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ScienceDirect

Energy Procedia 105 (2017) 551 – 556

Energy Procedia

The 8th International Conference on Applied Energy – ICAE2016

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

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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 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 Klason 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.

Peer-review under responsibility of the scientific committee of the 8th International Conference on Applied Energy.
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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Peer-review under responsibility of the scientific committee of the 8th International Conference on Applied Energy.
doi:10.1016/j.egypro.2017.03.355

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.

Table 1. Characterization of the untreated samples

	Stem wood	Bark	Stump
Higher heating value (MJ/kg, db^a)	19.78	20.14	18.57
Ash content (% m/m, ar^b)	0.31	2.43	0.43
Ca^{2+} (ppm, db^a)	1030	7803	1235
K^+ (ppm, db^a)	272	2011	245
Na^+ (ppm, db^a)	22	47	36
Si (ppm, db^a)	82	3602	253

^{a}dry basis, ^{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 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 amount of Klason 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].

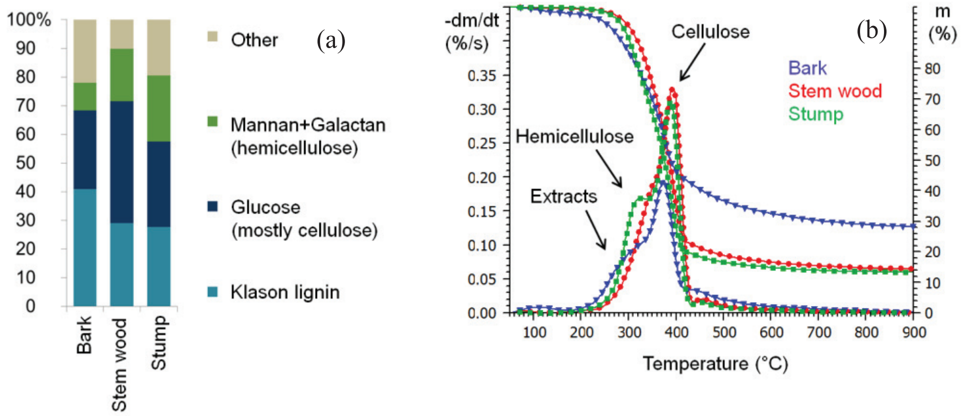

Fig. 1. (a) Composition of untreated bark, stem wood, and stump. (b) TG and DTG curves of untreated bark, stem wood, and stump.

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.

Sample	Treatement	Solid yield (%)	Glucan (%)	Mannan + Galactan (%)	Klason lignin (%)
Bark	Untreated	100	27.47 ± 0.7	9.68 ± 0.2	40.79 ± 0.3
	225°C, 30 min	90	28.38 ± 0.2	9.77 ± 0.2	49.61 ± 1.3
	225°C, 60 min	82	24.35 ± 0.6	8.75 ± 0.1	56.69 ± 0.8
	275°C, 30 min	73	12.26 ± 0.7	1.80 ± 0.1	78.84 ± 1.4
	275°C, 60 min	69	7.69 ± 0.3	0.81 ± 0.0	85.99 ± 1.2
	300°C, 30 min	63	2.68 ± 0.1	0.26 ± 0.0	90.04 ± 0.9
	300°C, 60 min	61	1.52 ± 0.1	0.14 ± 0.0	91.98 ± 0.4
Stem wood	Untreated	100	42.54 ± 0.9	18.26 ± 0.5	29.05 ± 0.8
	225°C, 30 min	92	44.74 ± 1.3	17.07 ± 0.4	30.63 ± 0.1
	225°C, 60 min	91	43.53 ± 0.9	16.59 ± 0.0	31.17 ± 0.5
	275°C, 30 min	79	45.64 ± 0.9	6.23 ± 0.3	42.69 ± 0.7
	275°C, 60 min	76	42.21 ± 1.4	4.74 ± 0.2	47.78 ± 0.3
	300°C, 30 min	70	12.80 ± 0.4	1.44 ± 0.1	80.16 ± 1.5
	300°C, 60 min	58	8.26 ± 0.3	0.75 ± 0.0	87.27 ± 1.4
Stump	Untreated	100	29.80 ± 0.3	22.97 ± 0.3	27.68 ± 0.7
	225°C, 30 min	93	28.21 ± 1.8	21.45 ± 0.4	34.30 ± 2.0
	225°C, 60 min	90	28.93 ± 1.3	20.92 ± 2.3	37.73 ± 2.4
	275°C, 30 min	72	29.69 ± 0.4	4.91 ± 0.2	57.18 ± 0.4
	275°C, 60 min	70	28.97 ± 0.4	4.61 ± 0.2	59.57 ± 1.0
	300°C, 30 min	56	25.64 ± 0.6	1.13 ± 0.0	68.58 ± 0.3
	300°C, 60 min	46	13.67 ± 0.5	0.41 ± 0.0	82.31 ± 0.5

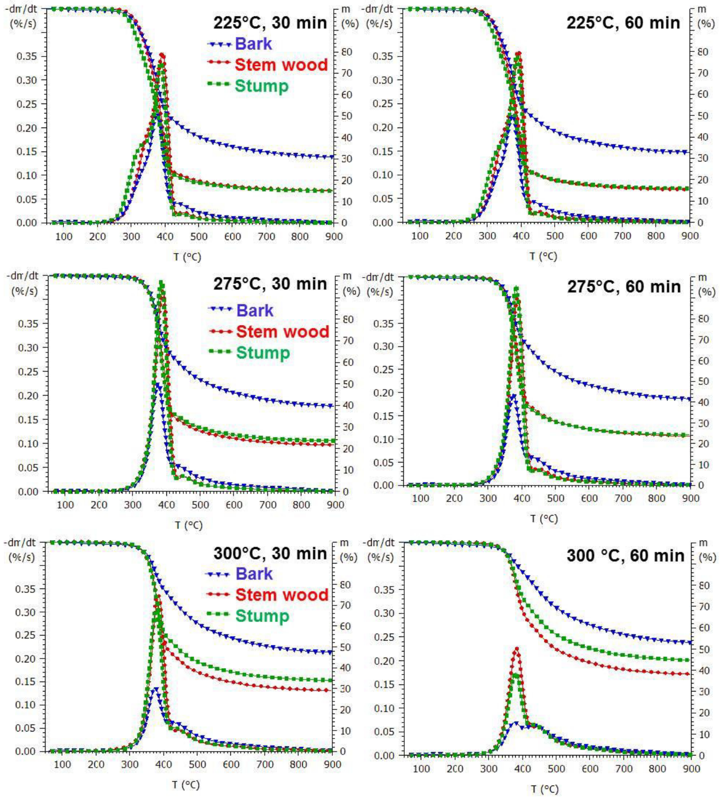

Fig. 2. TG and DTG curves of bark, stem wood, and stump after various torrefaction treatments

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

SINTEF acknowledges the financial support by the Research Council of Norway and a number of industrial partners through the projects BioCarb+ and GAFT. The authors are grateful to the NKFIH for financing the TÉT_13_DST-1-2014-0003 project and for “Bolyai János” research fellowship.

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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.