td>
<td>30.06 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>225°C, 30 min</td>
<td>92</td>
<td>44.74 ± 1.3</td>
<td>17.07 ± 0.4</td>
<td>31.73 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>225°C, 60 min</td>
<td>91</td>
<td>43.53 ± 0.9</td>
<td>16.59 ± 0.0</td>
<td>31.17 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>275°C, 30 min</td>
<td>79</td>
<td>45.64 ± 0.9</td>
<td>6.23 ± 0.3</td>
<td>42.69 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>275°C, 60 min</td>
<td>76</td>
<td>42.21 ± 1.4</td>
<td>4.74 ± 0.2</td>
<td>47.78 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>300°C, 30 min</td>
<td>70</td>
<td>12.80 ± 0.4</td>
<td>1.44 ± 0.1</td>
<td>80.16 ± 1.5</td>
</tr>
<tr>
<td></td>
<td>300°C, 60 min</td>
<td>58</td>
<td>8.26 ± 0.3</td>
<td>0.75 ± 0.0</td>
<td>87.27 ± 1.4</td>
</tr>
<tr>
<td>Stump</td>
<td>Untreated</td>
<td>100</td>
<td>29.80 ± 0.3</td>
<td>22.97 ± 0.3</td>
<td>27.68 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>225°C, 30 min</td>
<td>93</td>
<td>28.21 ± 1.8</td>
<td>21.45 ± 0.4</td>
<td>34.30 ± 2.0</td>
</tr>
<tr>
<td></td>
<td>225°C, 60 min</td>
<td>90</td>
<td>28.93 ± 1.3</td>
<td>20.92 ± 2.3</td>
<td>37.73 ± 2.4</td>
</tr>
<tr>
<td></td>
<td>275°C, 30 min</td>
<td>72</td>
<td>29.69 ± 0.4</td>
<td>4.91 ± 0.2</td>
<td>57.18 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>275°C, 60 min</td>
<td>70</td>
<td>28.97 ± 0.4</td>
<td>4.61 ± 0.2</td>
<td>59.57 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>300°C, 30 min</td>
<td>56</td>
<td>25.64 ± 0.6</td>
<td>1.13 ± 0.0</td>
<td>68.58 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>300°C, 60 min</td>
<td>46</td>
<td>13.67 ± 0.5</td>
<td>0.41 ± 0.0</td>
<td>82.31 ± 0.5</td>
</tr>
</tbody>
</table>

Fig. 2. TG and DTG curves of bark, stem wood, and stump after various torrefaction treatments
4. Conclusion

Untreated and torrefied stem wood, bark, and stump of Norway spruce were characterized and their thermal properties and chemical compositions were compared. It was found that the hemicellulose chain of each sample was thermally stable during torrefaction at 225°C; however, it degraded to a great extent at 275 °C as indicated by the chemical analysis. Significant decomposition of cellulose started only in bark sample at 275°C torrefaction temperature, which can be explained by the high alkali ion content of bark. The duration of torrefaction (30 vs. 60 min) did not have significant influence up to 275°C on the thermal behavior of the samples. At 300°C the residence time had a significant effect on the composition of the torrefied samples due to the intensive decomposition of cellulose.

Acknowledgements

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References


Biography

Eszter Barta-Rajnai is a PhD student in the Research Centre for Natural Sciences of the Hungarian Academy of Sciences. Her researches focus on the characterization of biomass materials using thermal analysis and analytical pyrolysis.
Impact of Torrefaction on Woody Biomass Properties

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Abstract

In this work, Norway spruce stem wood, stump and bark were torrefied in a tubular reactor. The effects of feedstock type and torrefaction process parameters such as torrefaction temperature and residence time on the grindability and chemical properties of the torrefied biomass samples were investigated. In comparison to torrefaction temperature, torrefaction residence time had smaller effects on the grindability of stem wood and stump. For raw bark, much less grinding energy is required compared to those for raw stem wood and stump. Torrefaction has minor effects on grindability of the bark. The cellulose contents of stem wood and stump were reduced slightly at a torrefaction temperature of 275 °C. On the contrary, the cellulose content of the torrefied bark drastically decreased already at a torrefaction temperature of 275 °C, with only trace amounts left in the 300 °C torrefied products.

1. Introduction

Faster development of bioenergy has been hindered by drawbacks of biomass properties, including low bulk density, poor grindability, high moisture content and relatively low calorific value. Torrefaction is an efficient way to upgrade biomass into high quality solid fuel [1]. Torrefaction is usually conducted in inert atmosphere in a temperature range from 200 to 300 °C, driving out the moisture, and parts of the volatile organic compounds in the biomass [2,3]. Torrefied biomass retains most of its chemical energy and can be grinded easily in comparison to the raw biomass. In addition, torrefied biomass has increased uniformity with respect to product quality in terms of physical and chemical properties [4].

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The Norwegian government has a goal to reduce the greenhouse gas emissions by 30% by 2020 according to _World Energy Outlook_ 2009 [5]. Bioenergy will play a significant role in meeting this goal. Norway has abundant forest resources and more than 40% of the land is covered by forest [1]. Biomass materials from the forest has a great potential to provide suitable feedstocks for bioenergy production. Stem wood is normally the main product of forest harvesting with harvesting or thinning residues such as tops and branches and stump wood as waste streams usually left behind in the forest, while bark is a waste product in the pulp and paper and sawmill industries. The tops and branches and stump wood represent a large bioenergy potential and is an underutilized resource for energy production, while the bark usually is burnt to produce heat in the mentioned industries. It has been reported that stump constitute 22-24% of the stem volume of a mature conifer tree, i.e. representing a very significant bioenergy potential [6].

Until now, the raw biomasses subjected to torrefaction studies have mainly been stem wood from different wood species, agricultural wastes and short rotation coppice [6]. Only a few studies have been carried out to investigate torrefaction behaviors of tops and branches, bark and stump and their properties after torrefaction treatment [2,3,6]. In addition, the studies have focused on the effect of process conditions on the mass loss of biomass and the properties of torrefied biomass for further thermal conversion applications. Less attention has been paid to the change of chemical composition and grindability of biomass upon torrefaction treatment.

The objective of the present work was to study the effects of torrefaction on the chemical composition and grindability characteristics of woody biomasses including stem wood, bark and stump from Norway spruce.

2. Materials and Methods

2.1 Raw biomass

In the present work stem wood, bark and stump from Norway spruce (_Picea abies_) were investigated. The Norway spruce trees harvested in South Norway were divided into three parts including trunk (with bark), stump and tops and branches. The tops and branches were not studied in this work. The trunk wood was debarked to get stem wood and bark. The stem wood was cut into strips and further into cubes with sides of 1 cm. The stump was shredded into chips and those with size of 3-5 cm were subjected to further experiments. The bark was chipped into pieces and the pieces with size of 5-7 cm were used. The stem wood cubes, bark and stump chips were dried at 105 °C for 24 hours for further analysis and torrefaction experiments.

2.2 Torrefaction experiments

The torrefaction experiments were conducted in a bench-scale tubular reactor. It includes a tubular vessel, an electrical gas pre-heater with a temperature controller, a condensate receiver and a gas supply system. For one torrefaction experiment, around 80 grams of raw biomass sample was loaded into the vessel for torrefaction treatment. After sample loading, the tubular vessel was closed tightly and connected with the gas supply system and the condenser as well. The tubular vessel was then placed inside an electrically heated furnace and purged with 1 l/min nitrogen to generate inert atmosphere. The sample was heated up at a heating rate of 15 °C/min to three final temperatures (225, 275 and 300 °C).

The residence time for one sample at each final temperature was 30 and 60 minutes, respectively. After each torrefaction experiment, the reactor was cooled down spontaneously and the torrefied biomass was discharged.
2.3 Assessment of torrefied biomass

For raw and torrefied biomass samples, the contents of carbohydrates were analyzed according to the slightly modified method reported by Sluiter et al. [7]. The raw and torrefied biomass samples were digested by a two-step acid hydrolysis. The suspensions of each digestion product were filtered and washed by distilled water through gas filter crucibles. The filtered supernatants were analyzed with high performance liquid chromatography (HPLC) for determining the sugar concentrations (glucan, mannan and galactan). The solid residues remaining after washing were dried at 105 °C until reaching a constant weight, and consist of acid-insoluble organics and ash. The dry solid residues were heated at 550 °C in air to determine the content of acid-insoluble ash. The Klason lignin content was calculated by deducting the acid-insoluble ash content from the dried acid-insoluble residue content.

The grindability of the raw and torrefied biomass samples was assessed by grinding them in a cutting mill. In the pre-grinding stage, the stem wood cubes and bark and stump chips with and without torrefaction treatment were fed into the cutting mill without a bottom sieve to reduce their sizes. Fine grinding of the grains and particles produced from the pre-grinding stage was carried out in the same cutting mill equipped with a 1 mm bottom sieve. The electricity consumed during the pre- and fine grinding stages was recorded by a digital wattmeter. The powder samples produced in the fine grinding stage were sieved by a vibrating sieving machine (Fritsch Analysette 3 Pro) with the following mesh sizes: 1 mm, 0.5 mm, 0.3 mm, 0.2 mm, 0.1 mm and 0.063 mm. The sample particles collected from the different sieves were weighed and presented as a percentage of the initial sample mass.

3. Results and Discussion

3.1 Torrefaction experiments

As can be seen in Table 1, the stump has similar properties as those of the stem wood. The fixed carbon content of the stump is even 1.3% higher than that of the stem wood. On the other hand, the bark contains as much as 23.0% fixed carbon, but also 2.1% ash. Fig. 1 shows the mass yields of the torrefied samples as a function of the final temperature and residence time. Obviously, temperature plays a critical role in realizing the mass yields in the performed torrefaction experiments. As the torrefaction temperature increased to 275 °C, there are significant mass losses for the three studied biomass samples, which is related mainly to the decomposition of hemicellulose. Compared to stem wood, the stump is more sensitive to temperature increase. At 300 °C torrefaction temperature, about 44 and 54% mass losses were recorded from the stump with holding time of 30 and 60 minutes, respectively, whereas stem wood lost only 30 and 42% mass, respectively.

Table 1. Properties of the studied fuels

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stem wood</th>
<th>Bark</th>
<th>Stump wood</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile matter content (wt%, dry basis)</td>
<td>88.1</td>
<td>74.9</td>
<td>86.7</td>
</tr>
<tr>
<td>Ash content (wt%, dry basis)</td>
<td>0.3</td>
<td>2.1</td>
<td>0.4</td>
</tr>
<tr>
<td>Fixed carbon content (wt%, dry basis)</td>
<td>11.6</td>
<td>23.0</td>
<td>12.9</td>
</tr>
</tbody>
</table>
3.2 Characterization of raw and torrefied samples

Compositional analysis of raw and torrefied biomass samples was carried out to understand the conversion behavior of the samples during torrefaction. As shown in Fig. 2, bark has the highest Klason-lignin content (40.8%), while stump has the highest hemicellulose content (23.0%). The stem wood has a similar composition as that of the stump, but an evident high cellulose content (42.6%). During torrefaction, lignocellulose materials decompose to different degrees upon torrefaction severity [7,8]. The decrease of glucan, mannan and galactan reflects decomposition of cellulose and hemicellulose in the samples. As also shown in Fig. 2, hemicellulose (measured as the sum of mannan and galactan) is the least thermally stable component of the studied biomass samples during torrefaction. After torrefaction at 275 °C, more than half of the hemicellulose content in the three studied biomass samples was degraded. The hemicellulose content of them further decreased and only a minor fraction was measured for samples torrefied at 300 °C. Fig. 2 also shows that the content of cellulose, indicated by the content of glucan, does not decrease evidently even at the torrefaction temperature 275 °C for stem wood and stump. However, a significant decrease is observed for bark. On the other hand, the Klason-lignin content of the torrefied samples increased considerably with increasing torrefaction temperatures.
3.2 Effect of torrefaction on grindability

Fig. 3 shows the total energy required for grinding the raw and torrefied biomass samples, which includes energy consumed for both the pre-grinding and fine grinding steps. For stem wood and stump, the energy required for grinding the samples was reduced significantly due to torrefaction treatment. This trend is in good agreement with those reported in literatures for the grinding of stem wood [1]. It indicates that significant energy savings associated with size reduction can be achieved by torrefying stem wood and stump, even at a mild torrefaction condition. Compared to stem wood and stump, much less energy is needed for grinding the raw bark, and the torrefaction treatment has no evident effects on the energy consumption for grinding bark. The differences in energy required for grinding stem wood, stump and bark are partially due to their compositional differences [6,8]. Fig. 4 shows the evident decrease of the amount of large particles (0.5 mm < d < 1 mm) of stem wood and stump after torrefaction at high temperature and prolonged holding time. For the raw bark, the percentage of large particles (0.5 mm < d < 1 mm) is quite small, in comparison to stem wood and stump. The major fraction of the raw bark particles has a size in the range of 0.3 mm < d < 0.5 mm, which decreases evidently after torrefaction treatment. Moreover, the percentage of fine bark particles (d < 0.063 mm) increases considerably upon the increase of torrefaction temperature.

Fig. 3. Energy required for grinding raw and torrefied samples.

Fig. 4. Particle size distributions for the stem wood, stump and bark as a function of torrefaction severity.
4. Conclusion

In the present work, the effects of torrefaction on the grindability and chemical compositions of Norway spruce stem wood, stump and bark were investigated. The results showed that both torrefaction temperature and residence time had effects on the grindability and chemical compositions of the studied biomass samples. However, the torrefaction temperature was more influential. The grindability of the stem wood and stump was significantly improved after the torrefaction treatment. For the stem wood and stump torrefied at 225 °C, only approximately half of the grinding energy was needed compared to those required for grinding the dried raw feedstocks. In addition, the coarse particles with sizes in the range of 0.5 to 1 mm were completely reduced after grinding when the stem wood and stump were torrefied at 275 °C. In addition, the hemicellulose contents of the torrefied stem wood and stump decreased with increase of torrefaction temperature and residence time, with only trace amounts left at 300 °C. Much less energy was required for grinding bark, and torrefaction did not affect the grinding energy requirement significantly. The fraction of fine particles (d < 0.063 mm) increased considerably in the ground torrefied bark. In addition, the cellulose content in the bark decreased evidently as the bark was torrefied at 275 °C.

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References


Biography

Liang Wang is a research scientist at SINTEF Energy Research in Trondheim Norway. His research focuses on characterization of biomass and wastes using combined analytical instruments and techniques, advanced biomass carbonization technology, experimental and kinetic study of torrefaction, pyrolysis, gasification and combustion, of biomass and charcoal, ash chemistry during biomass and waste thermal conversion.