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Cell wall components in torrefied softwood and hardwood samples

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ABSTRACT

Torrefaction – the process of soft pyrolysis (200–300 °C) in inert atmosphere – is considered to promote the usage of lignocellulosic biomass in various technologies. The initial raw material is not uniform in composition and we compared the effect of torrefaction on the samples of hardwood (birch) and softwood (pine). The major differences between the torrefied samples were observed between 225 and 250 °C and were largely connected with different behavior of hemicelluloses. Monosaccharide analysis revealed the decrease in detectable xylose from 26% to 1% (250 °C) of the raw sample in birch, and from 11% to 1%—in pine. Mannans were more resistant to degradation. Comparison of data from HPAEC, thermal analysis and IR-spectroscopy revealed that hemicelluloses are modified during torrefaction at 225–250 °C, rather than fully degraded and removed from the sample. This may lead to considerable modification of wood properties, more pronounced in hardwoods. The relative content of aromatic structures went up during torrefaction, part of the effect was due to condensation of modified carbohydrate units. Index of cellulose crystallinity increased in torrefied samples. The content of cellulose in birch samples remained the same as in raw sample up to 250 °C, while in pine it dramatically decreased after the torrefaction at 250 °C. Torrefaction at 300 °C made the samples of hardwood and softwood very much alike. The perspectives of usage of hardwoods and softwoods torrefied at different temperatures are discussed.

1. Introduction

Plant biomass is an important renewable feedstock. Conversion of lignocellulosic biomass to various products and fuels is an attractive idea in view of economic, environmental and social benefits. However, plant biomass usage faces the set of technological and organizational problems, which are due to the low energy density and the low bulk density (60–200 kg/m^3), the wide variations in particle size (10–100 mm) and in the moisture content (25–60%), the biodegradability and the dispersion of the biomass over the territory. One of the approaches that helps to partially solve the above mentioned problems is torrefaction—a mild pyrolysis process that is carried out in an inert atmosphere in the temperature range 200–300 °C and results in significant changes of biomass properties [1,2]. In contrast to pyrolysis, torrefaction does not destroy the cell wall polymers completely [3], allowing further usage of their properties. Varying of the thermal treatment conditions allows preservation of different polymer combinations that are desirable for the purposes of further biomass processing [1,2]. Thus, torrefaction can improve the efficiency of various biotechnological processes and help the development of novel products with new characteristics.

The features of torrefied wood are largely determined by the composition and architecture of cell walls. There are two types of wood that are significantly different in their properties—softwoods and hardwoods. The differences are due to several factors, including anatomical and morphological parameters, e.g. the cell diameter, the density of the cell packing, the proportion of different xylem elements (vessels, tracheids, fibers, parenchyma cells) [4]. But the most clearly manifested in the wood thermal processing features are the composition and the structure of cell walls. At that, the total compositions of softwoods and hardwoods are similar: cellulose comprises 40–50% of the dry weight, hemicelluloses—25–35%, lignin—15–30%, extractives—1–5%. The key difference is the composition of hemicelluloses: xylans are

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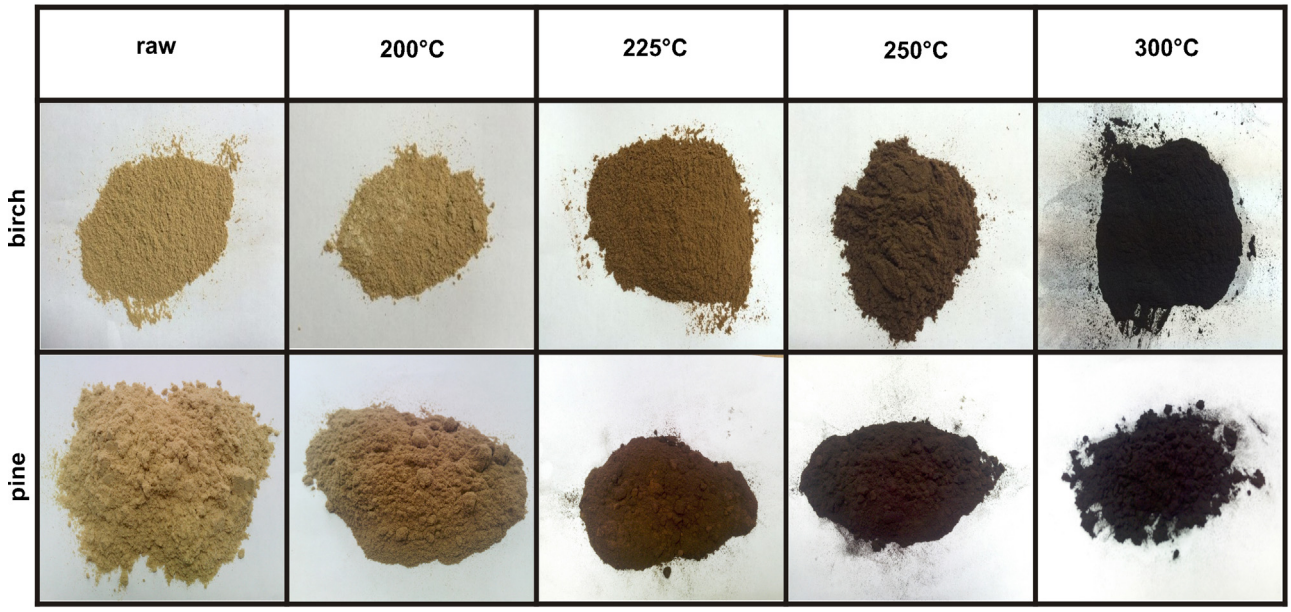

Fig. 1. The general view of torrefied samples.

the overwhelmingly dominant in hardwoods, while in softwoods mannans constitute the significant proportion [5]. In softwood, characteristic for gymnosperms, and for conifers in particular, the hemicelluloses usually include galactoglucomannans (10–30% of dry weight) and glucomannans (0–5%); arabinoglucuronixylans are also present (5–15% of dry weight). Hardwood that is produced by the flowering plants has the acetylglucuronoxylans as the main hemicellulose (20–30% of dry weight). Small amounts of glucomannans (2–5%) and galactoglucomannans (0–3%) can also be present in their cell walls [6,7].

It is known that hemicelluloses as the least stable cell wall polymers are the most degraded during torrefaction ones [8]. Thermal decomposition of the major commercially available model hemicelluloses showed that the mechanisms of their degradation are substantially different in many parameters, including the product composition. Xylan was the least stable of the analyzed polymers, while the most stable were the polymers based on β-glucan backbone [9]. The studies of the torrefaction process of isolated celluloses [10,11] and lignins [12] were also performed. However, in wood samples the complex interactions that affect the process course can take place both between the various components of cell walls, and between the products of their thermochemical modification [13]. Hence we compared the changes of cell wall substances in samples of pine (softwood) and birch (hardwood) during torrefaction process at different temperatures having in mind both the differences in their composition and the latest findings in pyrolysis mechanisms.

2. Materials and methods

2.1. Materials

Wood from debarked mature stems of pine and birch (70–90 years old) that were cut down in the central part of Volga Region was used as a raw material. The initial moisture of samples was 8–9%; ash content was 0.1–0.3%. The milling of both raw and torrefied samples was performed on a laboratory grinder with rotary knifes. Milled samples were passed through the sieve analyzer; the particles in fractions that were used for further analysis were between the sieves 0.08–0.16 mm. The calculations of the yield of torrefaction, the heating value and certain biomass components content in raw and torrefied samples were done per absolutely dry weight of raw samples.

2.2. Torrefaction of samples

Samples (20 g) of pine or birch wood (blocks 10 × 10 × 10 mm) were placed in a hermetic retort (diameter = 32 mm, length = 250 mm), heated in a furnace with the heating rate 7 °C/min up to the one of selected temperatures (200, 225, 250, or 300 °C) and maintained during 30 min in isothermal mode in nitrogen environment without blowing. The necessary time of torrefaction was determined in preliminary experiments to provide the uniformity of torrefied biomass. Temperature control was realized by chromel-alumel thermocouples that were installed inside and outside of the retort. At the end of the torrefaction, the retort was cooled down at room temperature during 30 min. Solid products that were formed during torrefaction (Fig. 1) were weighed and collected in a special tanks for further analysis.

2.3. Heating value measurement

The determination of the heat that is produced during the combustion was carried out on the calorimeter IKA® C 5000 (IKA®, Germany) under adiabatic conditions in an atmosphere of oxygen; sample masses were 0.5 g.

2.4. Analysis of monosaccharide composition of the carbohydrates hydrolyzed by trifluoroacetic acid (CF_3COOH)

Raw and torrefied wood samples (2 mg) were hydrolyzed for 1 h at 120 °C in 5 ml of 2 M trifluoroacetic acid (TFA). The obtained monosaccharides were analyzed by high pressure anion-exchange chromatography (HPAEC) on CarboPac-PA20 column (Dionex, USA). Detection was performed with pulse amperometric detector (Dionex, USA).

2.5. Uptegraff determination of crystalline cellulose content

Sample (10 mg) was placed in the test-tube, weighed, and incubated in acetic–nitric reagent (HNO_{3conc}:CH_3COOH_{conc} = 1:10) at 100 °C for 1 h. Then the remaining solid residue was washed three