



# Effect of steam explosion pretreatment on chosen saccharides yield and cellulose structure from fast-growing poplar (*Populus deltoides* × *maximowiczii*) wood

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## Abstract

The aim of this study was to determine the changes occurring in the wood cellulose of the fast-growing poplar (*Populus deltoides* × *maximowiczii*) under the influence of steam explosion (SE) pretreatment. Cellulose from native wood and after pretreatment at 160 and 205 °C was isolated. Cellulose polymerization degree by size exclusion chromatography (SEC) and cellulose crystallinity index by Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR) were determined. The profiles of sugars in the native wood and in the solid fraction after pretreatment (using the acid hydrolysis method) were also determined. In addition, the profile of monosaccharides in the liquid fraction obtained after steam explosion and in the liquid fraction after acid hydrolysis of the oligosaccharides were investigated using high-performance liquid chromatography (HPLC). This allowed to determine the change in the yield of hexoses and pentoses in the studied material.

The behavior of cellulose in wood subjected to steam explosion at 160 and 205 °C and isolated by the Kürschner–Hoffer method was studied by determining the absorption bands of FTIR-ATR spectra. The lateral order index (LOI) of cellulose was calculated from the ratio of the intensity of the corresponding absorption bands  $A_{1422}/A_{896} \text{ cm}^{-1}$ . Total crystallinity index (TCI) of cellulose was calculated from the ratio of the intensity of absorption bands  $A_{1372}/A_{2900} \text{ cm}^{-1}$ . TCI of Kürschner–Hoffer cellulose isolated from wood subjected to steam explosion at 160 and 205 °C decreased by 5.6 and 5.0%, respectively, with regard to the applied temperature. LOI increased in cellulose isolated from wood subjected to steam explosion at 160 °C (by 0.7%) and at 205 °C (by 19.2%) in relation to the index of cellulose isolated from native wood. Kürschner–Hoffer cellulose isolated from wood subjected to steam explosion at 160 and 205 °C exhibited, respectively, a reduced degree of polymerization of about 11% and about 8%. Polydispersity index in Kürschner–Hoffer cellulose was 1% lower after both pretreatments than native sample.

## Introduction

The wood biomass is a lignocellulosic complex consisting of glucose-based polysaccharide chain polymers—cellulose, pentose- and hexose-based polymers—hemicelluloses and aromatic polymer-like molecules—lignin (Ralph et al. 2008; Hendriks and Zeeman 2009). Both polysaccharides and lignin are the building materials of cell walls, and besides them there are extractives with different functions and separable using appropriate solvents.

The cellulose molecule is composed of  $\beta$ -D-glucopyranose mers linked by  $\beta$ -1,4-glucosidic bonds (Fengel and Wegener 2003; Klemm et al. 2005). The di-anhydro-D-glucopyranose form a mer repeating n-times in the cellulose molecule, accounting for its degree of polymerization. In the formula of the cellulose molecule, the two extreme glucosidic rings differ from the others, at the fourth carbon atom the –OH group is characterized by reducing properties, and at the first carbon it does not have these properties.

In wood, the degree of polymerization of cellulose is even about 15,000, and its average degree of polymerization varies from 9000 to 10,000 (Goring and Timell 1962; Fengel and Wegener 2003).

Under the influence of physico-chemical and mechanical factors acting on wood, the degree of polymerization of cellulose is significantly reduced. The action of high temperatures on cellulose causes a decrease in its degree of polymerization (Radomski et al. 2010; Antczak et al. 2016; Kučerová et al. 2016a, b; Zawadzki et al. 2016).

If cellulose molecules are arranged parallel to each other at small distances, then they are connected to each other by intermolecular hydrogen bonds. Hydrogen bonds are a form of association between a highly electronegative atom and a hydrogen atom bound by a covalent bond to an electronegative atom. In the cellulose molecule, the electronegative atom is an oxygen atom.

Currently, cellulose is assigned a crystalline-amorphous structure, containing crystalline and amorphous regions. Two cellulose molecules pass through a series of crystalline (oriented) areas, where the cellulose molecules are arranged parallel to each other, and areas of less oriented molecules (amorphous areas). In addition to crystalline and amorphous areas, paracrystalline areas characterized by an intermediate structure between crystalline and amorphous areas may be present in cellulose (Atalla 1993).

Several crystallographic variations of cellulose are known and are numbered with Roman numerals. Cellulose I is found in natural fibers and in this structure the cellulose molecules are arranged in parallel layers. The molecules in each layer are held together by hydrogen bonds, and the cohesion of adjacent layers is maintained by van der Waals forces. Cellulose II is the most thermodynamically stable type of cellulose and is mainly obtained from cellulose I, by mercerization (alkali treatment and regeneration, solubilization and subsequent recrystallization). Cellulose III and Cellulose IV can be formed from cellulose I and II, respectively, by treatment with liquid ammonia and reaction is reversible (Hayashi et al. 1975). Cellulose V and cellulose VI can be obtained by heating cellulose III and IV, respectively (Gardiner and Sarko 1985).

Glucose is a simple sugar formed mainly by the hydrolysis of cellulose, although a small amount is associated with the presence of heterogeneous hemicelluloses.

Cellulose, due to its crystalline-amorphous structure, is characterized by the difficult property of being stiff and elastic at the same time. High degree of crystallinity negatively influences its hydrolysis process. In contrast, amorphous cellulose exhibits from 3 to 30 times the efficiency of this process with respect to crystalline cellulose (Lynd et al. 2002). The crystalline areas of cellulose are resistant to chemicals and to the process of hydrolysis, and this occurs in the amorphous areas (Zhu et al. 2008). They are also temperature resistant, with the process in amorphous areas occurring above 150 °C and in crystalline areas above 180 °C (Yu et al. 2010). In the available literature there is a scarce information about using FTIR-ATR method to crystallinity analysis of cellulose from fast-growing poplars wood in a context of bioethanol production. Hence, in this respect the use of the above method to study the crystallinity can be interesting and noteworthy.

In wood, the polysaccharides accompanying cellulose are hemicelluloses, the molecules of which can be built from monomers of homogeneous and heterogeneous simple sugars. The most common monomers in hemicelluloses molecules are pentoses:  $\beta$ -D-xylopyranose,  $\alpha$ -D-arabinofuranose and hexoses:  $\beta$ -D-mannopyranose,  $\beta$ -D-glucopyranose,  $\beta$ -D-galactopyranose (Kačík and Solár 2000; Radomski et al. 2010). In this group of polysaccharides can be distinguished pentosans and hexosans and polyuronides. Among the pentosans, the main polysaccharide is xylan, whose molecule is built from  $\beta$ -D-xylopyranose residues, linked by an oxygen bridge 1,4. On average, seven out of ten D-xylopyranose units have acetyl groups in the C-2 or C-3 position, and every tenth unit is attached by a substituent 4-O-methylglucuronic  $\alpha$ -1,2 bond (Fengel and Wegener 2003).

Hemicelluloses show less resistance to physico-chemical agents compared to cellulose. They dissolve in alkaline media and hydrolyze more readily when exposed to dilute acids, and they degrade at range from 160 to 220 °C (Boonstra et al. 2007; Antczak et al. 2019, 2022).

Steam explosion is a physical and chemical method for pretreatment of lignocellulosic biomass (Brownell et al. 1986; Balan et al. 2020; Mankar et al. 2021). This method combines mechanical treatment with chemical treatment caused by wood autohydrolysis. The autohydrolysis of wood involves acetyl groups present in hemicelluloses and the water environment, which under conditions of elevated temperature and pressure have an action similar to that of acids. Autohydrolysis at elevated temperature results in reduction of hemicelluloses and plasticization of lignin, which forms a complex with hemicelluloses. This results in exposing the cellulose structure and reducing its degree of polymerization (Alvira et al. 2010; Tomás-Pejó et al. 2014; Kučerová et al. 2020). The polymerization degree of cellulose is a key parameter influencing the enzymatic hydrolysis of lignocellulosic biomass (Karimi and Taherzadeh 2016). It is known, that the shorter cellulose chains are more reactive to the enzymes, because the shorter chains contain lower hydrogen bonds and are more accessible to enzymes. Additionally, the reduction of cellulose polymerization degree by a pretreatment process causes a formation of more cellulose ends available to the exoglucanase. Based on literature information (Yang et al. 2011) no clear relation has been observed between polymerization degree of cellulose and

enzymatic hydrolysis yield. Hence, the research undertaken in this area is still valid and worth attention (Chandra et al. 2007).

The aim of this study was the investigation of glucose and xylose yields from *Populus deltoides* × *maximowiczii* wood before and after steam explosion pretreatment. Additionally, the polymerization degree of cellulose, polydispersity and total crystallinity index (TCI) and lateral order index (LOI) were studied.

## Materials and methods

### Materials

Wood of *Populus deltoides* × *maximowiczii* was obtained from 5-year-old stems cut at the end of the growing season and grown on plantations of the Department of Plant Genetics, Breeding and Biotechnology, Faculty of Horticulture, Biotechnology and Landscape Architecture, Warsaw University of Life Sciences, located in Wolica (52°08'42''N, 21°04'07''E). The wood was debarked and then chipped on a laboratory cutting mill. Tests were conducted on wood shavings with a fraction of the 0.43–1.02 mm fraction. They were dried to a moisture content of 5%, and before being pretreated with a steam explosion they were moistened to remove air from the wood pores. The weighed wood shavings were placed in a beaker and flooded with distilled water to 220 cm<sup>3</sup> by placing the beaker on a magnetic stirrer with a heating plate, heating to 90 °C for 20 min. Pretreatment by steam explosion was carried out in a high-pressure autoclave with a capacity of 250 cm<sup>3</sup>, made of acid-resistant steel (Antczak et al. 2022; Gałązka and Szadkowski 2021). Pretreatment with a steam explosion was carried out at 160 and 205 °C, without maintaining the temperature (once the target temperature was reached, there was a quick decompression of the system). Three repetitions were performed for every process temperature. The native material, the solid fraction obtained after steam explosion treatment at 160 and 205 °C, and the liquid fraction formed after pretreatment at both temperatures were used for chemical determinations. The pretreatment was carried out at the Department of Wood Science and Wood Protection, Warsaw University of Life Sciences in Poland. Chemical determinations were made at the Technical University in Zvolen, Slovakia. For this purpose, samples of the solid fraction were packed tightly into plastic containers and the resulting liquid fraction was frozen. The tightly packed material was transported between units and prepared there for further determinations.

### Methods

#### Acid hydrolysis of native wood and solid fraction obtained after pretreatment

In order to determine the yield of monosaccharides (glucose and xylose as the most promising for the production of biofuels from lignocellulosic materials), acid hydrolysis of wood before pretreatment and the solid fraction formed after pretreatment by

steam explosion at 160 and 205 °C was carried out. Wood samples before and after steam explosion pretreatment were dried to constant weight at  $104 \pm 1$  °C. Then, 0.1 g of the sample was placed in a 50 cm<sup>3</sup> flask and flooded with 1 cm<sup>3</sup> of 72% sulfuric acid (VI) (H<sub>2</sub>SO<sub>4</sub>) (Chempur, Gliwice, Poland). The samples were heated for 1 h at 30 °C. After adding 28 cm<sup>3</sup> of distilled water, they were heated for 2 h at 120 °C in an oil bath (glycerin, Agroekolab, Zvolen, Slovakia), and then cooled to room temperature. The hydrolysates were quantitatively poured into 50 cm<sup>3</sup> volumetric flasks and made up to the mark with distilled water. From the solutions obtained, 5 cm<sup>3</sup> of each were taken and transferred to beaker and neutralized with barium carbonate (BaCO<sub>3</sub>) to neutral pH, added 1 cm<sup>3</sup> of 5% cellobiose solution (an internal standard), it was filtered and washed with distilled water. The prepared samples were evaporated on a vacuum evaporator (Laborota 4000, Schwabach, Germany). Then the precipitate obtained was dissolved in 1 cm<sup>3</sup> of ultrapure water and filtered through a nylon filter with a pore diameter of 0.25 μm and subjected to HPLC (high-performance liquid chromatography) analysis (Kačík and Solár 2000; Kučerová and Výbohová, 2018; Kučerová et al. 2020). Each of the chemical determinations was carried out with triplicate, and standard deviations were determined.

### Direct analysis of liquid fraction obtained after pretreatment

The determination of free monosaccharides (glucose and xylose) in the liquid fraction obtained after steam explosion at 160 and 205 °C was carried out by taking 5 cm<sup>3</sup> of the solution, which was transferred to a conical flask, adding 1 cm<sup>3</sup> of 5% cellobiose solution as an internal standard. After neutralization with BaCO<sub>3</sub> to neutral pH, the solution was evaporated on a vacuum evaporator (Laborota 4000, Schwabach, Germany) to obtain a precipitate. The precipitate was dissolved in 1 cm<sup>3</sup> of ultrapure water and filtered through a 0.25 μm pore diameter nylon filter and analyzed by HPLC (Kačík and Solár 2000; Kučerová and Výbohová, 2018; Kučerová et al. 2020). Each of the chemical determinations was carried out with triplicate, and standard deviations were determined.

### Acid hydrolysis of liquid fraction obtained after pretreatment

In order to analyze the total yield of glucose and xylose in the liquid fraction obtained after pretreatment of *Populus deltoides* × *maximowiczii* wood subjected to steam explosion at 160 and 205 °C, assuming the presence of oligosaccharides in this liquid, their hydrolysis was performed. For this purpose, 20 cm<sup>3</sup> of solution was taken by placing in 50 cm<sup>3</sup> spherical flasks. 0.42 cm<sup>3</sup> of 96% sulfuric acid (VI) was added to the solution and placed under a reflux condenser above the hob for 4 h (the liquid boils). Then the solution was quantitatively transferred into 25 cm<sup>3</sup> volumetric flasks and made up to the mark with distilled water. From the solutions obtained, 5 cm<sup>3</sup> of each was taken and transferred to a beaker and neutralized with BaCO<sub>3</sub> to neutral pH, 1 cm<sup>3</sup> of 5% cellobiose solution (an internal standard) was added, then filtered and washed with distilled water. The prepared samples were evaporated on a vacuum evaporator (Laborota 4000, Schwabach, Germany). Then the precipitate obtained was dissolved in 1 cm<sup>3</sup> of ultrapure water and filtered through a nylon

filter with a pore diameter of 0.25  $\mu\text{m}$  and subjected to HPLC analysis (Kučerová and Výbohová, 2018; Kučerová et al. 2020). Each of the chemical determinations was carried out in triplicate, and standard deviations were determined.

### HPLC analysis of monosaccharides

Determination of glucose and xylose yield was carried out with an Agilent 1200 HPLC (Agilent Technologies, CA, USA) with a Benson BP-800 Pb column (Benson Polymeric Inc., Reno, NV, USA) at 80 °C, flow rate of 0.6  $\text{cm}^3/\text{min}$  and using refractive index detector. The mobile phase was ultrapure water. All analysis was performed four times per sample, and single standard deviations were calculated (Kačík and Solár 2000; Antczak et al. 2022).

### SEC analysis of cellulose isolated from native wood and solid fraction obtained after pretreatment

The degree of cellulose polymerization was measured by size exclusion chromatography (SEC) method. Cellulose samples were isolated using the Kürschner–Hoffer method (three cycles of a mixture of ethanol and nitric acid (V) were used to obtain cellulose) (Saeman et al. 1954; Krutul 2002; Gałazka and Szadkowski 2021) from native wood and solid fraction obtained after SE pretreatment. Before cellulose isolation, the samples were previously extracted with a chloroform-ethanol (93:7)<sub>w/w</sub> mixture (Antczak et al. 2006). Molecular weight distribution analysis of the cellulose samples was performed after their conversion into cellulose tricarbonylates (Kučerová et al. 2016a, b; Čabalová et al. 2009; Kačík et al. 2009). Cellulose tricarbonylates were dissolved in tetrahydrofuran and filtered through a Puradisc 25 NYL filter (Whatman International) with a pore size of 0.45  $\mu\text{m}$ . SEC analysis using a DAD detector was performed at 35 °C with tetrahydrofuran at a flow rate of 1  $\text{cm}^3/\text{min}$  on a two connected PLgel, 10  $\mu\text{m}$ , 7.5  $\times$  300 mm, MIXED-B columns (Agilent Technologies) preceded by a PLgel, 10  $\mu\text{m}$ , 7.5  $\times$  50 mm, Guard-column (Agilent Technologies). Data acquisitions were carried out with ChemStation software (Agilent Technologies) and calculations were performed with the Clarity GPC module (Data Apex). Numerical outputs were obtained for  $M_n$  (the number average molar mass),  $M_w$  (the weight average molar mass) and the values were recalculated to underivatized cellulose using Eqs. (1, 2).

$$M_w(\text{underivatized cellulose}) = M_w(\text{derivatized cellulose}) \cdot k \quad (1)$$

$$M_n(\text{underivatized cellulose}) = M_n(\text{derivatized cellulose}) \cdot k \quad (2)$$

where  $k = \frac{162 \text{ g mol}^{-1}}{519 \text{ g mol}^{-1}}$

Degree of polymerization ( $\text{DP}_w$ ) values were calculated by dividing the weight average molar mass of cellulose by the monomer equivalent mass of anhydroglucose using Eq. (3).

$$DP_w = \frac{M_w}{162} \quad (3)$$

Polydispersity index (PDI) of cellulose was calculated as the ratio of the weight average molar mass to the number average molar mass using Eq. (4).

$$PDI = \frac{M_w}{M_n} \quad (4)$$

Measurements were performed four times per sample, and single standard deviations were calculated.

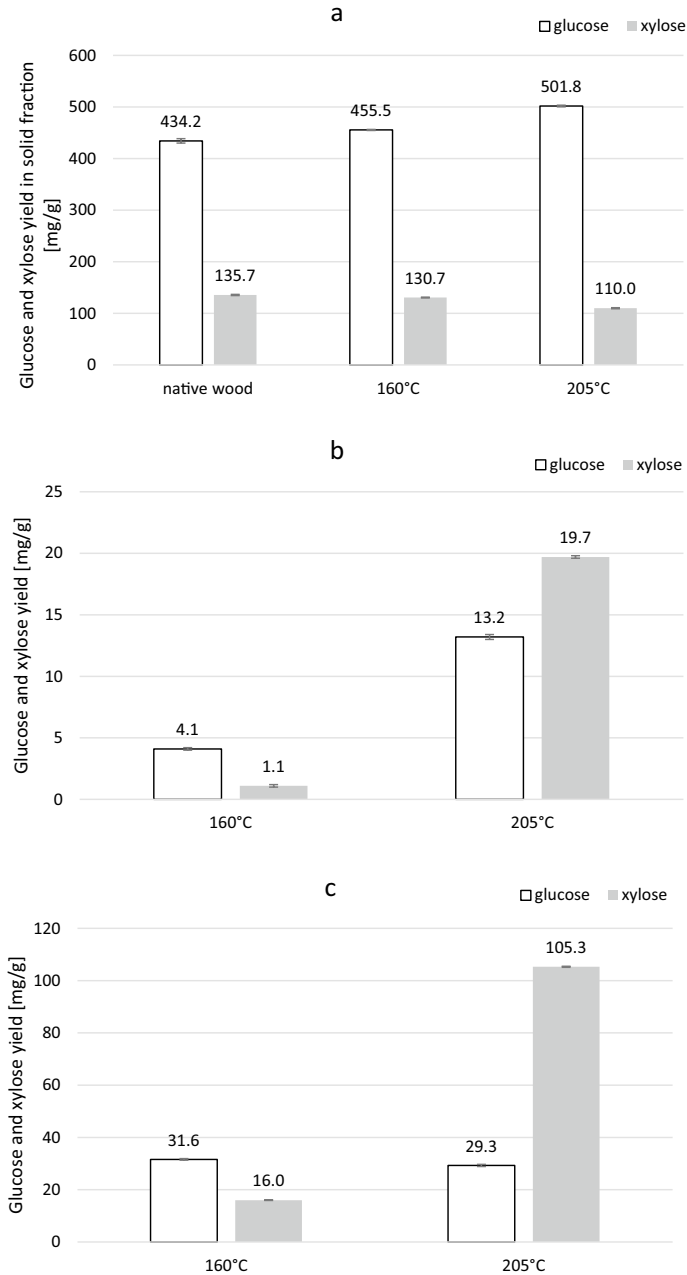
### FTIR-ATR analysis

Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR) spectra of native wood, solid fractions obtained after SE pretreatment and cellulose isolated from these materials were recorded on Nicolet iS10 FTIR spectrometer equipped with Smart iTR attenuated total reflectance (ATR) sampling accessory with diamond crystal (Thermo Fisher Scientific, Madison, WI, USA). Spectra were measured in the wavenumber range from 4000 to 650  $\text{cm}^{-1}$ . A resolution of 4  $\text{cm}^{-1}$  and 32 scans per sample were used. Measurements were performed on six replicates per sample and average spectra were created and evaluated. The obtained spectra of the wood samples were normalized at 1031  $\text{cm}^{-1}$ . The OMNIC 8.0 software (Thermo Fisher Scientific, Madison, WI, USA) was used to evaluate the spectra (Kačík and Solár 2000; Výbohová et al. 2018).

## Results and discussion

The glucose and xylose yield obtained after acid hydrolysis of native wood and SE pretreated solid fractions is presented in Fig. 1a. On the basis of the data presented in Fig. 1a, it can be concluded that the steam explosion process of *Populus deltoides* × *maximowiczii* wood, compared to native wood, increased the glucose yield from 434.2 to 455.5 mg/g (160 °C) and 501.8 mg/g (205 °C), respectively. However, the xylose yield decreased after pretreatment from 135.7 to 130.7 mg/g (160 °C) and 110.0 mg/g (205 °C).

Glucose is a simple sugar formed mainly by the hydrolysis of cellulose, although a small amount of glucose content is related to its presence in heterogeneous hemicelluloses, i.e., glucomannan. During the pretreatment process of *Populus deltoides* × *maximowiczii* wood, some saccharides pass into the post-reaction liquid. Figure 1b shows the data of glucose and xylose yield in the liquid fraction obtained after SE of wood at 160 and 205 °C. From the data shown in Fig. 1b, it can be seen that the glucose yield in the post-reaction liquid obtained at 205 °C was over three times higher with respect to its yield in the post-reaction liquid obtained at 160 °C. In contrast, the xylose yield in the post-reaction liquid obtained at 205 °C was about



**Fig. 1** **a** Glucose and xylose yield in native wood and solid fraction obtained after SE; **b** Glucose and xylose yield in the liquid fraction obtained after SE; **c** Glucose and xylose yield in the liquid fraction obtained after SE and acid hydrolysis



eighteen times higher with respect to its yield in the post-reaction liquid obtained at 160 °C.

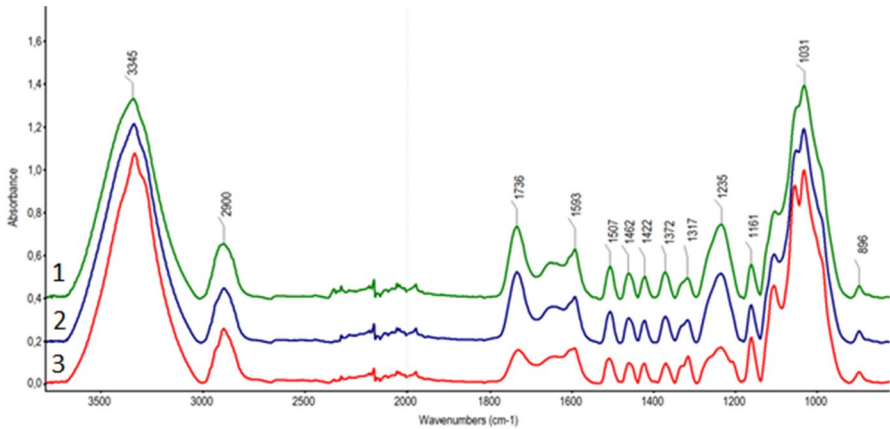
The total glucose and xylose yield was obtained by concentrating the post-reaction liquid and then hydrolyzing it with 72% H<sub>2</sub>SO<sub>4</sub>. The data presented in Fig. 1c show that the total yield of glucose in the liquid fraction obtained after wood pretreatment did not differ significantly from each other and was 31.6 mg/g (160 °C) and 29.3 mg/g (205 °C), respectively. On the other hand, the total xylose yield increased almost seven times when wood was pretreated at 205 °C with respect to its total yield (16.0 mg/g) in the liquid fraction obtained at 160 °C. The data obtained are consistent with the results of Carvalho et al. (2008).

The data of Marchwicka et al. (2015) showed that the glucose content of 3-year-old *Populus deltoides* × *maximowiczii* subjected to enzymatic hydrolysis at 24, 72, 150, 216 and 360 h without pretreatment increased gradually from 11.1 to 14.6%. On the other hand, if the wood was pretreated followed by enzymatic hydrolysis using the above-mentioned times, the glucose content also increased gradually and was from 15.6 to 24.1%. The increase in glucose content in wood subjected to steam explosion followed by enzymatic hydrolysis ranged from 28 to 40% compared to the control wood. From the data of Antczak et al. (2014), the glucose content of the wood of *Populus deltoides* × *maximowiczii* after extraction in chloroform-ethanol (93:7)<sub>w/w</sub> mixture and acid hydrolysis was 40.9%. From the above data, it can be concluded that the glucose yield from wood depends on the conditions and processes to which it is subjected.

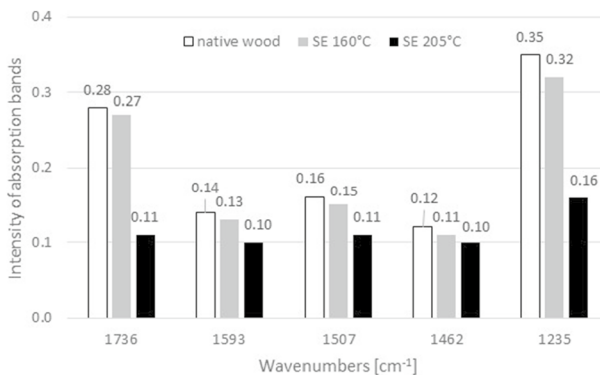
The xylose content after treatment of *Populus deltoides* × *maximowiczii* wood is related to its xylan content, although it also occurs as a component of e.g., glucuronoxylan. Hemicelluloses under steam explosion treatment at 205 °C are degraded and transformed to liquid and gaseous products.

Analyzing the results presented in Fig. 1b, c it can be seen that the SE pretreatment produces oligosaccharides which are not detectable under the applied conditions by HPLC analysis without additional acid hydrolysis. The total glucose yield after acid hydrolysis in the liquid fraction obtained at 160 °C was almost eight times higher and at 205 °C about twice higher than the yield of this sugar in the liquid fraction without additional acid hydrolysis. On the other hand, the total yield of xylose in the post-reaction liquid obtained at 160 °C after acid hydrolysis was over fourteen times higher and at 205 °C was over five times higher than the yield of this sugar in the liquid fraction without acid hydrolysis. Comparing the results shown in Fig. 1a, b, c, it can be observed that hemicelluloses are less heat resistant than cellulose (Rowell 2005; Gawron et al. 2014; Antczak et al. 2022).

One of the methods allowing tracing the changes occurring in the wood of *Populus deltoides* × *maximowiczii* before and after steam explosion at 160 and 205 °C is the analysis of FTIR-ATR (Figs. 2 and 3). The interpretation of FTIR spectra was performed based on the literature (Hon and Shiraiishi 2001; Kubovský et al. 2020; Bhagia et al. 2022). Celluloses isolated by the Kürschner–Hoffer method from native wood and from solid fraction obtained after steam explosion at 160 and 205 °C were used for the analysis. This method was chosen because it degrades cellulose less than the Seifert method and isolated cellulose is purer than cellulose obtained by Cross-Bevan method (Kačík and Solár 2000; Krutul 2002).



**Fig. 2** FTIR-ATR spectra of poplar (*Populus deltoides* × *maximowiczii*): 1—native wood, 2—solid fraction after SE pretreatment at 160 °C and 3—solid fraction after SE pretreatment at 205 °C



**Fig. 3** Relative intensity of selected absorption bands in FTIR spectra of wood samples

During the thermal treatment of wood, several processes take place simultaneously with different effects on the intensity of the absorption band with a maximum in the wavenumber at about 1736 cm<sup>-1</sup>. All components of the wood contribute to the change in the intensity of this band, but in most cases, lignin and hemicelluloses are the most important.

Based on the data of changes in the intensity of the absorbance band at the wavenumber 1736 cm<sup>-1</sup> it can be concluded that in the wood subjected to steam explosion, there was a decrease in the intensity of the absorbance band by 3.6% (160 °C) and 60% (205 °C) (Fig. 3) compared to the wood not subjected to this process, which indicates that at 205 °C xylan degrades more and goes into solution. On the other hand, the data of Výchová et al. (2018) show that during the process of the heat treatment of ash wood there was an increase in the absorbance of this peak.

For aromatic skeletal vibrations plus C=O stretch at  $1593\text{ cm}^{-1}$ , and aromatic skeletal C=C vibrations at  $1507\text{ cm}^{-1}$  the same decrease was detected for both process temperatures. At the temperature of  $160\text{ }^{\circ}\text{C}$  it was 7% for both absorption bands, and at  $205\text{ }^{\circ}\text{C}$  approximately 30%. The action on ash wood temperature 160, 180 and  $200\text{ }^{\circ}\text{C}$  increased the intensity of the peak  $1593\text{ cm}^{-1}$ , which may be due to the relative increase of lignin content in treated wood (Chen et al. 2012; Výchová et al. 2018).

From the above data, it is evident that in *Populus deltoides* × *maximowiczii* wood during high temperature pretreatment, lignin plasticizes and condenses with cellulose and hemicelluloses according to Fengel and Wegener (2003), Hill (2006), Nuopponen et al. (2004), Sun et al. (2016) and Antczak et al. (2018).

The decrease in the intensity of the absorption band at  $1462\text{ cm}^{-1}$ , for aromatic C–H deformation and asymmetric bending of groups  $-\text{CH}_3$  and  $-\text{CH}_2-$  saccharides at process temperatures of 160 and  $205\text{ }^{\circ}\text{C}$  was about 60 and 20% respectively, with respect to native wood, indicating transformation of lignin and polysaccharides.

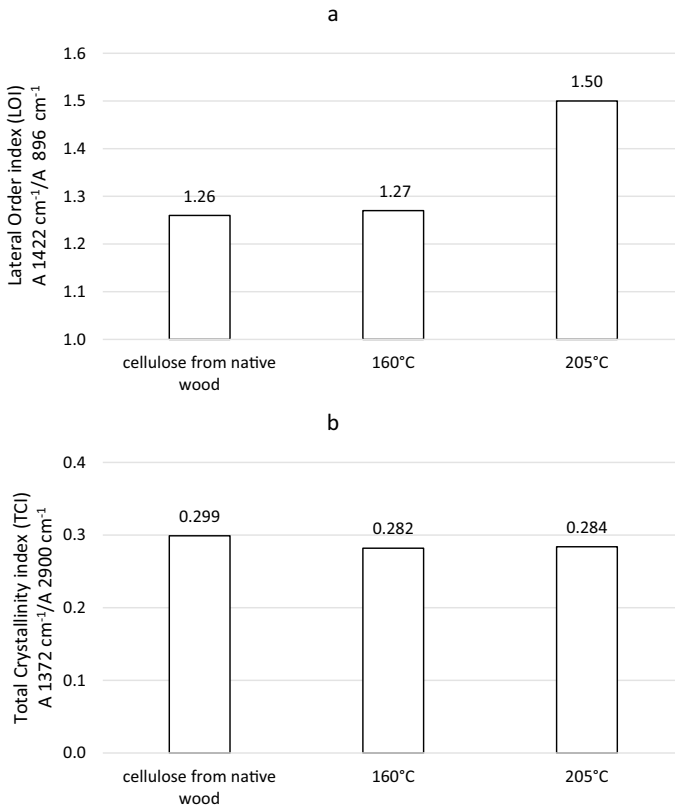
At the wavenumber of  $1235\text{ cm}^{-1}$  for syringyl ring and C–O stretching in lignin and xylan the reduction in intensity of this band in relation to native wood, respectively, to the applied temperature of 160 and  $205\text{ }^{\circ}\text{C}$  in the wood of *Populus deltoides* × *maximowiczii* subjected to the steam explosion was 7 and 53% (Fig. 3).

Based on the above data, it can be concluded that xylan was degraded and passed into solution after pretreatment of wood at  $205\text{ }^{\circ}\text{C}$ , while structural changes occurred in lignin. With increasing temperature, degradation and hydrolysis as well as dissolution of hemicelluloses occur, most of which goes into solution, and at the same time some of them are transformed into gaseous products (Jönsson and Martín 2016; Brethauer et al. 2020; Antczak et al. 2022).

Changes occurring in the cellulose isolated from *Populus deltoides* × *maximowiczii* wood by Kürschner–Hoffer method, subjected to a steam explosion at 160 and  $205\text{ }^{\circ}\text{C}$ , were investigated by analyzing the absorption bands of FTIR-ATR spectra. The cellulose crystallinity index was calculated from absorption bands TCI  $A_{1372}/A_{2900}\text{ cm}^{-1}$  and LOI  $A_{1423}/A_{896}\text{ cm}^{-1}$  (Fig. 4a, b). Band  $2900\text{ cm}^{-1}$  corresponds to stretching vibrations of  $-\text{CH}$  in  $-\text{CH}_2-$  and  $-\text{CH}_3$  groups, while  $1372\text{ cm}^{-1}$  to deformation vibration of C–H in cellulose (Poletto et al. 2012; Geffert et al. 2017). An empirical crystallinity index also known as lateral order index (LOI) was defined as ratio between intensity of the bands at  $1422\text{ cm}^{-1}$  (C–H bending vibrations) and at  $897\text{ cm}^{-1}$  ( $\beta$ -(1–4)-glycosidic bond and C–H deformation vibrations in cellulose) (Nelson and O’Connor 1964; Kumar et al. 2014).

The TCI is proportional to the degree of crystallinity of cellulose in wood and the LOI is correlated to the overall degree of order in the cellulose (O’Connor et al. 1958; Carrillo et al. 2004; Kumar et al. 2014).

Figure 4a shows data as a LOI  $A_{1422}^{-1}/A_{896}\text{ cm}^{-1}$  of Kürschner–Hoffer cellulose, from which it can be concluded that cellulose isolated from *Populus deltoides* × *maximowiczii* wood subjected to steam explosion at  $205\text{ }^{\circ}\text{C}$  was characterized by a 16.1% increase in LOI with respect to the cellulose index from native wood. On the other hand, the cellulose isolated from wood subjected to steam explosion at  $160\text{ }^{\circ}\text{C}$  characterized by a 0.6% increase in LOI with respect to the cellulose isolated from native wood. Based on the results, it can be concluded that the steam explosion



**Fig. 4** **a** Lateral Order Index (LOI)  $A_{1422}/A_{896}$   $\text{cm}^{-1}$ , **b** Total Crystallinity Index (TCI)  $A_{1372}/A_{2900}$   $\text{cm}^{-1}$

pretreatment at 205 °C of *Populus deltoides* × *maximowiczii* wood affected the increase of crystalline regions in cellulose isolated by the Kürschner–Hoffer method.

According to Auxenfans et al. (2017), a native poplar wood exhibited an LOI of  $1.77 \pm 0.4$  and decreased by about 18% after steam explosion of the biomass. From the data presented in Fig. 4a, b, it can be concluded that the changes in cellulose crystallinity index TCI and LOI in *Populus deltoides* × *maximowiczii* wood subjected to steam explosion depended on the applied temperature of the biomass pretreatment process.

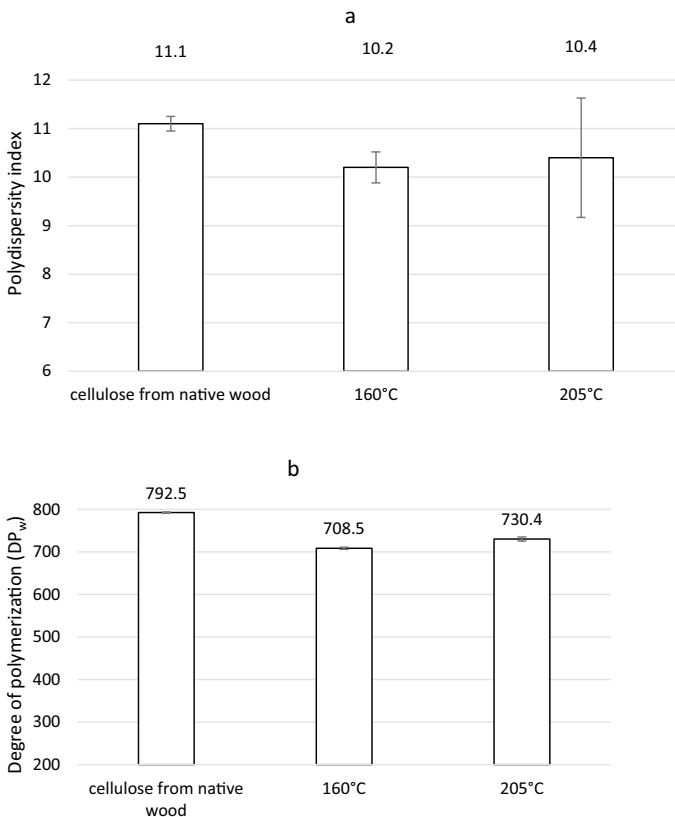
On the basis of the data presented in Fig. 4b, it can be concluded that the total crystalline index of cellulose isolated from wood by the Kürschner–Hoffer method, decreased with a comparable rate in the case of both treatment temperatures, namely approximately by 5%. Geffert et al. (2017) reported that the total crystalline index investigated in steamed beech wood increased by 13.2% compared to native wood. This is probably due to the partial degradation of hemicelluloses and amorphous cellulose regions by the influence of high temperature.

Yildiz and Gümüřkaya (2007) found that cellulose isolated from spruce and beech wood samples treated by thermal modification at 150, 180 and 200 °C by

6 and 10 h was characterized by an increase of TCI and LOI. As a result of these modifications, it was concluded that hemicelluloses and less ordered cellulose deteriorated and as a consequence the degree of cellulose crystallinity increased.

According to the literature and the analyzed data, the impact of a steam explosion on wood at 160 and 205 °C resulted in the degradation of hemicelluloses, cellulose with a lower degree of polymerization, and the degradation and change in the structure of lignin. As a result, the observed change in the total crystallinity index was low.

One of the important characteristics of cellulose is its degree of polymerization. The cellulose with degree of polymerization above 200 (i.e.,  $\alpha$ -cellulose) is characterized by higher resistance to acids, alkalis in comparison to  $\beta$ -cellulose (degree of polymerization around 200) and  $\gamma$ -cellulose (degree of polymerization below 100). Figure 5a shows the polydispersity index data of K urschner–Hoffer cellulose isolated from *Populus deltoides*  $\times$  *maximowiczii* wood before and after steam explosion at 160 and 205 °C. Figure 5b shows the degree of polymerization of cellulose after steam explosion at 160 and 205 °C.



**Fig. 5** **a** Polydispersity index of cellulose, **b** degree of polymerization of cellulose

Figure 5b shows an increase in the share of cellulose with a higher degree of polymerization as the pretreatment temperature increases.

Based on the data presented, it can be concluded that after taking into account the standard deviation, the cellulose isolated from pretreated wood had a similar polydispersity index with respect to the cellulose isolated from native wood. The data obtained are consistent with the results relating to slight changes in the degree of polymerization of cellulose (Alvira et al. 2010; Tomás-Pejó et al. 2011; Sun et al. 2016).

In summary, it can be stated that for cellulose isolated from wood before and after pretreatment by steam explosion at 160 and 205 °C by the Kirschnner–Hoffer method, a slight decrease in TCI was observed for cellulose isolated from wood after pretreatment, while for LOI it increased with increasing treatment temperature. In the case of polydispersity index and degree of cellulose polymerization, a decrease in these parameters was observed for pretreated cellulose relative to the native material. The cellulose isolated from wood after pretreatment at 205 °C had higher polymerization and polydispersity index than the cellulose obtained from wood after treatment at 160 °C.

## Conclusion

Based on the data presented, it can be concluded that:

1. The change in cellulose structure was observed as a result of the pretreatment by steam explosion at 160 and 205 °C applied to *Populus deltoides* × *maximowiczii* wood.
2. Pentosans (xylan) were not resistant to the temperature of 160 and 205 °C used in the steam explosion of wood, hence the xylose yield in the liquid fraction was three times higher than the glucose yield.
3. TCI ( $A_{1372}/A_{1900} \text{ cm}^{-1}$ ) of Kirschnner–Hoffer cellulose isolated from *Populus deltoides* × *maximowiczii* wood subjected to steam explosion at 160 and 205 °C decreased by 5.6 and 5%, respectively, to the applied temperature relative to the crystallinity index of Kirschnner–Hoffer cellulose isolated from native wood.
4. LOI ( $A_{1429}/A_{896} \text{ cm}^{-1}$ ) of Kirschnner–Hoffer cellulose isolated from *Populus deltoides* × *maximowiczii* wood subjected to steam explosion at 205 °C increased by 19% with respect to the index of cellulose isolated from native wood, whereas Kirschnner–Hoffer cellulose isolated from wood subjected to steam explosion at 160 °C did not differ highly in index (LOI) from cellulose isolated from native wood.
5. Kirschnner–Hoffer cellulose isolated from *Populus deltoides* × *maximowiczii* wood subjected to steam explosion at 160 and 205 °C had a reduced degree of polymerization of about 11% and about 8%, respectively, according to the temperature used.
6. Kirschnner–Hoffer cellulose isolated from *Populus deltoides* × *maximowiczii* wood subjected to steam explosion at 160 and 205 °C had a similar polydispersity index with respect to cellulose isolated from native wood.

7. The higher temperature of the steam explosion process results in the decomposition of saccharides with lower degrees of polymerization and crystallinity thus allowing for higher values of these parameters than the process at lowers.

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## Declarations

**Conflict of interest** The article does not contain any conflict of interest.

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