brought to you by 🐰 CORE

Journal of Analytical and Applied Pyrolysis 116 (2015) 102-113



Contents lists available at ScienceDirect

# Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap



## Cell wall components in torrefied softwood and hardwood samples



Sergey A. Pushkin<sup>a</sup>, Liudmila V. Kozlova<sup>a,b,\*</sup>, Alexandr A. Makarov<sup>a,c</sup>, Andrey N. Grachev<sup>a</sup>, Tatyana A. Gorshkova<sup>b</sup>

<sup>a</sup> Kazan National Research Technological University, 68 Karl Marx Street, Kazan 420015, Russian Federation

<sup>b</sup> Kazan Institute of Biochemistry and Biophysics, Kazan Scientific Center, Russian Academy of Sciences, 2/31 Lobachevskii Street, Kazan 420111, Russian

Federation

<sup>c</sup> Kazan Federal University, 18 Kremlevskaya Street, Kazan 420008, Russian Federation

#### ARTICLE INFO

Article history: Received 22 June 2015 Received in revised form 17 September 2015 Accepted 30 September 2015 Available online 9 October 2015

Keywords: Torrefaction Birch Pine Hemicelluloses Cellulose Lignin

### 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 220 °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.

© 2015 Elsevier B.V. All rights reserved.

### 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  $(60-200 \text{ kg/m}^3)$ , 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

*E-mail addresses:* serega\_pushkin90@mail.ru (S.A. Pushkin), liudmilakibbksc@gmail.com (L.V. Kozlova), smakarov86@gmail.com (A.A. Makarov), energolesprom@gmail.com (A.N. Grachev), gorshkova@kibb.knc.ru (T.A. Gorshkova). 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

<sup>\*</sup> Corresponding author at: Kazan Institute of Biochemistry and Biophysics, Kazan Scientific Center, Russian Academy of Sciences, 2/31 Lobachevskii Street, Kazan 420111, Russian Federation.