THE CONCENTRATION OF SELECTED HEAVY METALS IN POPLAR WOOD BIOMASS AND LIQUID FRACTION OBTAINED AFTER HIGH TEMPERATURE PRETREATMENT

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ABSTRACT

The concentration of selected heavy metals: chromium (Cr), manganese (Mn), iron (Fe), nickel (Ni), copper (Cu) and zinc (Zn) in 5-year-old wood of *Populus trichocarpa* before and after steam explosion (SE) and liquid hot water (LHW) pretreatments was studied. The concentration of the above heavy metals in the liquid fraction obtained after pretreatments was also studied. The studied problem of heavy metals in lignocellulosic biomass is an interesting and important issue in the context of bioethanol production technology. An X-ray fluorescence spectrometer (XRF) was used to analyse the concentration of heavy metals. The change of concentration of the tested elements in wood biomass after pretreatment was small (except for iron). On the other hand, the average concentration of iron in wood biomass of a 5-year-old *Populus trichocarpa*, after SE and LHW with duration of the pretreatments 15 and 60 min, increased about 24-fold to 28-fold, comparing to its average concentration in native wood. During the pretreatment process, wood biomass absorbed the iron that at high temperatures passed from the pretreatment equipment to the solution. The average concentration of the elements under research in liquid fraction obtained during SE and LHW of wood biomass with duration of the pretreatments 15 and 60 min was at a low level.

KEYWORDS: *Populus trichocarpa*, poplar, steam explosion, liquid hot water, liquid fraction, heavy metals.

INTRODUCTION

Nowadays biomass hydrolysis is preferably performed via the enzymatic process, although acidic hydrolysis is better known. Acidic hydrolysis causes a higher negative impact on the natural

environment and that is why the application using enzymes has been focused on. Enzymatic hydrolysis is basically a well known process and has been used many times by different authors (Mansfield et al. 1999, Palonen et al. 2004, Martin et al. 2008, Kumar and Wyman 2009, Studer et al. 2011, Antczak et al. 2018, Antczak et al. 2019), but the high cost of the enzymes to be used make the process unprofitable. The content of possible enzymatic hydrolysis inhibitors in raw material is also a very important factor which should be taken in to account.

The technological process of biofuel production from wood biomass can be hindered by organic and inorganic inhibitors. Among organic substances, it is worth mentioning furan aldehydes created mostly as a result of decomposition and further transformations of hemicelluloses to furfural, 5-hydroxymethylfurfural, as well as soluble phenolic compounds appearing due to lignin degradation (Palmqvist and Hahn-Hägerdal 2000a, b, Klinke et al. 2002, Garcia-Aparicio et al. 2006, Alvira et al. 2010, Horn et al. 2011, Tomás-Pejó et al. 2011, Chandel et al. 2013, Jönsson et al. 2013).

Poplar is a known fast-growing species which can be used for biofuel production. It may be useful as a raw material further processed to biogas or liquid biofuels (Antczak et al. 2014, Antczak et al. 2018).

Inorganic inhibitors include some heavy metals which can accumulate in the trees depending on their growth environment, as well as in the wood during the process of its impregnation finish, as well as during pretreatment of lignocellulosic biomass during its preparation for biofuel production. The source of contamination with metals can be compounds and alloys used to manufacture the blades of industrial wood grinders, as well as reactors, in which the pretreatment processing takes place (Palmqvist and Hahn-Hägerdal 2000a,b). During pretreatment, high temperature and pressure can facilitate the transfer of metals from the machines into wood biomass. Metals can also pass to the liquid fraction created after pretreatment (Warzee et al. 1966). The salts of chromium, iron, nickel and copper are metal compounds considered to be inhibitors in wood biomass pretreatment processes and its fermentation (Warzee et al. 1966, Chandel et al. 2013). Moreover, some of metal ions may additionally bind to lignin, causing a change in the energy potential of the biomass leading to an increase of enzymatic hydrolysis efficiency (Liu and Zhu 2010, Akimkulova et al. 2016). The process of enzymatic hydrolysis of wood biomass leads to ions of such metals being combined with proteins, which causes their denaturation and deactivation, and as a consequence: lower efficiency of glucose production. In the available literature, there is scarce information on studies of heavy metals concentration released during pretreatment such as steam explosion and liquid hot water of poplar wood biomass.

The aim of this paper was to investigate the concentration of selected heavy metals in 5-year-old *Populus trichocarpa* wood biomass before and after SE and LHW pretreatments. The concentration of the above heavy metals in liquid fraction obtained after pretreatments was also studied.

MATERIAL AND METHODS

Material (mixed sapwood and hardwood) were obtained from the trunk of an about 5-year-old *Populus trichocarpa*. The high temperatures used in pretreatment processes of plant biomass cause the transmission of chemical compounds from the solid fraction to the liquid fraction used as reaction environment.

The measurement of heavy metal concentration in the wood was performed for such metals as Cr, Ni, Cu, Mn, Zn and Fe, after the wood was burnt and converted to ashes. On the other hand, in the liquid fraction generated after pretreatment, the measurement was conducted directly.

The heavy metal concentration was measured with an X-ray fluorescence spectrometer Spectro Midex M. The spectrometer was equipped with a 540 x 600 x 2500 mm chamber, with test bench positioning with the precision of 2.5 µm. Measurement points were set with the help of a system of two cameras controlled by the Spectrum X-labro software, permitting very precise location of the measurement points and the position of the sample in relation to the detector. Moreover, the device was equipped with an X-ray lamp cooled with air, containing a molybdenum anode. The maximum power was 30 W, and the maximum voltage, 50 kV. The heavy metal concentration was measured for wood biomass of *Populus trichocarpa* before and after SE and LHW processes.

Wood biomass was converted into ashes in a muffle furnace, which took 6 hours at 600°C. The increase at temperature from 20°C to 600°C lasted for additional 2.5 hours. Samples were converted to ashes in order to concentrate them (Harju et al. 1997).

Wood biomass was subjected to steam explosion in a stainless steel autoclave. According to the technical specification (Explo Solution company), the autoclave was made of 316Ti stainless steel (complaint with the PN-EN 10088-1) characterized by the following composition: C- max. 0.080%, Mn- max. 2.00%, Si- 0.75%, P- 0.045%, S- 0.030%, Cr- 16.00 ÷ 18.00%, Ni- 10 ÷ 14.00%, Mo- 2.00 ÷ 3.20%, Ti- max. 0.70%, N- max. 0.10%. The interchangeable elements of the apparatus, in accordance with the technical specification (Explo Solution company), are made of CuZn33 brass (complaint with the PN-EN 1652), composed of: Cu- 66.0 up to 68.0%, Pb- max. 0.05%, Al- max. 0.02%, Fe- max. 0.05%, Ni- max. 0.3%, Sn- max. 0.1% and Zn- 31.5%.

The wood biomass of a 5-year-old *Populus trichocarpa* was subjected to the processes of SE and LHW. The processes were done in a stainless-steel reactor with a total volume of 250 cm^3. To each of pretreatment process about 20 g of size reduced (fraction between 0.43 and 1.02 mm) wood was used. Before the pretreatment, the wood in the reactor was supplemented with distilled water to a volume of 250 cm^3. The ratio of wood to distilled water was 1:12.5. The SE and LHW processes were conducted at temperatures of 160°C, 175°C and 190°C, with duration of the pretreatments 15 and 60 min. The concentration of selected metals in the liquid fraction obtained after pretreatments was tested in drops, whose volume amounted to about 0.3 cm^3 of liquid. In addition, the concentration of heavy metals in distilled water, which was used during the pretreatment, was tested. For each processing temperature and pretreatment kind (SE and LHW) at least three drops of the same volume were tested, and one point of measurement was set in each of them. The test made use of a 2 x 2 mm shutter and time of exposure of 300 sec.

RESULTS AND DISCUSSION

The results of the concentration of selected metals in native wood (biomass before the pretreatments) of a 5-year-old *Populus trichocarpa*, in wood after high temperature pretreatments with different residential times (15 and 60 min), in distilled water and in liquid fraction are presented in Figs. 1-6. On the basis of the data presented in Fig. 1, we can conclude that the chromium concentration in wood biomass subjected to steam explosion, independently of the temperature and time of pretreatment, doubled or tripled, comparing with the concentration of this metal in native wood and in distilled water. The average concentration of chromium in liquid fraction oscillated between 26.0-29.0 ppm, independently of the steam explosion temperature and heating temperature residential time.

The data provided by Zielenkiewicz et al. (2016) indicate that the concentration of chromium in a native wood of 2.5-year-old *Populus trichocarpa* amounted to 11 ppm, which is consistent with the data obtained for a native wood of 5-year-old *Populus trichocarpa* (10.0 ppm). The average

concentration of chromium in the wood biomass of the 5-year-old *Populus trichocarpa* after the LHW process with residential times of 15 and 60 min it was similar to its concentration in wood biomass after steam explosion, and fell in the range between 17.0 ppm and 41.0 ppm (Fig. 1).
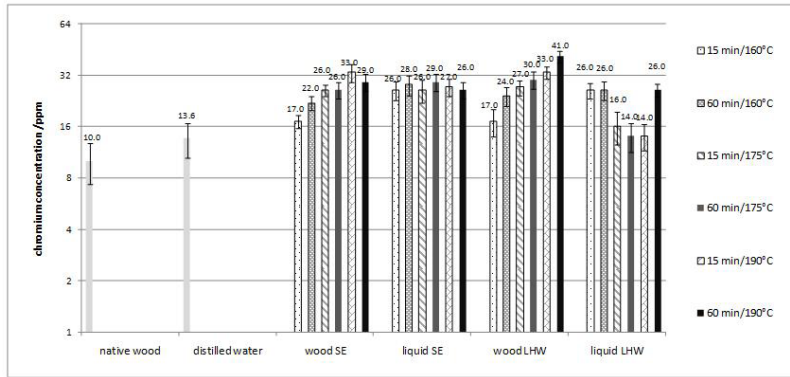

Fig. 1: Chromium concentration in native wood of a 5-year-old Populus trichocarpa, in wood after high temperature pretreatments (SE and LHW) with different residential times (15 and 60 min), in distilled water and in liquid fraction obtained after above pretreatments.

In the wood biomass of a 2.5 year-old *Populus trichocarpa* subjected to steam explosion at the temperatures of 160°C and 190°C, the concentration of chromium was 17 ppm and 32 ppm, respectively. In the wood biomass of a 5 year-old *Populus trichocarpa* subjected to steam explosion at the temperatures of 160°C, 175°C and 190°C, the average concentration of chromium was from 17.0 ppm to 33.0 ppm, in both heating times: 15 and 60 min. To sum up, it can be concluded that both native wood and wood biomass after steam explosion have a low concentration of chromium. Similarly, in the liquid fraction obtained after SE and LHW, the average concentration of this element fell in the range between 14.0 ppm and 29.0 ppm (Fig. 1).

On the basis of data presented in Fig. 2, it can be concluded that the concentration of nickel in the wood of the 5-year-old *Populus trichocarpa* and wood biomass after high temperature treatment was similar to the chromium concentration (Fig. 1). In wood biomass after steam explosion at the temperatures of 175°C and 190°C, with residential times of 15 and 60 min, the average concentration of nickel was two and three times higher than its average concentration in native wood or in distilled water, and fell in the range between 34.0 ppm and 51.0 ppm. According to Zielenkiewicz et al. (2016), in the wood biomass of a 2.5 year-old *Populus trichocarpa* subjected to steam explosion at the temperatures of 160°C and 190°C, with residential times of 15 and 60 min, the concentration of nickel amounted to 16 ppm and 40 ppm, respectively. For the liquid fraction obtained after steam explosion treatment of the wood biomass of a 5-year-old *Populus trichocarpa* at the temperatures of 160°C, 175°C and 190°C, with residential times of 15 and 60 min, the average concentration of nickel fell in the range between 38.0 ppm and 41.0 ppm (Fig. 2). Similarly to the concentration of chromium and nickel, the average concentration of copper in the native wood of a 5-year-old *Populus trichocarpa* was low and amounted to 14.0 ppm (Fig. 3).
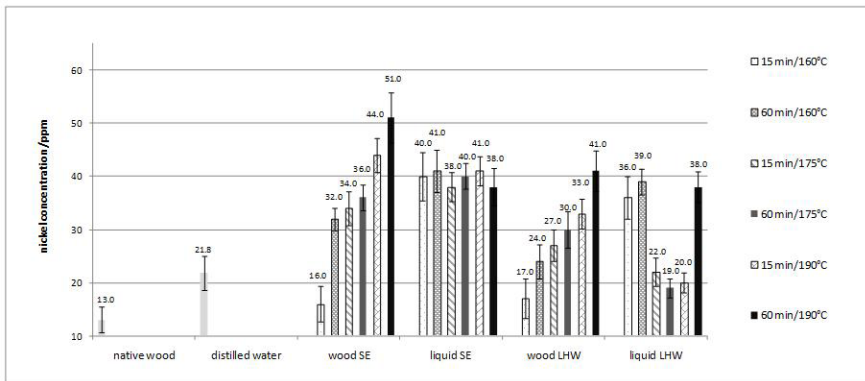
Fig. 2: Nickel concentration in native wood of a 5-year-old Populus trichocarpa, in wood after high temperature pretreatments (SE and LHW) with different residential times (15 and 60 min), in distilled water and in liquid fraction obtained after above pretreatments.
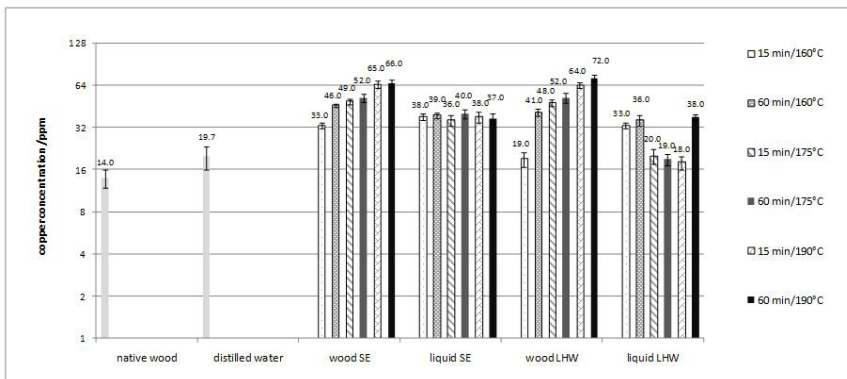

Fig. 3: Copper concentration in native wood of a 5-year-old Populus trichocarpa, in wood after high temperature pretreatments (SE and LHW) with different residential times (15 and 60 min), in distilled water and in liquid fraction obtained after above pretreatments.

Also according to Zielenkiewicz et al. (2016), the concentration of copper in the wood of a 2.5-year-old *Populus trichocarpa* amounted to 12 ppm and its concentration increased 6-fold in the biomass after steam explosion treatment at 130°C, 3-fold after the treatment at 160°C, and 5-fold after the treatment at 190°C. On the basis of data presented in Fig. 3, we can see that the copper average concentration in wood biomass subjected to pretreatment with SE and LHW, with residential times of 15 and 60 min, at the temperature of 190°C increased 4- and 5-fold comparing to its average concentration in native wood and increased 3-fold comparing to its average concentration in distilled water. The average concentration of copper in the liquid fraction changed irregularly together with the increase of process temperature and residential time during which the heating temperature was maintained.

Fig. 4 presents data concerning the concentration of manganese in the native wood of a 5-year-old *Populus trichocarpa*, in biomass after SE and LHW processes, as well as in distilled water and in the liquid fraction. The native wood of the 5-year-old *Populus trichocarpa* had

a manganese average concentration of 118.0 ppm, which was similar to its concentration in the wood of a 2.5-year-old *Populus trichocarpa*, amounting to 120 ppm (Zielenkiewicz et al. 2016). The average concentration of manganese in wood biomass after pretreatment with steam explosion, independently of the temperature and the residential time, did not change, while wood biomass after LHW contained about 10% more of manganese comparing to its average concentration in native wood. In the liquid fraction obtained after pretreatment processes of wood biomass and in distilled water, the manganese average concentration was low and fell in the range between 12.0 ppm and 31.0 ppm (Fig. 4).
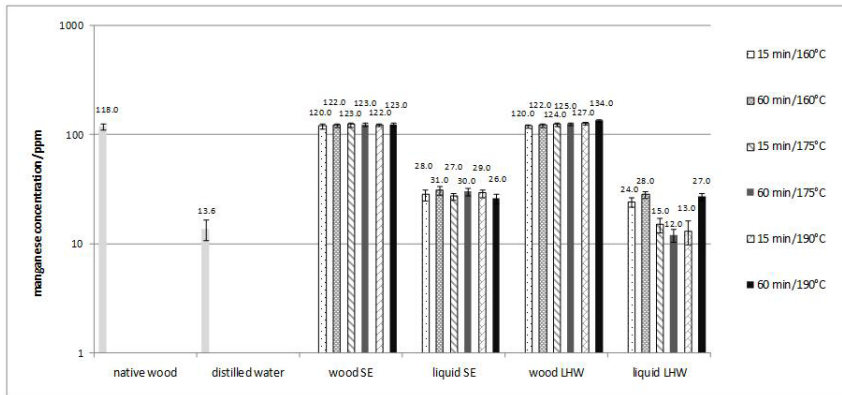

Fig. 4: Manganese concentration in native wood of a 5-year-old Populus trichocarpa, in wood after high temperature pretreatments (SE and LHW) with different residential times (15 and 60 min), in distilled water and in liquid fraction obtained after above pretreatments.

The average concentration of zinc in the native wood of a 5-year-old Populus trichocarpa amounted to 155.0 ppm (Fig. 5) and was similar to its concentration in a 2.5-year-old *Populus trichocarpa*, where it amounted to 160 ppm (Zielenkiewicz et al. 2016). The concentration of zinc in wood biomass after SE and LHW processes increased together with the increase in process temperature and residential time, from about 10% to about 30%.
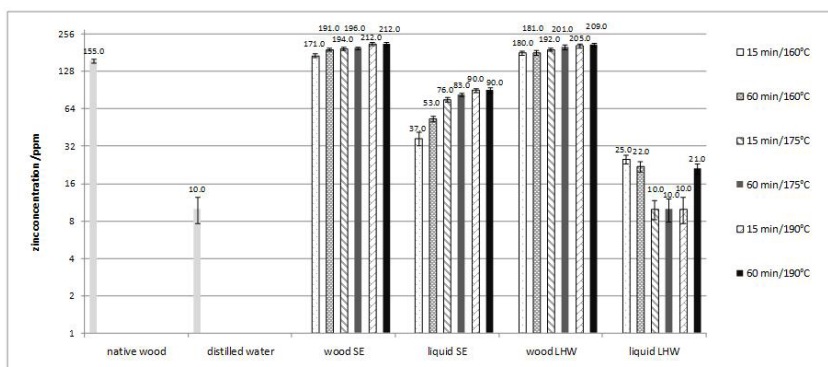

Fig. 5: Zinc concentration in native wood of a 5-year-old Populus trichocarpa, in wood after high temperature pretreatments (SE and LHW) with different residential times (15 and 60 min), in distilled water and in liquid fraction obtained after above pretreatments.

According to Zielenkiewicz et al. (2016), the wood biomass of a 2.5 year-old *Populus trichocarpa* subjected to steam explosion at the temperature of 130°C, with residential time of 15 min, the concentration of zinc increased two-fold comparing to its concentration in native wood; while after the process at 160°C it did not change; and it increased by 20% after the steam explosion process at 190°C. On the other hand, the concentration of zinc in the liquid fraction, generated as a result of pretreatment of wood biomass of a 5-year-old *Populus trichocarpa* both with SE and LHW, changed irregularly together with the increase in process temperatures and residential time during which the heating temperature was maintained.

On the basis of data presented in Fig. 6, we can conclude that the average concentration of iron in the wood of a 5-year-old *Populus trichocarpa* was low and amounted to 54.0 ppm. The iron average concentration in wood biomass after pretreatment processes (SE and LHW) at the temperatures of 160°C, 175°C and 190°C, with residential times of 15 and 60 minutes, grew from about 24 to 28 times, comparing to the iron average concentration in native wood. On the other hand, the average concentration of iron in the liquid fraction, generated as a result of pretreatment of wood biomass of a 5-year-old *Populus trichocarpa* both with SE and LHW, was low, as in distilled water, between 16.0 ppm and 40.0 ppm. On the basis of the presented data, it can be concluded that during the SE and LHW pretreatment processes, wood biomass absorbed the iron that passed from the pretreatment equipment to the solution due to high temperatures. The data obtained are in line with the findings of Zielenkiewicz et al. (2016), suggesting that the wood biomass of a 2.5 year-old *Populus trichocarpa* subjected to steam explosion at the temperatures of 130°C, 160°C and 190°C, without maintaining the heating temperature, contained a 43-times and 24-times higher iron concentration than the native wood.
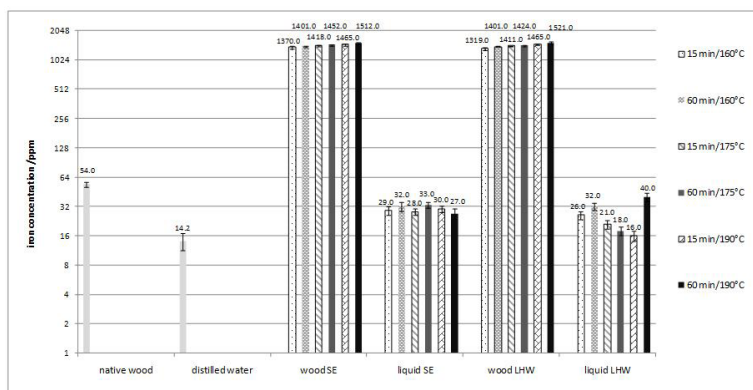

Fig. 6: Iron concentration in native wood of a 5-year-old Populus trichocarpa, in wood after high temperature pretreatments (SE and LHW) with different residential times (15 and 60 min), in distilled water and in liquid fraction obtained after above pretreatments.

According to Roberge (1999), an increase in the content of metallic elements in wood biomass is caused by the corrosion process of the equipment used for pretreatment by high temperature hydrolysis and steam explosion and the contact of steel with substances released from wood biomass during these processes. The raw lignocellulosic biomass is prone to absorb heavy metals (Kord and Kord 2011).

Out of all the tested elements that can inhibit the bioethanol production process (chromium, nickel, copper and iron), the biggest variations happened in case of the concentration of iron

in wood biomass, both after SE and LHW, independently of the process temperature and its residential time.

On the other hand, the average concentration of iron in the liquid fraction generated during the SE and LHW pretreatment processes of a 5-year-old *Populus trichocarpa*, with residential times of 15 and 60 min, was low and fell in the range between 16.0 ppm and 40.0 ppm.

CONCLUSIONS

The average concentration of all the tested elements that can inhibit the bioethanol production process (chromium, nickel, copper and iron) was quite low in native wood and ranged between 10.0 ppm and 54.0 ppm. The average concentration of manganese and zinc in the native wood was higher, at the level of 118.0 ppm and 155.0 ppm, respectively.

The concentration of iron in wood biomass of the 5-year-old *Populus trichocarpa* after pretreatment processes of SE and LHW at the temperatures of 160°C, 175°C and 190°C, with residential times of 15 and 60 min, increased from about 24 to 28 times, comparing to its average concentration in native wood. This means that during the pretreatment process, wood biomass absorbed iron that passed from the pretreatment equipment to the solution due to high process temperatures. The iron is an element considered to be a potential inhibitor in bioethanol production technology. The average concentrations of the tested elements: chromium, nickel, copper, zinc, manganese and iron, in the liquid fraction obtained during the pretreatment of wood biomass of a 5-year-old *Populus trichocarpa* in SE and LHW processes, with residential times of 15 and 60 min, were low and fell in the range between 10.0 ppm and 90.0 ppm.

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