Steam explosion of wood particles from fibreboard and particle board with indirect control by enzymatic hydrolysis

Andrej Pažitný

Pulp and Paper Research Institute, Dúbravská cesta 14, 841 04, Bratislava, Slovak Republic
pazitny@vupc.sk, ORCID: Andrej Pažitný 0000-0003-2269-953X

Abstract: Pretreatment of particles obtained from lignocellulosic materials by steam explosion with indirect control by enzymatic hydrolysis has been studied. The dendromass pretreatment model has been applied for recycled fibreboard and particle board based on softwood. Their structure and chemical composition partly predetermine these lignocellulosic materials consisting of a mixture of spruce and fir particles also for bioethanol production. Optimum steam explosion temperature of 205 °C was determined based on the concentration of total monosaccharides — glucose, xylose and arabinose, among all experimentally prepared hydrolysates. This corresponds to basic conditions for fine disintegration of biomass to lignocellulosic structure with good holocellulose accessibility. Particles obtained from fibreboard and particle board primarily consisting of softwood without steam explosion pretreatment provide relatively low cellulose accessibility for commercial enzymes activity while monosaccharides concentration is partly reduced because of torrefaction at high temperatures. The concentration of monosaccharides in hydrolysates was determined for original sample and each steam explosion temperature. Based on the steam explosion conditions, the effect of severity factors was investigated to find optimum pretreatment conditions to increase accessibility of softwood cellulose and hemicelluloses. The identified optimum severity factor $R_O = 4.09$ matches the optimum steam explosion temperature of 205 °C and the residence time of 10 minutes.

Keywords: biofuel industry, dendromass, fibreboard, particle board, severity factor, steam explosion

Introduction

Middle density fibreboards (MDF) and particle boards (PB) are the most produced wood based panels for furniture industry (Irle and Barbu, 2010). Generally, fibreboards and particle boards based on softwood are very useful materials also in building industry (Lühr et al., 2018). European production of wood chips and particles for MDF and PB boards manufacturing was about 86 million m³ in 2018 which is 15 % of predicted wood consumption in 2020. From this amount, about 45 million m³ of PB were produced in 2018. According to the FAO, it is assumed that wood consumption for energy generation in the European Union will grow from 346 million m³ in 2010 to 573 million m³ in 2020 and could reach as much as 752 million m³ in 2030 (Moskalik and Gendek, 2019). Slovak republic participates with the production of about 830 thousand m³ of chips and 630 thousand m³ of particle boards. Urea-formaldehyde (UF), melamine-urea-formaldehyde (MUF), and melamine-urea-formaldehyde resins combined with a phenolic resin (MUPF) for external environment have been used for the production of fibreboards and particle boards considering the humidity of the environment of their use. Formaldehyde used for resin condensation is gradually released from boards during their lifetime. Formaldehyde is a colourless, highly toxic, and flammable gas. It is slightly heavier than air at room temperature and its releasing, especially from furniture boards, is strictly monitored. Just the amount of formaldehyde included in waste agglomerated boards significantly reduces the possibility of their recycling (Ihnát et al., 2017).

However, after a few decades of using fibreboards and particle boards their end-of-life comes and wood waste is formed. The used waste wood based panels are classified among municipal waste which may not be put on landfills but should be recycled or energy utilised. In general, recycling of wood waste is difficult due to the presence of harmful chemicals contained both in glue used during the manufacturing process (Risholm-Sundman and Vestin, 2005) and in additives originally protecting it from moisture and wood decaying fungi, increasing its fire resistance and so on (Erbreich 2004). There are also efforts to use wood waste in combination with other organic waste, e.g. with polyurethane since urea-formaldehyde resin is the main synthetic component in the fibreboard and particle board production and the obtained composite panels containing a certain amount of urea-formaldehyde resin and polyurethane show good mechanical properties (Liu et al., 2019). Additionally, researchers in our work group assume that the amounts of urea-formaldehyde resin from waste fibreboard and particle board materials gra-

dually reduce after boiling water treatment due to its hydrolysis and the obtained materials with reduced urea-formaldehyde resin are suitable for the production of recycled and agglomerated materials (Ihnát et al., 2017; Ihnát et al., 2018). Recycled fibreboards can also be combined with other biomass species like straw pulp to prepare insulating fibreboards (Ihnát et al., 2015).

In Slovakia, commonly available softwood (Petráš et al., 2019) is used for the production of agglomerated materials such as MDF and PB, especially spruce. There often are combinations of spruce with deciduous trees, mainly beech. Their ratio and resulting composition are subject to availability of natural lignocellulosic sources. In the past, PB was produced mainly from deciduous trees — beech trees with a small addition of other ones (V. Ihnát, personal communication). Such lignocellulosic materials have considerably high holocellulose content and thus the particle boards and fibreboards contained a considerable amount of cellulose since they were produced from natural lignocellulosic materials (Arévalo and Peijs, 2016). Lignocellulosic materials are the most widespread natural form of cellulose, which is the most common biopolymer on Earth. Its annual worldwide production is estimated to be up to 10^{10} tonnes (Alvira et al., 2010; Sánchez and Cardona, 2008). Many research activities refer to thermo-mechanical or thermo-hydro-mechanical refining processes that can be optimised and applied in particle boards and fibreboards refining pretreatment (Xing et al., 2008). Optimal conditions can result in structural recalcitrance reduction and enhanced cellulose accessibility. These facts can be generalised for all lignocellulosic biomass species such as wheat straw, beech sawdust, etc. (Pažitný et al., 2019a; Pažitný et al., 2019b). Steam explosion is such an alternative (Yin et al., 2007). This pretreatment process can be controlled indirectly by enzymatic hydrolysis which is a very useful process common in industrial technologies (Pažitný et al., 2019a). Numerous experiments of enzymatic hydrolysis on bioconversion of pretreated sugarcane bagasse have been studied (Patel et al. 2017). The main advantage of enzymatic hydrolysis performance is also obtaining information about the hydrolysates content. This can vary significantly depending on biomass species, stiffness of starting material, and enzymatic hydrolysis conditions (Gigac et al., 2017).

Materials and Methods

Materials
Two types of recycled holocellulose sources: recycled fibreboards (Kronospan Mielec Ltd. Co., Poland) and particle boards (Bučina Zvolen JSC, Slovak Republic) were used. The raw material was recovered as waste from these lignocellulosic materials. Cellic CTec3 was used as a ready-to-use stabilised enzyme complex supplied by Novozymes A/S (Bagsværd, Denmark) for lignocellulosic raw material consumption to fermentable monosaccharides. The enzyme activity was measured to be 1.700 BHU (Biomass Hydrolysis Units)/g product in our laboratory.

Preparation of wood chips from waste particle boards
Initial destruction of large dimension materials, thickness of 18 mm, was carried out by cutting to smaller pieces of approximately 100 mm × 100 mm. Disintegration of waste particle boards glued with UF adhesives was carried out on a wet (soaking in water/cooking) basis employing a process provided by our workplace (Ihnát et al., 2017). Samples of 100 × 100 mm particle boards bonded with UF glues without surface foils on either side were dipped/soaked and cooked in water and weighed to determine the water absorbance. The samples were soaked for 48 hours in cold water and subsequently cooked for 180 minutes under stirring. The samples were disintegrated freely into individual particles after 180 minutes of cooking. Thus prepared samples were disintegrated and dried at 105 °C and particles obtained were sieved to fractions. Distribution of the prepared particles was determined by the laboratory sieving after drying at 105 °C, whereas the prepared particles were dried and sieved at pilot plants.

Preparation of wood fibre from waste MDF boards
Waste MDF based on UF resins was obtained from old furniture based on MDF boards. It was destructed to parts with edges of not more than 5 cm and fibre was prepared according to the process described in our previous paper (Ihnát et al., 2018). Particles of MDF were cooked at constant stirring in water for 3 minutes until the relative humidity of at least 45 % was achieved. The particles were hydro-mechanically defibered by wet milling on the Sprout Waldron (Sprout, Waldron & Co., Inc., USA) at the minimum temperature of 80 °C.
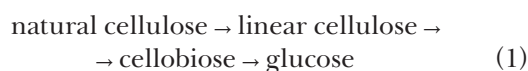
Steam explosion
The prepared samples of recycled fibreboards and particle boards were impregnated with fresh water so that the final moisture content of samples before the steam explosion was at least 85 % w/w. That is the amount of water in which a sample was soaked prior to its pretreatment and which was calculated to be 15 % w/w of the used lignocellulosic material.

The samples were soaked in water at 20 °C for at least 1 hour prior to steam explosion pretreatment. Quick determination of dry matter in the samples was performed on a moisture analyser Denver IR35 that uses infrared sample heating. The samples (100 g o.d.) were finally pretreated in a 2 L stainless steel batch reactor for steam explosion (Amar Equipments Pvt. Ltd., India). The reactor was used for steam reactions at three different temperatures (185 °C, 205 °C and 235 °C). Retention time of each thermo-hydro-mechanical experiment with the recycled lignocellulosic materials (steam explosion — STEX) was 10 minutes.

Enzymatic hydrolysis

Enzymatic hydrolysis (EH) of original particles and those pretreated with Cellic Ctec3 at a dose of 15 % w/w (g of Cellic Ctec3/100 g of cellulose) was carried out at 50 °C, pH = 5.0 for 96 hours and 12.5 % w/w of particles. The pH value was adjusted continuously during the process using 0.1 N sulphuric acid and 0.1 N sodium hydroxide. The hydrolysate samples were collected after 24, 48, 72 and 96 hours. The procedure of cellulose decomposition is well described (Whistler and Smart, 1953) by the chemical equations scheme represented by Eq. (1).

$$\text{natural cellulose} \rightarrow \text{linear cellulose} \rightarrow$$
$$\rightarrow \text{cellobiose} \rightarrow \text{glucose} \qquad (1)$$

HPLC analysis

Concentration of monosaccharides was determined using the procedure of the National Renewable Energy Laboratory (NREL 2008; Sluiter et al., 2011). Monosaccharides (glucose, xylose and arabinose) were determined in hydrolysates by the HPLC (High Performance Liquid Chromatography) method using a Rezex ROA (organic acid) H^+ column. The mobile phase was 0.005 N sulphuric acid at the flow of 0.5 mL·min⁻¹ and the temperature was set to 30 °C. Chromatography data were processed by the software Clarity version 5.3.0.180 (DataApex Ltd., Czech Republic).

Results and Discussion

Recycled fibreboards and particle boards as perspective substrates in 2G bioethanol production

A good model for dendromass behaviour in partial processes of biofuel production can be obtained using of recycled fibreboards and particle boards due to their high holocellulose content. The mentioned substrates are based mostly on spruce and, in lower extent, also on beech; holocellulose content in these natural materials ranges from 71 % (Kurth and Ritter, 1934; Bodîrlău et al., 2012) to 85 % (Gawron et al., 2011). Among the recycled fibreboards, MDF boards are very often used in furniture industry. However, these contain also resin and other additives that are blended with the fibres (Piekarski et al., 2014). There are no reliable literary sources referring to 2G bioethanol produced from fibreboards and particle boards and this work has the ambitions to change this.

Steam explosion of recycled fibreboards and particle boards as a pretreatment method and its evaluation

Various methods of pretreatment and their evaluation have been described in our previous papers as well as in other scientific papers (Pažitný et al., 2019a, 2019b; Kokta and Ahmed, 1998; Simangunsong et al., 2018). In this work, steam explosion of recycled fibreboards and particle boards at 185 °C, 205 °C and 235 °C was studied. Samples prepared for the steam explosion experiment were soaked in water at 20 °C for at least 1 hour and then they were subjected to steam explosion at appropriate temperatures. The corresponding severity factors are listed in Table 1.

Tab. 1. Effect of pretreatment process temperature on the severity factor at constant retention time of 10 minutes.

Steam explosion temperature (°C)	Retention time (minutes)	Severity factor
185	10	3.50
205	10	4.09
235	10	4.97

The severity factor computation for corresponding temperatures and constant retention time was based on the integral form of the equation for severity factor determination (Eq. (2)) introduced in other scientific papers (Hashemi et al., 2019; Batista et al., 2019).

$$R_O = \int_0^t exp\left[\frac{T_r - T_b}{14.75}\right] dt \qquad (2)$$

where R_O is the severity factor, T_r reaction temperature (°C), T_b base temperature (100 °C), t retention time in biomass hydrothermal reaction (minutes), 14.75 is an empirical temperature value based on the conventional activation energy assuming first order kinetics (kJ·mol⁻¹). Eq. (2) can be written in a simplified form (Pažitný et al., 2019a) and it quantifies as a reaction coordinate for steam explosion. Table 1 clearly shows the increasing trend of the severity factor depending on the temperature increase.

Tab. 2. Availability of samples obtained from enzymatic hydrolysis of particles prepared by steam explosion.

Sample type	Steam explosion temperature (°C)	Availability of samples from enzymatic hydrolysis
Particle boards	Without steam explosion	Available
Fibreboards	Without steam explosion	Unavailable
Particle boards	185	Available
Fibreboards	185	Unavailable
Particle boards	205	Unavailable
Fibreboards	205	Available
Particle boards	235	Unavailable
Fibreboards	235	Available

Several enzymatic hydrolysis experiments with samples obtained from steam explosion were excluded from the analysis due to the difficult removal of hydrolysates and problems with torrefaction of the lignocellulosic material at the steam explosion temperature of 235 °C, mainly in case of particles obtained from particle boards. The most common material for particle boards and fibreboards production in our region is spruce wood which can be torrefied at temperatures ranging from 230 °C to 290 °C (Manouchehrinejad and Mani, 2018). However, steam explosion of particles based on fibreboards at 235 °C was successful and enzymatic hydrolysis was performed with removable hydrolysate. Availability of samples obtained from enzymatic hydrolysis is shown in Table 2.

Elution time of all monosaccharides (Table 3) was equal for each sample and at all times of hydrolysates sampling (Fig. 1 a) — d)).

Tab. 3. Retention time of analysed monosaccharides obtained from enzymatic hydrolysis.

Analysed component	Elution time (minutes)
Glucose	11.80 ± 0.01
Xylose	12.60 ± 0.02
Arabinose	13.85 ± 0.02

Figure 1 a) shows an HPLC chromatogram overlay of hydrolysates obtained from the particles without steam explosion pretreatment. It confirms
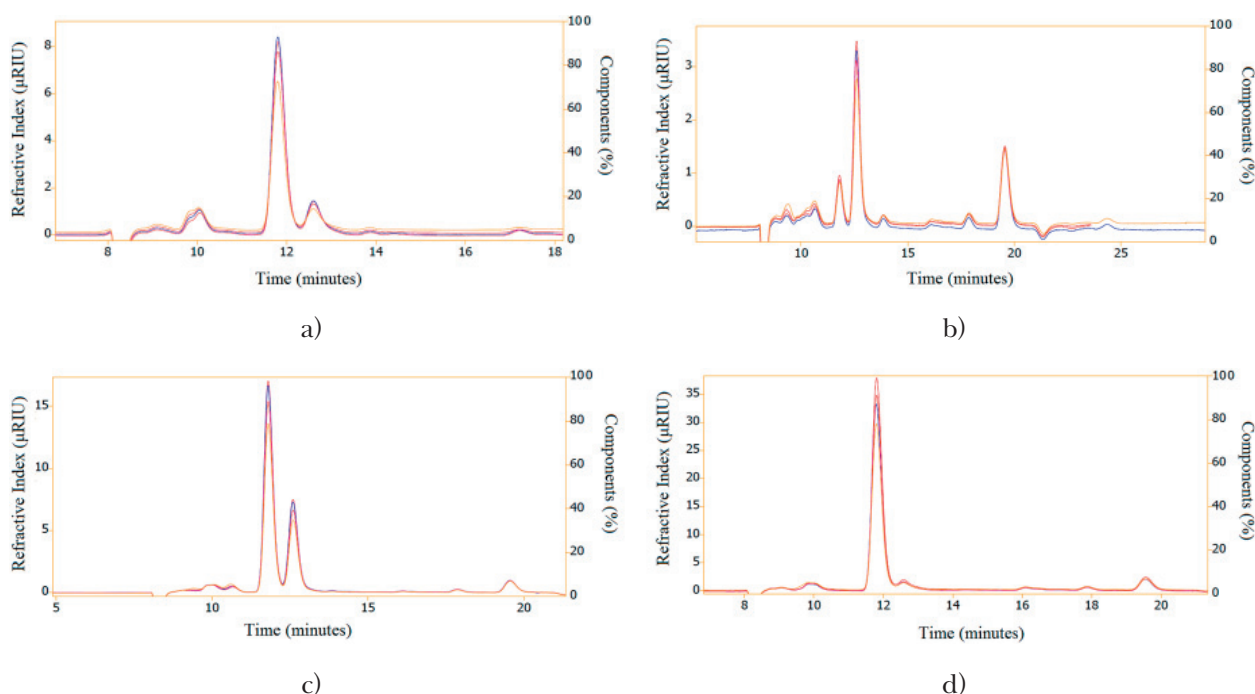

a)

b)

c)

d)

Fig. 1. HPLC chromatogram overlays of hydrolysates obtained from particles without steam explosion pretreatment *(a) particle boards* and pretreated by steam explosion at different temperatures, *b) particle boards, 185 °C, c) fibreboards, 205 °C, d) fibreboards, 235 °C)*, elution time of analysed monosaccharides is shown in Table 3 *(EH 24 hours — orange, EH 48 hours — red, EH 72 hours — blue, EH 96 — light red).*

the characteristic presence of glucose and lower concentration of xylose and arabinose expected based on lower holocellulose accessibility without pretreatment (Pažitný et al., 2019b). Figure 1 b) — d) shows HPLC chromatograms of hydrolysates obtained from the particle boards or fibreboards pretreated by steam explosion. In Figure 1 a), c) and d), the most significant peak belongs to the glucose monomer which indicates high content of accessible cellulose. It was found that hydrolysate obtained from fibreboards pretreated by steam explosion at 235 °C contains the highest proportion of the glucose monomer based on the highest signal (Fig. 1 d)). Thus, the best splitting of recalcitrant structure and the most accessible fibreboard cellulose are at the highest used temperature of steam explosion which is very close to the torrefaction temperature (Manouchehrinejad and Mani, 2018). Additionally, Figure 1 b) shows higher signal for the xylose monomer compared to that for the glucose monomer which is probably caused by the lower pretreatment temperature. The holocellulose decomposition mechanism during thermo-hydro-

mechanical refining processes is known. The rate of this decomposition is higher for hemicelluloses, much lower for cellulose and the lowest for lignin (Sandberg et al., 2013). This implies that the cellulose decomposition requires higher temperatures. It should be noted that Figure 1 a) — d) gives qualitative analysis of monosaccharides in hydrolysates — glucose, xylose and arabinose monomers. However, the recorded chromatograms show several smaller peaks that are difficult to analyse due to their overlap. As expected, the concentration of monosaccharides recovered in the liquid phase is very low for non-pretreated samples and it increases as shown by leaps and bounds for pretreated samples, which is in accordance with our previous results (Pažitný et al., 2019a). It is also clear that steam explosion temperature of 185 °C is insufficient to achieve splitting of recalcitrant structure of the lignocellulosic material used as the signal for the refractive index for glucose is relatively low (approximately 3 µRIU). Figure 2 a) — b) gives information about the concentration of individual monosaccharides in hydrolysates. It is shown that the highest concentration of
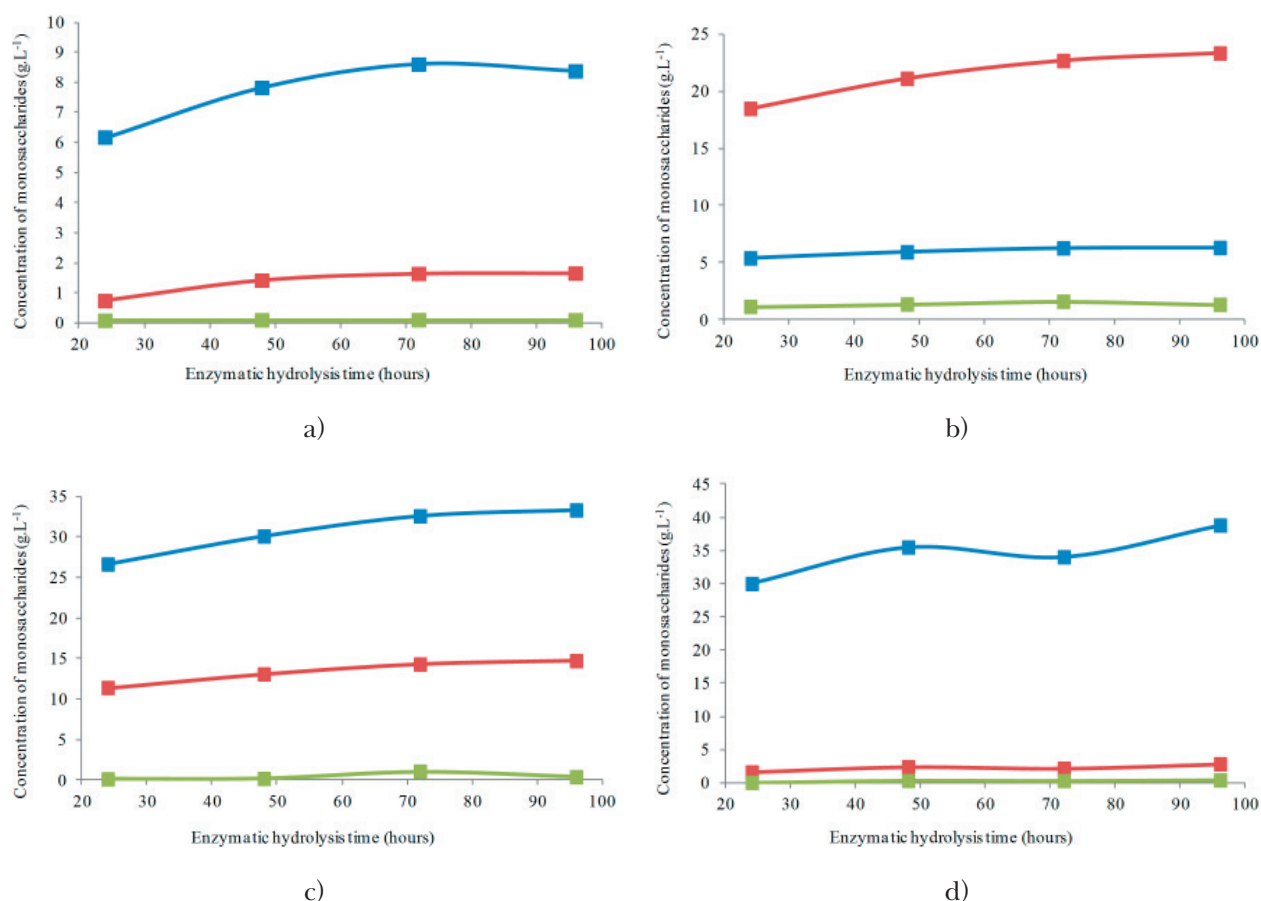

Fig. 2. Time-dependence of monosaccharides concentration *(glucose – blue, xylose – red, arabinose – green)* for hydrolysates obtained from particles without steam explosion pretreatment *(a) particle boards)* and pretreated by steam explosion at different temperatures *(b) particle boards, 185 °C, c) fibreboards, 205 °C, d) fibreboards, 235 °C).*

glucose (38.8 g·L⁻¹) results in steam explosion of fibreboard particles at 235 °C. However, the highest total concentration of monosaccharides (42 g·L⁻¹) is provided by steam explosion of fibreboard particles at 205 °C. It should be added that this pretreatment temperature of lignocellulosic material based on wood was identified as the optimum because higher pretreatment temperatures enhance the production of fermentation inhibitors (Stankovská et al., 2018) which are not suitable for further treatment in second generation biofuel production. As mentioned above, analogically to chromatograms evaluation, the highest concentration of identified pentose − xylose and arabinose was found for steam explosion pretreatment of particle boards at 185 °C. The maximum concentration of xylose (23.3 g·L⁻¹) and arabinose (1.58 g·L⁻¹) was achieved after 96 hours and after 72 hours of enzymatic hydrolysis, respectively.

The obtained results on hydrolysates composition can help to formulate input mixture of raw materials suitable for the production of second generation liquid biofuels. Based on these results, fibreboard seems to be a more suitable lignocellulosic material with relatively low severity factor R_O = 4.09 (pretreatment temperature of 205 °C, retention time of 10 minutes).

Conclusions

HPLC analysis was used to characterise hydrolysed lignocellulosic materials based on dendromass, the materials were subjected to mechanical, hydro-mechanical and thermo-hydro-mechanical refining processes. Dramatic changes in the basic composition of particles based on fibreboard and particle boards were observed when thermo-hydro-mechanical pretreatment − steam explosion, was used. Enzymatic hydrolysis was used as an indirect control of the pretreatment process.

Analysis of hydrolysates from enzymatic hydrolysis showed that the optimum pretreatment process was achieved by steam explosion of fibreboard particles at 205 °C, which corresponds to the severity factor (R_O) of 4.09 (pretreatment temperature of 205 °C, retention time of 10 minutes). For this temperature, the highest concentration of total monosaccharides (42 g·L⁻¹) with relatively high proportion of glucose (38.8 g·L⁻¹) was obtained. Significantly higher pretreatment temperatures enhance the concentration of fermentation inhibitors resulting from reduced concentration of monosaccharides at the pretreatment temperature of 235 °C. This temperature is also very close or even corresponds to the torrefaction temperature of the lignocellulosic materials studied. However, this pretreatment temperature provided

the highest concentration of glucose in case of steam explosion of particles based on fibreboards. In contrast, the concentrations of xylose and arabinose were reduced. The maximum concentration of xylose (23.3 g·L⁻¹) and arabinose (1.58 g·L⁻¹) were obtained in case of steam explosion pretreatment of particle boards at 185 °C after 96 hours and after 72 hours of enzymatic hydrolysis, respectively.

The hydrolysates composition results can help in the formulation of the input mixture of raw materials suitable for the production of second generation liquid biofuels as well as in the field of enzymology and wood processing industry.

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