



Torrefaction Process of Needles, Cones and Bark of Spruce (*Picea Abies* (L.) Karst) and Pine (*Pinus Sylvestris* L.)

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Abstract: *The actual problems related with the depletion of fossil resources and the accentuated increase of global warming requires rapid shift to renewable and eco-friendly alternatives. Biomass forestry residues are valuable candidates that can be used as sustainable resources. Torrefaction is a mild thermal treatment that can convert biomass into value-added liquid and solid products. Here we performed torrefaction at 250 °C of needles, cones and bark from spruce and pine, as representative coniferous species in Romanian Carpathians. The elemental analysis of solid materials was performed and the calculated O/C and H/C atomic ratios showed that torrefaction placed the solid materials in the region of coals, close to the origin of the Van Krevelen diagram. The calorific values were improved, leading to higher energy density. The energy yield was close to the unit, indicating that torrefaction is a highly efficient process. The liquid products had complex composition, with compounds coming from the compositional and structural changes in the forestry residues. Terpenes are the dominating compounds from volatile extractives. Furans, from which furfural and 5-methylfurfural were the main compounds produced from degradation of hemicelluloses, while phenol derivatives were produced from lignin. Exploratory data analysis revealed differences between samples from spruce and pine but also between needles, cones and bark.*

Keywords: *forestry residues, coniferous waste, thermal treatment, energy density, GC-MSD*

1. Introduction

Over the last two decades, global energy demand has been growing exponentially, with fossil fuels being the most dominating source of energy (about 80 % is covered by fossil fuels) [1]. In 2020, due to transport restrictions and lockdown measures from COVID-19 global pandemic, it was registered an important drop of the primary energy consumption with the lowest levels recorded since 1990. However, long term reductions must be taken into consideration to achieve the European Union's (EU) energy objectives for 2030 and 2050. The EU goal is to cut greenhouse gas emissions by 80 - 95 %, before 2050 [2]. Therefore, it is essential to produce energy from other sources than fossil fuels. The International Energy Agency (IEA) carefully analyzes the energy issues including oil, gas and coal supply and demand, as well as the renewable energy sources. According to their report [3], in all scenarios, it is intended to achieve before 2050 at least 55 % of renewable energy sources.

Sustainable bioenergy could come from energy crops, organic by-products and residues from agriculture, forestry, municipal solid waste and wastewater. Biomass is considered one of the best renewable solutions for the replacement of fossil fuels, by converting biomass into valuable chemicals and/or fuels [4]. Forestry coniferous residues are a major source of lignocellulosic biomass including branches, leaves/needles, low grade wood, bark, etc., which are usually considered of no economic use for further processing [5,6].

Spruce and pine forests dominate in Europe and Carpathian mountains. The main species are represented by *Picea abies* (L.) Karst. and *Pinus Sylvestris* L., with a long tradition of cultivation. Spruce trees can grow up to 50 - 60 m, with rigid light to dark green needles of 1 - 2.5 cm long and cylindrical cones of 12 - 15 cm long and orange brown bark [7]. Pine trees are medium-sized conifers with 23 - 27m height and live for 400 years or even more. The bark color depends on the tree position, having reddish-orange colour on the upper part, while the lower part is furrowed brown to grey-brown and becomes

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deeply fissured. It has blue-green or grey-green needles of 5 - 7 cm long and cones are cylindrical with 5 - 8 cm in size [8].

From the beginning of civilization biomass was used as major source of energy, especially for heating and for food preparation. Biomass usually contains high amounts of moisture and thus has high susceptibility to decay. It is also largely heterogeneous in composition of properties depending on species, geographical and climatic particularities during growing, age, among others [9,10]. Depending on source, it also can have low density and energy content. This becomes more pronounced in the case of biomass waste or residues. Besides energy production, biomass can be converted into value added chemicals or into biochars. Thermal treatments (e.g. torrefaction, pyrolysis and gasification) are the main involved methods since they offer great versatility for various types of biomass [11]. Especially, torrefaction is largely used to improve the quality of biomass before further processing by other thermal methods. Torrefaction is a thermal treatment in mild conditions (temperatures of 200 - 300°C) in oxygen-free atmosphere [12].

We previously studied needles, bark and cones from silver fir, one of the most important tree at high altitudes in Romanian Carpathians [13], reporting on the characterization of these forestry residues [14] and on their thermochemical conversion by torrefaction and pyrolysis [15]. Here we report on torrefaction of needles, cones and bark from spruce and pine, other two significant coniferous species in Romania. Material and energy yield of the process and the composition of the solid and liquid products are discussed, to determine differences among species and type of material. Torrefaction is the key pretreatment process for subsequent thermochemical conversion including pyrolysis, as it improves the physical properties, chemical composition, and energy content of biomass. The current work attempts to shed more light on the possibility on torrefaction of forest coniferous residues located in the north-eastern mountain region of Romania. These insights are highly valuable to extend the knowledge about the torrefaction of forestry biomass and to promote the potential of converting these forestry residues to energy and value-added products.

2. Materials and methods

2.1. Material preparation

Needles, cones and bark from spruce (*Picea Abies* (L.) Karst) and pine (*Pinus Sylvestris* L.) from forests of about 100 years old in the northeastern mountain region of Romania were collected in the summer of 2020. A specialist helped with proper authentication of specimens. Samples were conditioned for one month in a shadowed and ventilated space, then were grinded and sieved in particles with the size below 500 μm . Grinding to small size is necessary for a proper heat and mass transfer during thermal processes [16,17]. Samples were coded using capital letters "S" for spruce and "P" for pine, followed by lower case letters "n" for needles, "c" for cones and "b" for bark. "To" stands for the torrefied samples. For example, the "ToSn" code represented the torrefied needles from spruce.

2.2. Torrefaction experiments

Torrefaction experiments were performed in a semi-batch reactor schematically presented in Figure 1. The torrefaction temperature was selected in accordance to a previous study conducted on torrefaction of silver fir bark [18], where it was proved that 250°C is a suitable temperature for an energy efficient process.

Samples of about 10 g were heated for 60 min at 250°C under self-generated atmosphere. The condensable liquid products were separately collected as an aqueous and an oil fraction, while the solid residue remaining inside reactor was collected at the end of experiments. The solid and liquid yields were determined gravimetrically and the gas yield was calculated by difference.

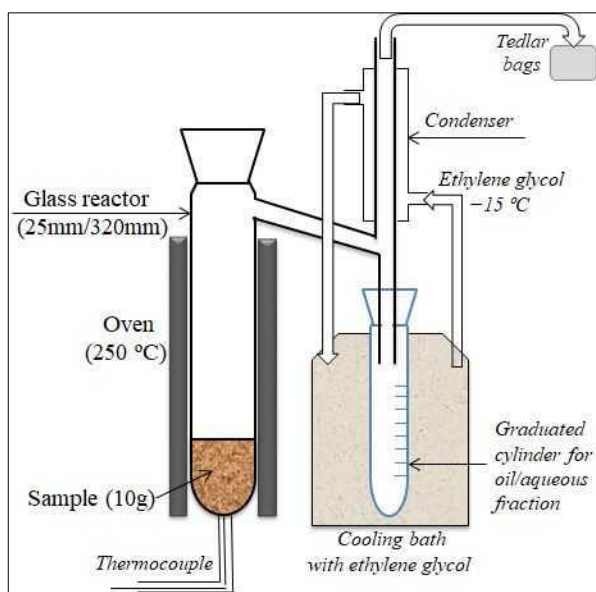


Figure 1. Experimental set-up for torrefaction of needles, cones and bark from spruce and pine

2.3. Characterization of torrefaction products

The ultimate analysis of solid materials (the needles, cones and bark from spruce and pine, before and after pyrolysis) was performed to determine the content of carbon and hydrogen (by Pregl method), nitrogen (by Kjeldahl method) and sulfur (Schonninger method). Oxygen content was calculated by difference. Each determination was made in triplicate and the average values were reported. The results were expressed on moisture free basis. The hydrogen, carbon and oxygen mass percent content were used to calculate the H/C and O/C atomic ratios [19].

The high heating values (HHV) of solid materials, expressed in MJ/kg, were calculated based on elemental composition [20], as following:

$$\text{HHV} = 0.3491\text{C} + 1.1783\text{H} + 0.1005\text{S} - 0.1034\text{O} - 0.0151\text{N} - 0.0211\text{Ash} \quad (1)$$

The energy density and energy yield of torrefaction were calculated based on the high heating values of the initial (HHVi) and of the thermal treated samples (HHVt) and on the solid yield of torrefaction (SY) [21], as following:

$$\text{Energy density (ED)} = \text{HHVt}/\text{HHVi} \quad (2)$$

$$\text{Energy yield (EY)} = \text{SY} \times \text{ED} \quad (3)$$

The aqueous and liquid products were analyzed by gas chromatography coupled with mass spectrometry detection (GC-MSD) on a 6890N Agilent chromatograph coupled with a 5975 inert XL Agilent mass selective detector, under the following conditions: HP5-MS column (30 m x 0.25 mm x 0.25 μm), temperature program of 2 min at 40°C then ramped at 10°C min^{-1} up to 320°C, inlet temperature of 230°C, transfer line of 280°C, 1 mL/min He flow. Identification was performed based on NIST14 database library. A quality of recognition above 85 % was used as selection criteria.

3. Results and discussions

Torrefaction produced ~ 75 - 80 wt% solid material, most part of the initial forestry residues being converted mainly to an aqueous product (~ 14 - 17 wt%) (Figure 2a). Non condensable gases, such as CO, CO₂ and C1 - C5 light hydrocarbons represented about ~ 5.5 - 9 wt% of the initial material. Only small amounts of torrefaction oils below 2 wt% were obtained from the needles and cones of spruce and pine. Instead, no oil could be separately collected from the torrefaction of barks. The torrefied coniferous residues had calorific values in the range of 26 - 30 MJ/kg, much higher than initial materials, of 21 -

22.5 MJ/kg (Figure 2a). The energy density of torrefied materials was of 1.2 - 1.33, leading to an energy yield of the torrefaction process of 98 - 105 % (Figure 2b).

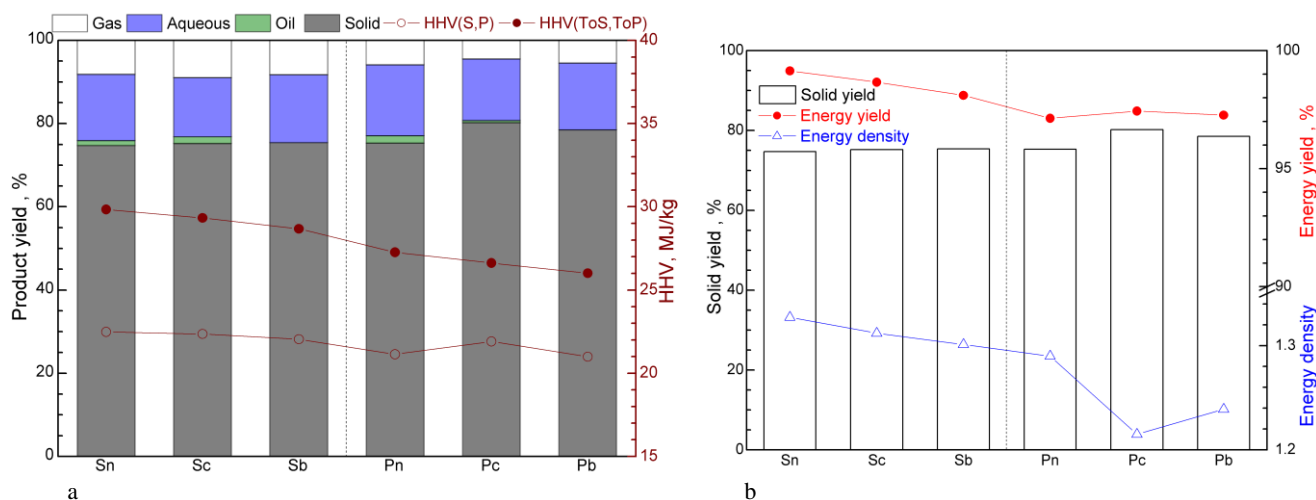


Figure 2. Product yield (a) and energy yield (b) from torrefaction of needles, cones and bark from spruce and pine forestry residues

The elemental composition in Table 1 shows that torrefaction changed the content of carbon, hydrogen and oxygen in solid materials. Carbon content strongly increased from 50 - 54 wt% in initial biomass residues up to 71 - 75.5 wt% in the torrefied materials. Instead, hydrogen was decreased by torrefaction, from about 6 wt% down to ~ 3 - 4.5 wt%. The strongest effect was observed on oxygen content, which decreased from 36 - 39 down to only 17 - 23 wt%. These changes decreased both the O/C atomic ratio (from ~ 0.5 - 0.6 to ~ 0.2) and the H/C atomic ratio (from ~ 0.5 - 0.6 to ~ 0.2).

Table 1. Elemental composition (wt%), O/C and H/C atomic ratios and high heating values (MJ/kg) of needles, cones and bark from spruce and pine before and after torrefaction at 250°C

Sample	C	H	N	S	Ash	O*	O/C	H/C	HHV
Sn	52.90	6.56	0.18	1.02	3.12	36.22	0.51	1.49	22.49
Sc	53.78	6.25	0.41	0.40	2.78	36.38	0.51	1.39	22.35
Sb	52.70	6.32	0.54	0.86	2.55	37.03	0.53	1.44	22.04
Pn	50.30	6.38	0.15	1.38	2.93	38.86	0.58	1.52	21.13
Pc	51.72	6.61	0.25	0.99	1.83	38.60	0.56	1.53	21.91
Pb	50.72	6.21	0.28	0.93	2.53	39.33	0.58	1.47	20.99
ToSn	75.45	4.46	0.17	0.82	1.74	17.36	0.17	0.71	29.84
ToSc	74.97	4.25	0.39	0.67	1.52	18.20	0.18	0.68	29.33
ToSb	74.27	4.02	0.49	0.55	1.24	19.43	0.20	0.65	28.68
ToPn	72.15	3.62	0.13	0.78	1.74	21.58	0.22	0.60	27.26
ToPc	71.52	3.36	0.22	0.65	1.69	22.56	0.24	0.56	26.62
ToPb	71.25	2.96	0.25	0.62	2.05	22.87	0.24	0.50	26.01

*oxygen calculated by difference

The needles, cones and bark from spruce and pine forestry residues are placed in the upper right region of the Van Krevelen diagram (Figure 3). Torrefaction moved the samples close to the origin of the diagram, in the region of coals. Clear distinctions can be observed according to the species of the coniferous material, spruce samples being separated from the pine ones. Spruce was placed on the lower left part of pines for the initial materials but to the upper left part for the torrefied ones. This was due to lower oxygen and higher hydrogen content in spruce after torrefaction, compared with pine.

The liquid products from torrefaction had complex composition (Figure 4), with chemical compounds distributed mainly in the C6 - C20 range of the NP-grams (Figure 5). The NP-gram curves show the amount of compounds (based on the percentage area from the GC-MSD chromatograms) versus the corresponding carbon number, n, of the corresponding normal paraffins [22,23]. For example,

all compounds appearing in the chromatogram after the retention time of octane (C8) but before the retention time of nonane (C9) are considered to have the carbon number of nine (C9). The carbon numbers are indicated in red on the X axis of chromatograms in Figure 4.

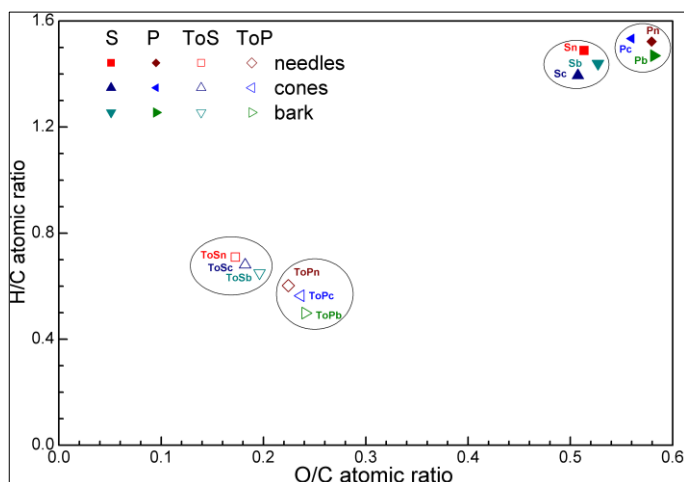


Figure 3. The Van Krevelen diagram for forestry residues before and after torrefaction

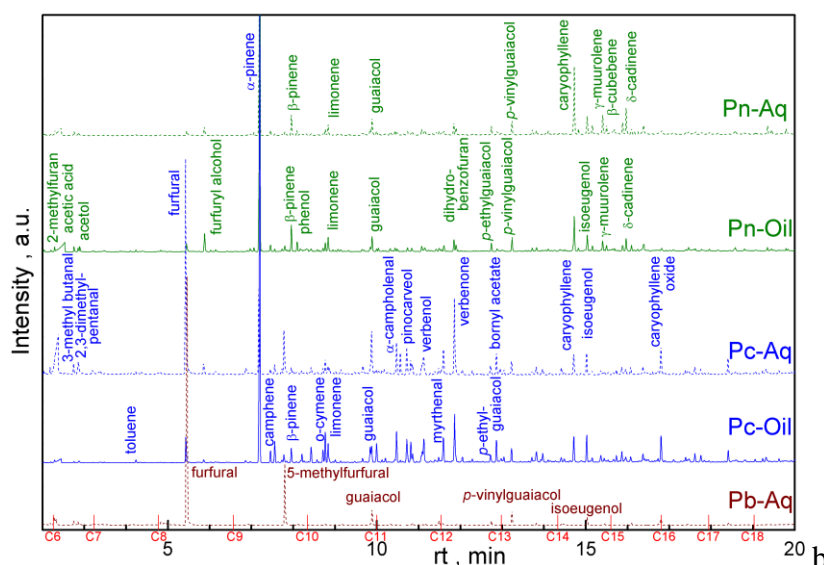
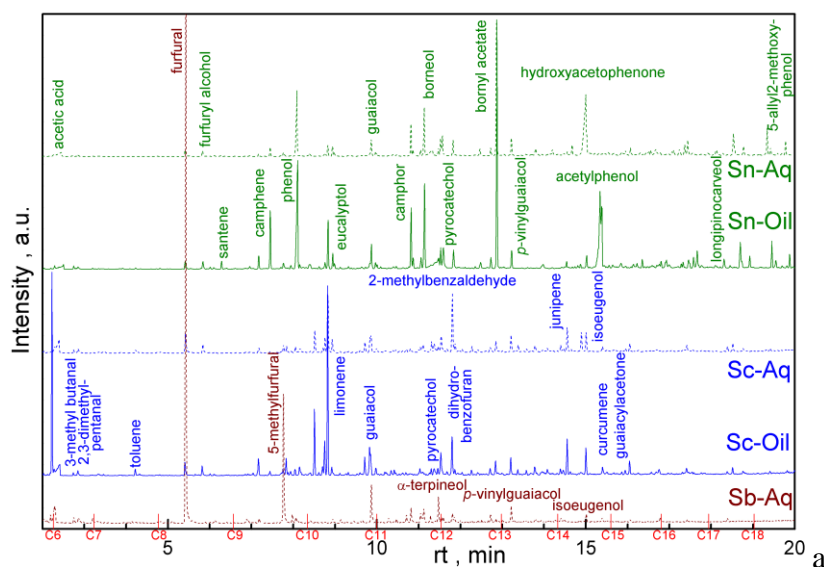


Figure 4. The GC-MSD chromatograms and the main identified compounds in the aqueous and oil fractions from torrefaction of spruce (a) and pine (b) forestry residues

The organic compounds produced from the torrefaction of coniferous forestry residues partitioned between the aqueous and the organic fractions. Differences could be observed in global composition of the liquid products, according to species (spruce or pine) and type (needles, cones or bark) of residue.

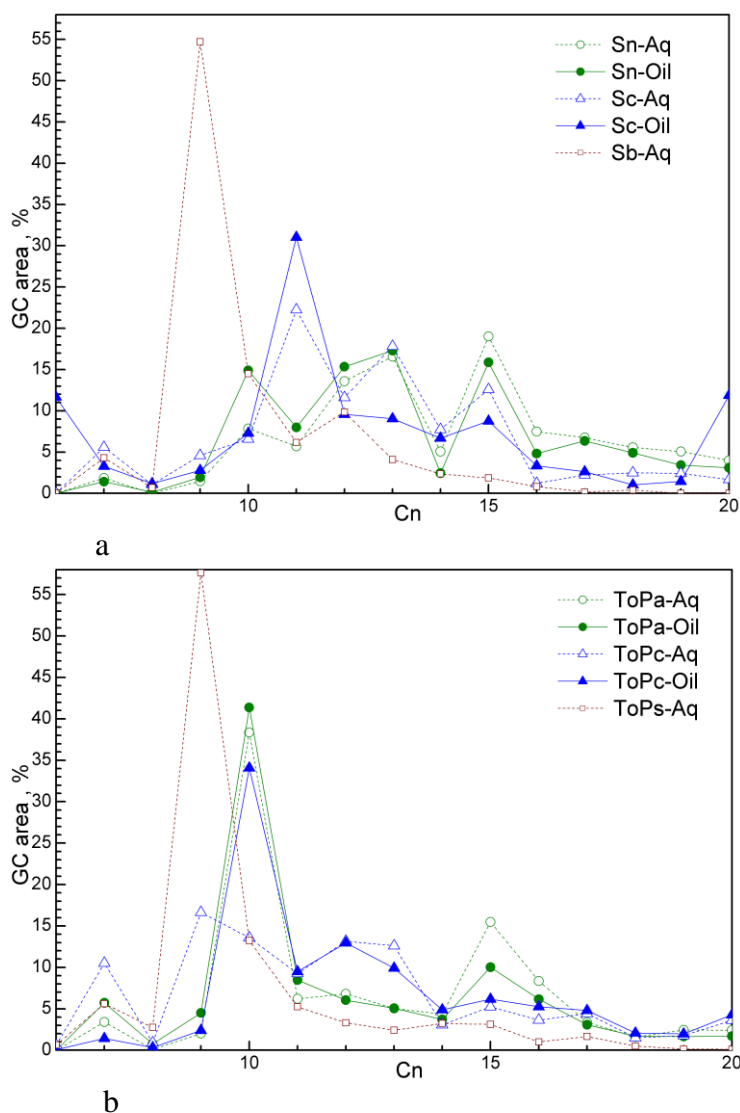


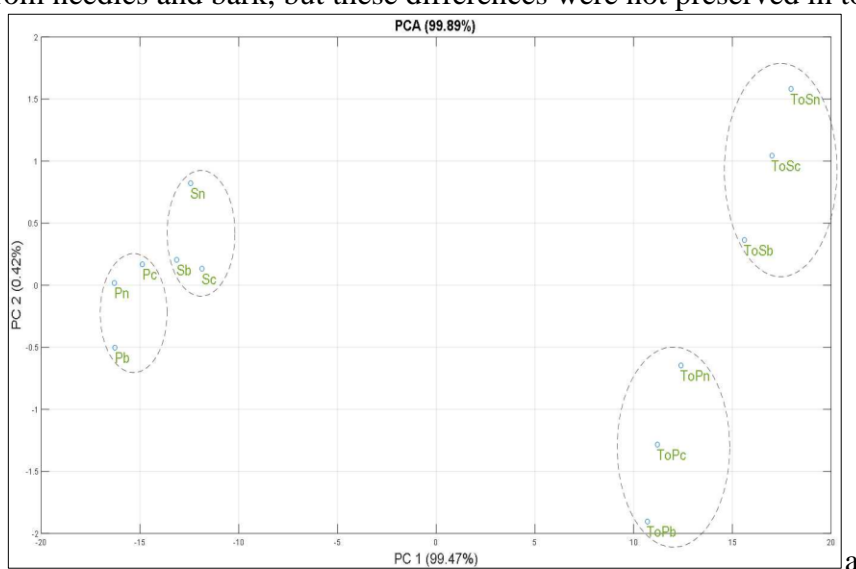
Figure 5. The distribution of compounds in the aqueous and oil fractions from torrefaction of spruce (a) and pine (b) forestry residues

Acetic acid was the main compound at C7, being followed in the case of pine by butanal and pentanal derivatives. Furfural was the main compound at C9 and represented more than 50% of the organic compounds in the aqueous fraction from barks. Terpenes (α -pinene and camphene) were the main compounds at C10 in the liquid products from the cones, especially those from pine. Instead, 5-methylfurfural was the main compound from barks in this range, while phenol was a major compound from needles, especially those from spruce. The C11 range of NP-grams is dominated by terpenes, especially limonene from the cones of spruce. Guaiacol, coming from degradation of lignins, is also a significant compound in this range, regardless of sample type. Campholenal, pinocarveol and verbenol were terpenes found in high amounts at C12 in the liquid products from the cones of pine, while camphor and borneol were produced in this range by the needles from spruce. Barks had α -terpineol as the main compound at C12. Spruce generates at C13 high amounts of bornyl acetate terpene from needles and dihydrobenzofuran from cones, while verbenone was a significant compound from the cones of pines. Hydroxyacetophenone and acetylphenol were main compounds at C15 from needles of spruce. Caryophyllene at C15 and caryophyllene oxide at C17 were significantly produced by pine, especially from cones. Isoeugenol at C15 was observed in most samples.

Biomass torrefaction is well known as a process capable of improving the physicochemical properties and potential energy of biomass. However, comprehensive information on operating conditions such as residence time and temperature are needed for implementation of torrefaction as upscale technology, from the laboratory to pilot and further to industrial scale. As a valuable start, this study gives clear knowledge of how torrefaction of spruce and pine residues operates at laboratory level.

The main effect of torrefaction is removal of water, both the physically adsorbed by sample as moisture, and the chemically bounded one that is liberated when the weakest structures in biomass start to thermally degrade. This lead to formation of high amounts of aqueous fraction observed from the product yield in Figure 2, and explains the strong decrease of oxygen and hydrogen content of samples (Table 1). The carbon content in samples increased as a consequence. Water has high vaporization enthalpy, its evaporation adsorbing large amounts of the energy produced by combustion of biomass. Therefore, removal of large amounts of water and the strong decrease of oxygen content and the increase in carbon content strongly increased the calorific values of the torrefied materials. These were higher for the torrefied needles, cones and bark from spruce compared with their corresponding counterparts from pine, due to increasing amounts of hydrogen, as listed in Table 1. This increased the energy density of the solid materials. The calculated energy yield was above 97% showing the high efficiency of the torrefaction process. This indicates that the increased energy density of the torrefied material compensates in very large amount the energy spent during the process for removal of humidity, volatilization of extractives and scission of the labile chemical bonds in biomass. These results are comparable with those obtained by Wang et al. [24] which analyzed the properties of torrefied pellets produced from spruce stem wood, bark, and forest residues, over a temperature range of 225-275°C. The authors observed that both O/C and H/C ratios of torrefied spruce pellets decreased and correlated to dehydration, decarboxylation, and depolymerization of the organic fraction during the torrefaction process. Also, similar results of increasing HHV trend upon torrefaction treatment has been reported by McNamee et al. [25], where the fixed carbon and HHV of torrefied North American pine increased while the moisture and volatiles contents decreased.

The exploratory data analysis based on the characterization data of the solid materials presented in Table 1 showed clear distinction between the forestry residues before and after torrefaction, but also between the studied species (Figure 6). Needles, cones and bark were grouped together in clusters that are spatially distinct. The initial forestry residues are placed on the left side of the PCA diagram in Figure 6.a while the torrefied ones are placed on the right side. Distinction was also observed between the clusters of the spruce and those of pine. The dendrogram in Figure 6.b evidences the magnitude of differences among samples. Great difference in terms of composition appeared between the initial and torrefied samples, but also between materials from spruce and from pine. Cones from initial spruce and pine are distinct from needles and bark, but these differences were not preserved in torrefied samples.



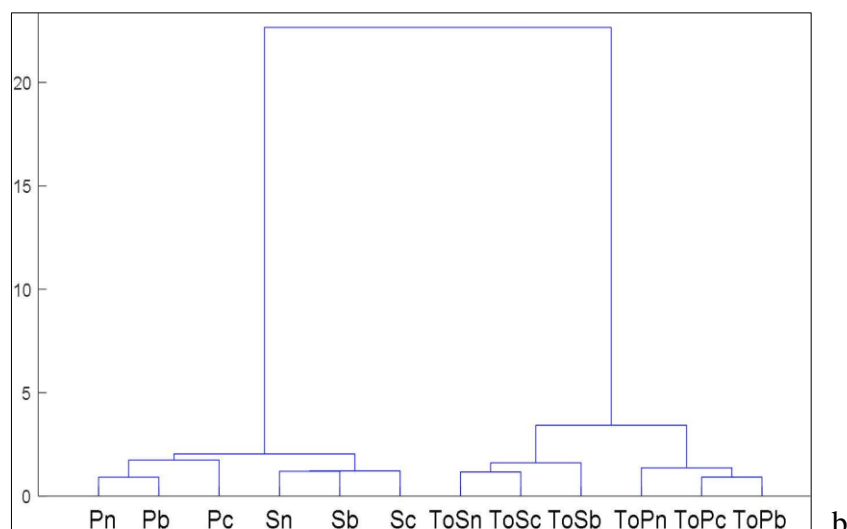


Figure 6. The PCA plot (a) and the hierarchical clustering (b) of needles, cones and bark from spruce and pine before and after torrefaction, according to composition data in Table 1

Non condensable gases such as CO and CO₂ are also formed by torrefaction these being degradation products of oxygenated structures with lower thermal stability, especially from hemicelluloses.

Volatile compounds are also liberated from the composition of woody biomass samples. Terpenes are the most relevant volatiles, especially from needles and from cones. Furans are produced from degradation of hemicelluloses, furfural and 5-methylfurfural being the main compounds from torrefaction of barks. Phenol derivatives, such as pyrocatechol, ethyl- and vinyl- guaiacol, isoeugenol and guaiacylacetone are degradation products of lignin. Composition of liquid products indicated that besides removing humidity torrefaction released the volatile terpenes, and degrades the most labile structures in the composition of biomass. Hemicelluloses mainly affected but signs of degradation of lignin were also evidenced. The last observation is in good agreement with Brebu et al. [26] which reported that degradation of lignin starts at low temperatures, soon after removal of humidity.

4. Conclusions

Torrefaction of forestry residues was performed at 250°C and self-generated atmosphere, in a semi-batch glass reactor. Spruce and pine were considered as representative coniferous species in Romanian Carpathians. Needles, cones and bark from spruce and pine were collected from 100 year old forests in Eastern Romania. Torrefaction removed the moisture from the biomass samples and strongly decreased the oxygen content of the solid materials. Hydrogen content also decreased, this being eliminated together with oxygen mainly in the form of water. Consequently, carbon content increased in the torrefied samples. This leads to improved calorific values and higher energy density of the torrefied solids. The energy yield was close to the unit, indicating the efficiency of the torrefaction process. The O/C and H/C atomic ratios decreased in the torrefied materials compared with the initial ones. This placed the torrefied samples close to the origin of the Van Krevelen diagram, similar with coals. Removal of volatile compounds from the extractive fraction and the thermal degradation of the most labile bonds in the structural units in biomass samples lead to organic compounds that partitioned between the aqueous and oil fractions. These have complex composition, including terpenes as volatile compounds from extractives, furans from degradation of hemicelluloses and phenols originating from lignin structural units in forestry biomass. The exploratory data analysis indicates differences between samples according to the species (spruce vs. pine) and to origin (needles vs. cones vs. bark). Upon the torrefied samples, spruce needles, closely followed by cones and bark, exhibited the highest HHV, and the greatest energy yield. Therefore, from the energy point of view, spruce needles can be considered the best material for the production of torrefied biomass and may be upscaled from the laboratory to the



pilot scale. It is also necessary to understand how torrefaction can be integrated into biomass processing technology, namely pyrolysis, being the objective of our next research.

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