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Abstract

In this work, steam explosion (STEX), microwave assisted extraction (MAE) and high voltage electrical discharges (HVED) pretreatments have been evaluated for their impact on the physicochemical characteristics of extracted hemicellulosic polymers and on the resulting hemicellulose-based films. Extraction was carried out on spruce sawdust pre-soaked in water (WPS) or 1 M NaOH solution (SPS). The results have shown that STEX pretreatment gave the highest hemicellulose yields (64 and 66 $mg.g^{-1}$ of dry wood from WPS and SPS respectively) followed by MAE and HVED whilst MAE pretreatment produced the highest molecular mass (M_w~66 kDa of arabinoglucoronoxylans from SPS and 56 kDa for galactoglucomannans from WPS). A relatively high acetylation degree was found for STEX WPS (acetylation degree ≈ 0.35) and a high lignin content for STEX SPS (≈ 12%). Films have been produced by casting using sorbitol as plasticizer. Low oxygen barrier and light transmittance properties were observed for the films obtained from hemicelluloses extracted from SPS due to their high molecular mass and to intermolecular bonding of hemicelluloses and lignin.

Key words: Hemicelluloses, spruce wood, film formation, pretreatment of biomass, steam explosion

46

47

48 **Abbreviation**

AD	Acetylation degree
AcGGM	Acetyl-Galactoglucomannan
AD	Acetylation degree
AGX	Arabinoglucoronoxylan
ASL	Acid soluble lignin
ASTM	American Society for Testing and Materials
DW	Dry wood
kDa	Kilo Dalton
GGM	Galactoglucomannans
HPLC	High performance liquid chromatography
HVED	High voltage electrical discharges
M	Mole
MAE	Microwave assisted extraction
OTR	Oxygen transmission rate
PD	Polymerization Degree
RH	Relative humidity
SD	Standard Deviation
SF	Severity Factor
SPS	Sodium hydroxide Pre-soaked Sawdust
STEX	Steam explosion
W	Weight
WPS	Water pre-soaked sawdust

1. Introduction

Hemicelluloses represent a very promising resource and are gaining an increasing interest in their recovery and transformation into functional products. Spruce hemicelluloses are composed principally of acetyl-galactoglucomannans (AcGGM) 20 % of wood and arbinoglucuronoxylans (ARX) 5 – 10 % (Timell, 1967). AcGGM has a backbone of β-D-(1→4) -glucopyranosyl and β-D-(1→4)-mannopyranosyl units in a linear or slightly branched chain. Single α-D-galactopyranose units are attached to the main chain by (1→6)-bonds. The mannopyranosyl units are acetylated at C-2 or C-3 with a degree of acetylation ≈ 0.5 (Timell, 1967) and for water-soluble AcGGM a galactose-to-glucose-to-mannose ratio ≈ 0.5–1.1:1:3.5–4.5 (Sjöström, 1993). ARX are composed of a backbone of (1→4)-linked β-D-xylopyranose units and side groups at C-2 of 4-O-methyl-α-D-glucuronic acid groups on the average of two residues per ten xylose units.

One of the most promising applications of polymeric hemicelluloses is the film production because of their film-forming properties, their biocompatibility and biodegradability. The films can be produced by solution-casting from water and a plasticizer such as sorbitol, xylitol or glycerol is usually employed in order to achieve a good film flexibility (Pomes 1971). In addition, like most polysaccharides, hemicelluloses-based films are known to exhibit gas barrier properties especially toward oxygen [2] which makes them interesting for bio-packaging since the oxygen permeability is critical for many food stabilization processes [3]. Hartman et al. [4] have developed films with GGM obtained from thermomechanical pulping (TMP) with low oxygen permeability and good mechanical properties using polysaccharides and a plasticizer such as alginate and carboxymethylcellulose. Mikkonen et al. [5] have shown

that GGM recovered from TMP process and crosslinked with glyoxal exhibited high mechanical performance and low oxygen permeability and water vapor permeability.

The valorization methods of spruce hemicelluloses described in the literature generally rely on the recovery of solubilized hemicelluloses in TMP process by filtration or ethanolic precipitation [6–11]. Studies dedicated to the extraction from wood of high molecular weight hemicelluloses are scarce. The extraction of polymeric hemicelluloses from wood is limited by the structure of the plant cell walls. In fact, the inherent structure and the composition of native lignocellulosic materials make the access to hemicelluloses hindered [12]. Overcoming the recalcitrance of lignocellulosic biomass through physico-chemical pretreatments has been the subject of extensive literature in the context of 2G bioethanol [13,14]. These pretreatments act either by decomposing the structure of the lignin and carbohydrates of the vegetal matrix and/or by creating cracks in the fiber wall to make the cellulose more accessible to enzymes. Hemicelluloses extraction have been described by hydrothermal treatment at high temperatures (≥170 °C) [10,15], by chemical extraction (alkaline) [16–19] and ionic liquids [20], by pressured hot water [21,22], and by microwave heat-fractionation (> 180 °C) [23–25].

In previous papers, we described the optimization of hemicelluloses extraction from spruce wood using physical activations including steam explosion (STEX), microwave assisted extraction (MAE) and high voltage electrical discharges (HVED) [26–28]. In this work we assessed the effect of these pretreatment technologies on the extraction of high molecular weight hemicelluloses and thus the effect on the resulting films properties. Extracts have been fully characterized, hemicelluloses-based films have been produced by casting and the oxygen permeability, light transmittance and the mechanical properties have been examined. The impact of the pretreatment step on the properties of the hemicelluloses and the films produced is discussed.

2. Materiel and method

2.1 Raw material

Spruce sawdust with a particle size of 1 to 5 mm was produced from a spruce tree from the Lorraine region in France and stored at room temperature in sealed polyethylene bags in the dark until extraction. The average moisture content of the raw material was 9.93% w/w. The hemicelluloses content of the sawdust (~30% w/w dry wood) was calculated by analyzing noncellulosic monosaccharides of spruce wood according to NREL/TP-510-42618 method [29].

2.2 Impregnation

For HVED and MAE a mass of 20 g of spruce sawdust was pre-soaked with a solution of 1M sodium hydroxide or water (ratio solid:liquid = 1:7). The sawdust was left for one night 15h) before treatment at room temperature. The same procedure was followed for STEX pretreatment, but with 50 g of sawdust instead of 20 g. In next paragraphs, Water Pre-soaked Samples are named (WPS) and Sodium hydroxide Pre-soaked Samples are named (SPS).

2.3 Extraction procedure

2.3.1 HVED pretreatment

A. Pretreatment

HVED pretreatment was carried out using a high voltage pulsed power 40 kV-10 kA generator (Basis, Saint Quentin, France), coupled to a 1-liter cylindrical batch treatment chamber. The HVED treatment chamber was equipped with needle-plate geometry electrodes. The diameters of stainless-steel needle and the grounded disk electrodes were 10 and 35 mm,

120 respectively. The distance between the electrodes was 10 mm. The energy was stored in a set
121 of low-inductance capacitors, which were charged by the high-voltage power supply. The
122 electrical discharges were generated by electrical breakdown in the medium of extraction
123 (liquid) at the peak pulse voltage of 40 kV.

124 In all experiments the liquid-to-solid ratio was fixed at 15 (w/w). The HVED generator
125 (40 kV, 10 kA) provided pulses of a sine form with a pulse repetition rate of 0.5 Hz.

126 **B. Diffusion**

127 The diffusion step was added in order to facilitate the transfer of hemicelluloses chains from
128 wood matrix to the extracellular medium. Temperature during HVED treatment was 50 °C. In
129 order to maintain mild conditions of extraction (low temperature, low decrease of pH), the
130 diffusion was carried out in an Erlenmeyer flask under reflux at 50°C during 3 h with
131 agitation.

132 A pretreatment at 4 ms was chosen as a reference for extraction with HVED based on
133 previous work [28].

134 **2.3.2 Microwave pretreatment**

135 **A. Pretreatment**

136 MAE experiments for the extraction of hemicelluloses from spruce sawdust were carried out
137 using a microwave laboratory system (230V-50 Hz, NEOS-GR, Milestone, Italy). This mono-
138 mode apparatus operates at 2.45 GHz with maximum delivered power of 900 W regulated in
139 10-Watt increments with a temperature and power feedback/control. This instrument was
140 equipped with time controller. The experiments were performed at atmospheric pressure.
141 Time and power were controlled and followed by the software. The MAE experiments were
142 conducted in a glass extraction vessel. The samples were treated for 1h using different

selected powers. Indeed, the effects of microwave irradiation, nature of solvent and consumed energy were studied. The liquid-to-solid ratio was fixed at 7 during microwave treatment.

B. Diffusion

After microwave treatment, supplementary diffusion step was done by a heating under reflux at low temperature to avoid degradation of polymeric chains (70 °C for 3 h). The liquid-to-solid ratio was fixed at 15 (w/w).

A treatment at 573 Watts was chosen as reference for MAE based on previous studies [26].

2.3.3 Steam explosion

Soaked sawdust was placed into a 2-liter reactor with heat jacket and automatic control for steam pressure and sampler residence time. The biomass was treated at different temperatures by injecting a saturated steam into a pressure resistance chamber. After a given reaction time, the steam saturated biomass was released into a discharge tank as well the biomass.

A treatment at 190 °C for 10 min was chosen as reference for steam explosion extraction based on previous work [27] .

The reference conditions chosen for HVED, MAE, and STEX are based on the previous studies. For each pretreatment, these conditions gave hemicelluloses with the highest molecular mass [26, 27,28].

2.4 Hemicelluloses recovery

After extraction, the obtained suspension was filtered on qualitative filter paper with retention particle size of 5–13 µm (VWR International, Fontenay-sous-Bois, France). The volume and final pH of the extract solutions were measured at room temperature shortly after the extraction. The liquid fraction from 1M NaOH impregnated sawdust was neutralized to a pH of 5.5-6 by a solution of 72 % H_2SO_4. 10 mL were taken from the

filtered extract for analyses. The extract solution was concentrated by vacuum evaporation using a water bath at 50 °C. To precipitate high-molecular weight hemicelluloses, four volumes of ethanol (95%) were added to the liquid extracts. The liquid phase was separated from the precipitated hemicelluloses by settling at room temperature and decantation. Hemicelluloses were further separated from the remaining liquid by centrifugation at 3724 g for 10 min at room temperature. The precipitated hemicelluloses were re-dissolved in distilled water and then dialyzed with a dialysis membrane with a cut-off of 3.4 kDa (Spectrum Laboratories, Inc., Rancho Dominguez, CA, USA). Finally, dialyzed hemicelluloses solutions were freeze-dried.

Calculated yield represents the weight of recovered hemicelluloses powder related to dry wood weight.

2.5 Measurement of monosaccharides and uronic acids using HAPE-PAD

The monosaccharides content of the soluble fraction was analyzed by ionic chromatography according to NREL/TP-510-42618 procedure. After acid hydrolysis of samples, sugars and uronic acids were quantified by HAPE-PAD (ICS-3000 Dionex, Dionex Corp., Sunnyvale, USA) equipped with a Dionex CarboPac^{TM} PA-20 (3 × 150 mm) analytical column. Filtered (0.20 µm) samples (20 µL) were eluted at 35°C and at 0.4 mL.min^{-1} with the following composition: pure water 99.2 %/250 mM NaOH 0.8%: 0–20 min; pure water 75 %/250 mM NaOH 20%/ $NaOCOCH_3$ (1 M)- NaOH (20 mM) 5% 20–37 min; and pure water 40%/250 mM NaOH 20%/$NaOCOCH_3$ (1 M)- NaOH (20 mM) 40 % 37–41 min. Each elution was followed by a wash and a subsequent equilibration step. External sugar and uronic acid standards were used for calibration (7 points per curve). The reagents and standards are provided by Sigma-Aldrich and Fisher Scientific.

2.6 Acetyl content

Acetyl content of extracted hemicelluloses was calculated by measuring the acetic acid concentration after a saponification reaction. Acetic acid was analyzed according to NREL/TP-510-42623 method using an Ultimate 3000 HPLC system.

Acetic acid was separated in 45 min on an Agilent Hi-Plex H column at 55 °C with an isocratic flow rate of 0.4 mL.min^{-1} with sulfuric acid (5. 10^{-3} M) as an eluant and detected by UV at 210 nm. An external calibration was performed with six calibration points per standard. Reagents and standards were provided by Sigma-Aldrich.

2.7 Gel filtration chromatography

A Shimadzu Prominence HPLC system was used to estimate the relative molecular weight distribution of hemicelluloses by gel permeation chromatography. The stationary phase was composed of two columns linked in series: Phenomenex Polysep GFC-P as a guard column (7.8×35 mm), Phenomenex Polysep GFC-P3000 and GFC-P2000 as analytical columns (7.8×300 mm). Sodium nitrate (0.25 M) was used as an eluent with a 0.5 mL.min^{-1} flow rate. Samples were solubilized in sodium nitrate (0.25 M) solution and filtered (0.45 µm) and 20 µL are injected. Samples were separated at 30 °C and detection was done with a Refractive Index Detector (Shimadzu RID-20A). Solutions (1 mg.ml^{-1}) of dextran standards with molecular weights of 1; 5; 12; 24; 50 and 80 kDa were used to prepare the calibration curve.

2.8 Soluble lignin

The acid-soluble lignin (ASL) content of hemicelluloses was determined by solubilizing hemicelluloses and measuring the absorbance at 205 nm according to the laboratory analytical procedure (LAP) provided by the National Renewable Energy Laboratory [29]

$$\%\ \mathrm{ASL} = \frac{(Abs_{205\,nm} \times V_t \times Dilution \times 100)}{\varepsilon \times DM_i \times Pathlength} \qquad Eq.(1)$$

where V_t is the total volume of sample (L); ε is the absorptivity of biomass at specific wavelength and DM_i is the initial dry matter (g).

2.9 Preparation of films

Films were prepared from hemicelluloses extracted by pretreatments according to the proposed procedure of Mikkonen (2010). Hemicelluloses powder were dispersed in distilled water (10 $g.L^{-1}$) under magnetic stirring at 90 °C for 10 min. Sorbitol was then added at 40 wt% of the weight of hemicelluloses. Sorbitol was used as plasticizer for all films, because was recently shown in hemicellulose films to result in more stable plasticization (less migration of plasticizer) [30]. The suspension was dispersed a second time under magnetic stirring at 60 °C for 5 min, then degassed by ultrasonication, cast into Teflon Petri dishes, and dried at 60 °C.

2.10 Characterization of films

2.10.1 Mechanical properties

The mechanical properties of the prepared films were determined at 46 % RH using a universal testing machine Lloyd instrument (AMETEK, United Kingdom) according to ASTM D882. These properties consisted of elongation at break (%), tensile strength (kPa) and Young's modulus (kPa). Sample films of 2 cm × 6 cm (analyzed area = 3.5 cm × 2 cm) uniaxially stretched (with a constant speed of 10 $mm.min^{-1}$). The stress–strain curves were recorded and analyzed with Nexygen software.

2.10.2 Oxygen permeability determination

A. Oxygen transmission rate

The oxygen transmission rate (OTR) was measured with an oxygen permeation analyzer (8001 Oxygen Permeation Analyzers, SYSTECH Illinois) at 23 °C and 0 % RH. The apparatus allows a direct measurement of the oxygen without using complex extrapolations. The oxygen permeability (OP) ($cm^3.\mu m.m^{-2}.day^{-1}.kPa^{-1}$) was then calculated by the flowing equation:

$$OP = OTR\ x \frac{X}{\Delta p} \qquad Eq.(2)$$

where, X is the film thickness (µm) and Δp is the partial pressure difference of O_2 across the film (kPa).

B. Thickness measurement

The thickness of the films was photographed by a scanning electron microscope (HITACHI, TM 3000). The thickness of the films was then measured by the software (Image Pro Premier). No preparation was made before the analysis, the films were cut in the form of small rectangles and placed directly on the microscope. The thickness was taken in 3 points on each film and then the average of three films was calculated (µm).

2.10.3 Light transmittance

The light transmittances of the films were scanned from 190 to 900 nm wavelength using a Shimadzu UV-vis spectrophotometer (Libra S32, Biochrom, Lagny-sur- Marne, France).

2.11 Statistical analysis

All experiments were conducted at least in duplicates. The means and error bars were calculated and were represented in all figures.

3. Results and discussion

3.1 Hemicelluloses extraction yields and molecular weights

Fig. 1 shows the extraction yields and molecular weight of polymeric hemicelluloses recovered after neutral and basic pretreatment (WPS and SPS respectively). Three different pretreatment technologies have been compared: steam explosion (190 °C, 10 min), microwave at atmospheric pressure (100°C, 1 h) and high voltage electrical discharges (50 °C, 4 ms).

It appears from Fig. 1. A that STEX gave higher extraction yields (64 and 66 $mg.g^{-1}$ DW for WPS and SPS respectively) than MAE (12.8 and 31.8 $mg.g^{-1}$ DW for WPS and SPS respectively) and HVED (8 and 19.8 $mg.^{-1}$ DW for WPS and SPS respectively). STEX relies on the extraction of hemicelluloses chains from wood matrix by autohydrolysis (due to an auto-catalyzed acid hydrolysis). During the steaming stage of STEX performed at 190 °C - 10 min after a water impregnation (WPS), hemicelluloses carboxylic acids generated acidic conditions which are responsible for the hydrolysis of glycosidic bonds. As a result, hemicellulosic chains with a relatively low molecular weight (M_w ~ 20 kDa) (Fig. 1. B) and high amount of monomer sugars (2 $mg.\ g^{-1}$ DW) have been isolated. For basic impregnation (SPS), significantly higher molecular mass of hemicelluloses (M_w ~ 52.4 kDa) have been recovered associated with a lower concentration of monosaccharides (less than 0.1 $mg.\ g^{-1}$ DW).

283 The molecular weight of hemicelluloses extracted by MAE (56.30 kDa and 66 kDa from WPS
284 and SPS fraction respectively) were higher than those obtained by STEX and HVED. Based
285 on literature data, microwave irradiations involve the disruption of wood fibers which is due
286 to the selective interaction of microwaves with the inhomogeneous lignocellulosic materials
287 [31]; The HVED pretreatment gave hemicelluloses with $M_w \approx 44.7$ and 55.4 kDa from WPS
288 and SPS fraction respectively. HVED pretreatment primarily relies only on the physical and
289 mechanical effects caused by electrical discharges since the reached temperature during the
290 pretreatment is relatively low (50 °C). The application of HVED-treatment results in
291 generation of shockwaves. These shockwaves may play an important role in the raw material
292 fragmentation, thus facilitating hemicelluloses extraction [32]. The formation of the shock
293 waves in liquid medium is often followed by the formation of cavitation bubbles. The
294 combined effect of shockwaves and cavitation bubbles may improve the disruption and the
295 destabilization of cell walls [32–34].

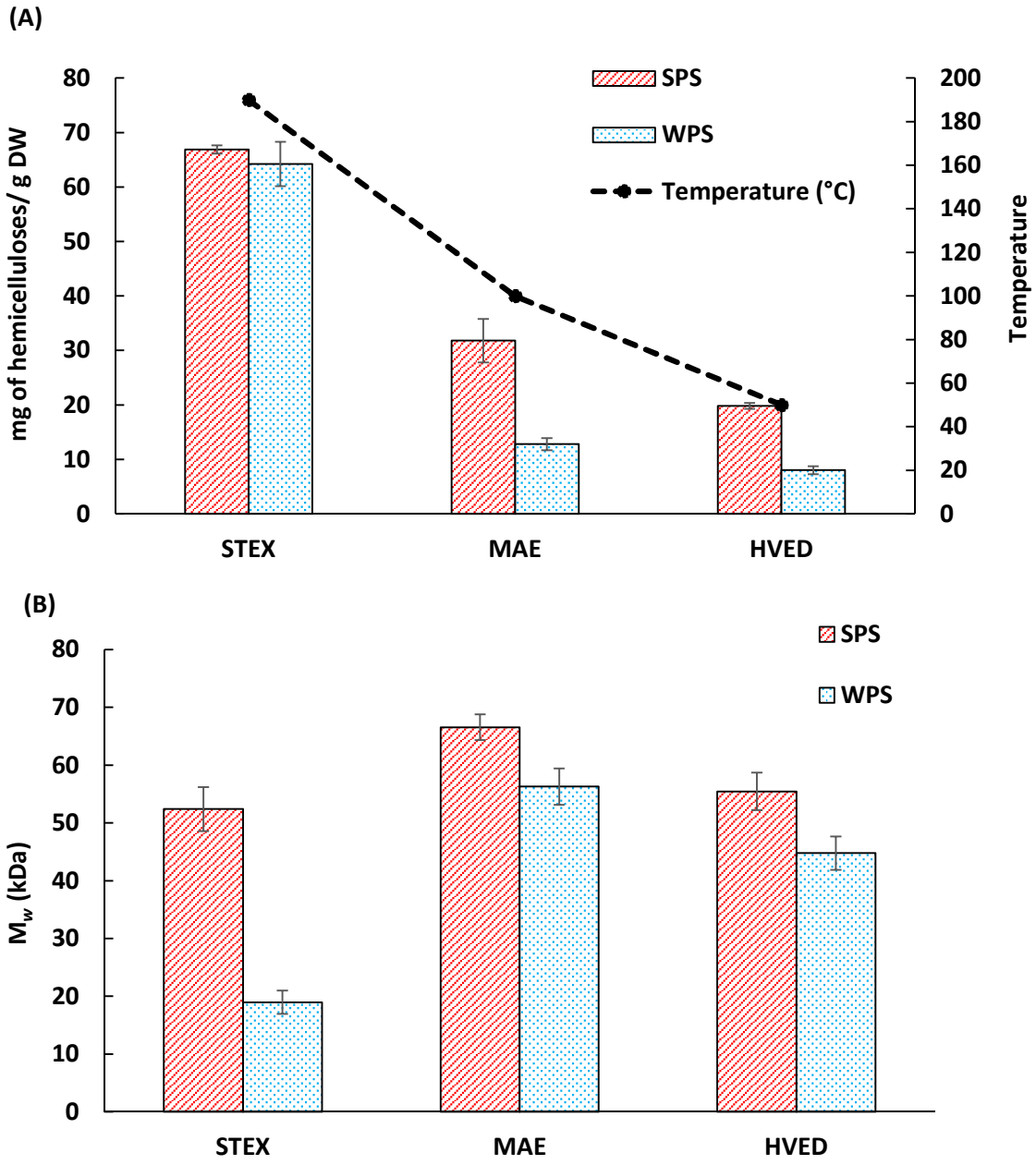
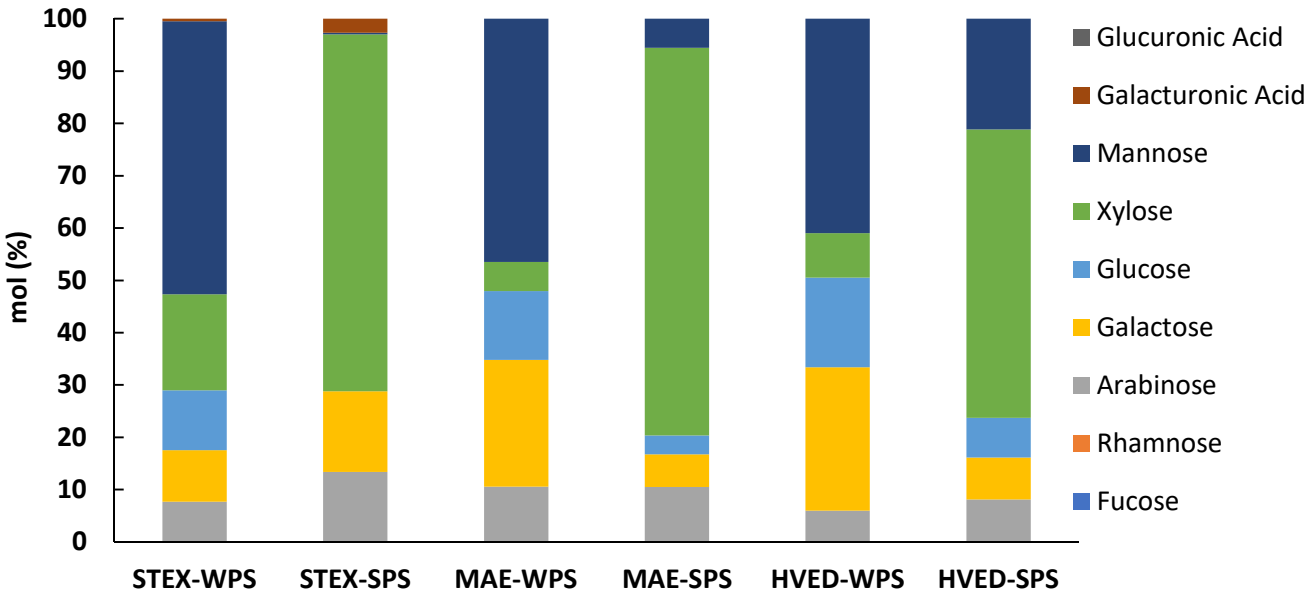


Fig. 1. Yield of extraction of hemicelluloses (A) and molecular mass analysis (B).

3.2 Sugar composition, acetylation degree and phenolics content of extracted hemicelluloses

The monomeric sugar compositions of the hemicellulosic fractions have been established after acid hydrolysis by ionic chromatography. From Fig. 2 it appears that the presoaking conditions strongly influenced the selectivity of extraction. For WPS, mannose is the

304 dominant sugar (41–52%), followed by galactose (10–28%), glucose (12–18%). Concerning
305 SPS, xylose and arabinose are the most abundant (55–69% and 8–13% respectively), and
306 mannose is present in low amounts. These observations are in agreement with those reported
307 by Perez et al. [35] who have found that spruce hemicelluloses extracted in acidic conditions
308 are primarily composed of galactoglucomannans with a high proportion of mannans (at least
309 45%, up to 57%), then glucans (16 to 25%) and galactans (13 to 19%). Some arabinoxylans
310 are also present (>15%), while, the hemicelluloses obtained in basic conditions are a mixture
311 of arabinoxylans and galactoglucomannans with a heavily contamination with lignin (> 18%).
312 According to Svard et al. [36], the sugar composition of hemicelluloses extracted from
313 lignocellulosic biomass is a function of the extraction pH because their solubility is affected
314 by the substituents on the polymeric chain [37]. As a result, neutral and acidic media could
315 promote the solubilization of water soluble AcGGM [25]. On the other hand, basic medium
316 yielded a xylose-rich extract because of the methyl glucuronic acid and arabinose substituents
317 of AGX [38,39]. It can also be observed that with STEX-WPS and HVED-SPS, higher
318 amounts of xylose and mannose were detected respectively.



3

320 Fig. 2. Sugar composition of extracted hemicelluloses from WPS (A) and SPS (B)

The acetylation degree of extracted hemicelluloses from WPS has been determined by HPLC after saponification and are given in Fig. 3. The molar Ac/Man ratios were used as a measure for the acetylation degree (AD). As expected, hemicelluloses recovered from SPS are totally deacetylated due to the saponification of acetyl moieties in basic conditions (results are not shown). After water presoaking, the AD for hemicelluloses extracted by STEX (AD = 0.36) is closed to the values reported for native AcGGM, determined by NMR and titration methods [8,40] and higher compared to those reported in previous studies for AcGGM recovered from TMP process and from spruce wood [41,42]. Hemicelluloses from MAE and HVED displayed a lower AD (0.1 and 0.07 respectively). From this result, it can be concluded that STEX pretreatment allows to extract slightly modified and highly acetylated AcGGM oligomers from spruce.

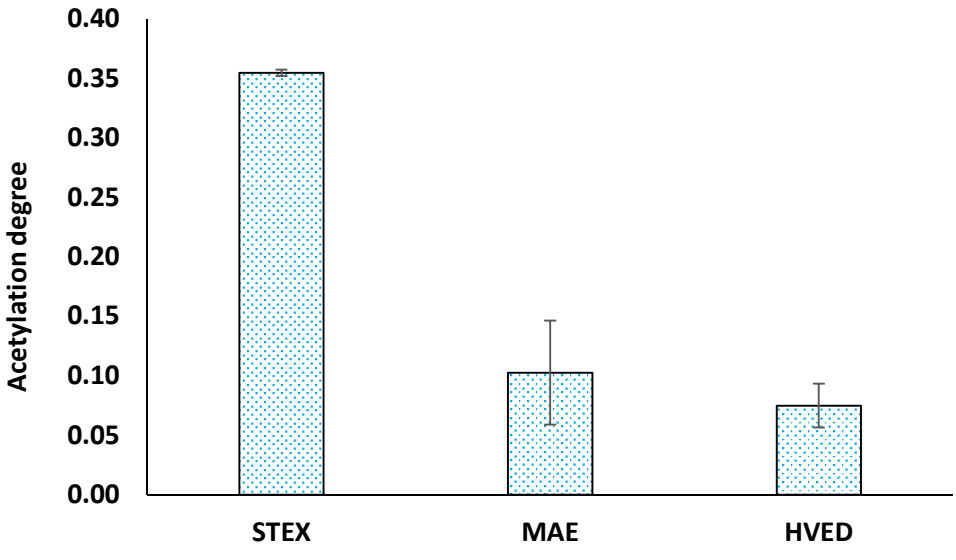


Fig. 3. Acetylation degree of extracted hemicelluloses from WPS

The hemicellulosic fractions recovered after precipitation and dialysis contained minor amounts of lignin. As shown in Fig. 4, the lignin content is a function of the extraction conditions. Higher amounts of lignin were detected for hemicelluloses extracted from SPS. This can be explained by the well-known delignification reactions in basic media, producing small fragments of soda lignin recovered in the liquid stream with the polysaccharides. Higher

lignin contents were observed for STEX compared to MAE and HVED because of the higher temperature used during the steaming step. The presence of lignin fraction co-extracted with hemicelluloses in basic conditions (lignin-hemicellulose complexes), may restrict the dissolution of certain hemicellulose fractions especially for (STEX SPS) and could affect their molecular mass.

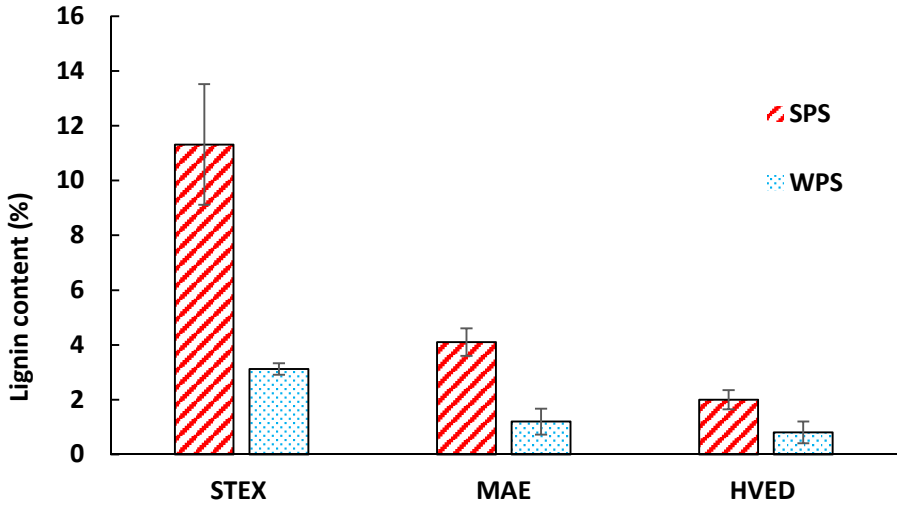


Fig. 4. Lignin content of extracted hemicelluloses

3.3 Characterization of films

The extracted hemicelluloses from each pretreatment and from both conditions (SPS and WPS) were used to prepare films by a casting procedure in the presence of 40% of sorbitol used as a plasticizer. The resulting films (Fig. 5) have been analyzed in terms of oxygen permeability, mechanical strength and light transmittance and then compared to starch film.

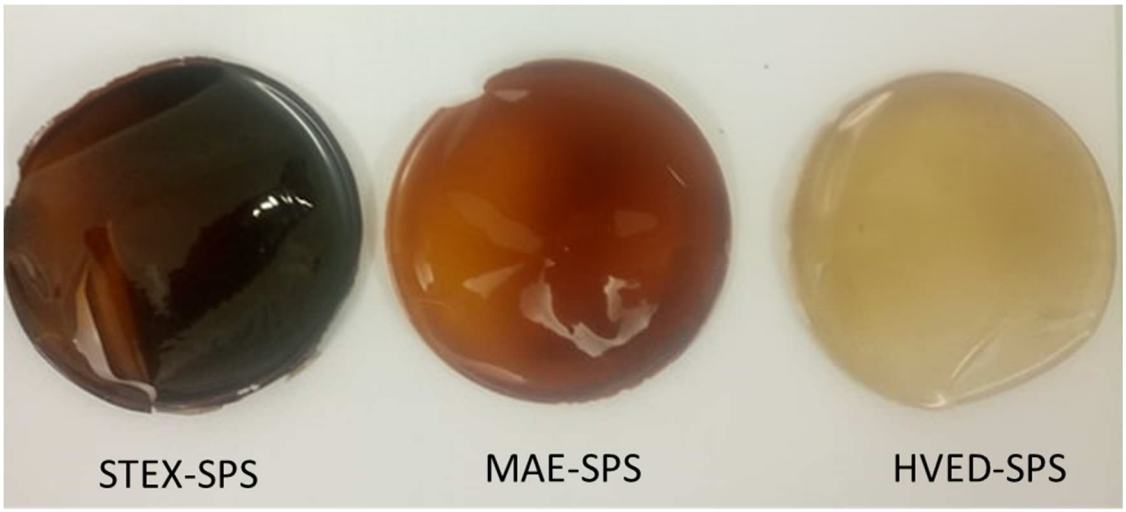


Fig. 5. Aspect of film made from hemicelluloses extracted from SPS.

3.3.1 Mechanical strength

Results of mechanicals tests are given in Table 1. Elongation at break is the ratio between changed length and initial length after breakage of the film (elastic and plastic deformations). This factor indicates the ability of the film to resist to the changes of the shape without cracking. The highest elongation was found for MAE SPS (6.55%) followed by HVED SPS (6.3%), HVED WPS (5.65%) and MAE WPS (4.95%). The elongation of starch film was 8.45%. Films from STEX showed low elongation, especially for STEX WPS, which is due principally to the low molecular weight of hemicelluloses (M_w~14 kDa). Considering the films composition (cf. Fig. 4), the higher lignin content of films obtained after STEX SPS might be responsible for their lower mechanical properties. In accordance with Westbye et al. (2007), the relatively high lignin content in the hemicelluloses extract (≈ 11% w/w, Fig. 4) could impact the film formation and decrease its mechanical performance because of lignin agglomeration and uniform dispersion that had a negative effect on the mechanical strength of films.

Tensile tests measure the force required to break the sample and the extent to which the specimen stretches or elongates to that breaking point. The tensile strength of films was

interestingly found to be independent on the type of pretreatment and the composition of hemicelluloses. In comparison, the tensile strength of films from hemicelluloses extracted from SPS was higher than those from WPS. Thus, the tensile strength of HVED SPS (16.48 MPa) films was higher compared to STEX SPS and MAE SPS films (8.85 and 8.44 MPa respectively).

Mikkonen et al. [5] have found that the tensile strength and the elongation at break of films is dependent on the degree of polymerization (DP) of hemicellulose chains. The elongation at break of guar gum-based films reached a maximum at medium low polymerization, and the tensile strength reached a maximum at medium high and medium low polymerization. In our study a DP between 254 and 406 was found to be the optimum value for high elongation at break (> 4.95 %) which match with HVED SPS, HVED WPS, MW WPS and MAE WPS films. The high amount of lignin in STEX SPS films reduces its elongation at break. The highest value of tensile strength was for HVED SPS films (16.48 MPa) which means that DP of 338 is the optimum value for high tensile strength.

Young's modulus (E) is a mechanical property that measures the stiffness of a solid material. The values of E was very close for all films made from hemicelluloses extracted in basic medium due to their high DP (>238). For STEX WPS film, the Young's modulus is very low (E = 42.4 MPa) due to the lowest DP of hemicelluloses (DP = 85).

The mechanical properties of pure spruce hemicellulose films can be improved by mixing them with other polysaccharides. For example, addition of microfibrillated cellulose (MFC) as reinforcement can enhance film performance. GGM from spruce reinforced with MFC gave films with a high Young's modulus (0.8–1 GPa) and elongation at break at 3–5% [43]. Arabinoxylan from rye blended with MFC resulted in higher film characteristics (Young's modulus: 2–2.5 GPa and elongation at break: 5–10%) [44].

393 Table 1: Mechanical properties of hemicellulose films

	Young's Modulus (MPa)		Tensile Strength (MPa)		Elongation at break (%)	
	Average	SD	Average	SD	Average	SD
HVED WPS	149.5	19.1	3.0	0.2	5.7	0.3
HVED SPS	402.4	5.0	16.5	1.3	6.3	0.5
MAE WPS	255.1	20.1	5.2	0.0	5.0	0.3
MAE SPS	331.4	15.0	8.4	2.8	6.6	0.4
STEX WPS	42.4	2.3	0.9	0.1	3.3	0.0
STEX SPS	366.3	0.2	8.9	0.0	0.1	0.1
Starch	1279.1	46.1	23.1	2.2	8.5	0.0

394

395 ### 3.3.2 Oxygen permeability

396 Polysaccharides are generally a good oxygen barrier. The hydrogen bonds of polysaccharides
397 contribute to good packing of the material and thus a low permeability of gas. The oxygen
398 permeability (OP) of prepared films is shown in Table 2. The results show that values of the
399 OP of films from hemicelluloses are lower than 10 $cm^3.\mu m.day^{-1}.kPa^{-1}$, thus they can be
400 considered as a good oxygen barrier for food packaging [45]. The oxygen permeability of
401 films made from hemicelluloses extracted from SPS is slightly lower than those extracted
402 from WPS. The high amount of lignin present in these films and the sugar composition of
403 hemicelluloses can explain this difference. In fact, it was reported that the presence of lignin
404 and native intermolecular and intramolecular hemicelluloses–lignin interactions in
405 hemicellulose-based coatings applied on polyethylene terephthalate films decrease the OP up
406 to more than 5-fold compared with the coatings obtained with purified spruce hemicelluloses

[46]. This property of lignin could provide a new application of spruce hemicelluloses without delignification of wood or high refining procedure. In this sense, the pretreatment with STEX of SPS might be thought to be more advantageous compared to other pretreatments since the lignin contents of these hemicelluloses was significantly higher and could lead to better oxygen barrier properties on the basis of our results and those reported by Zhu Ryberg et al. [46] and Bahcegul et al. [47].

The type of pretreatment (STEX, MAE, HVED) did not significantly affect the OP of the resulting films. The OP of spruce hemicellulose films in our study are near to films from AcGGM–alginate (0.6 $cm^3.\mu m.day^{-1}kPa^{-1}$) [4], Rye bran arabinoxylan (0.87 cm^3 $\mu m.day^{-1}.kPa^{-1}$at 50 % RH) [48] and lower than those from Konjac tuber glucomannan (6.1 $cm^3.\mu m.day^{-1}.kPa^{-1}$at 50 % RH) [30], Locust bean galactomannan (18 $cm^3.\mu m.day^{-1}.kPa^{-1}$at RH 50–75%) [30]. Furthermore the OP obtained for those films are lower than those of conventional petroleum-based barrier materials at (23 °C - 50 % RH), such as polyethylene terephthalate 1,000-5,000 $cm^3.\mu m.m^{-2}.day^{-1}.atm^{-1}$ which correspond to 10-50 $cm^3.\mu m.m^{-2}.day^{-1}.kPa^{-1}$, and polypropylene 50,000-10,000 $cm^3.\mu m.m^{-2}.day^{-1}.atm^{-1}$ which correspond to 500-100 $cm^3.\mu m.m^{-2}.day^{-1}.kPa^{-1}$ [49].

Table 2: Oxygen permeability of films

	OP ($cm^3.\mu m.\ m^{-2}.day^{-1}.\ kPa^{-1}$)	
Film	Average	SD
HVED SPS	0.75	2.25E-03
HVED WPS	0.83	2.25E-03
STEX SPS	0.73	4.50E-03
STEX WPS	0.80	2.25E-03
MAE SPS	0.67	0.00E+00
MAE WPS	0.81	2.25E-03
Starch	0.7	0.00E+00

3.3.3 Light transmittance

Light exposure may lead to some adverse effects on foods. It is well known that the light exposure may catalyze some reactions which are considered to be complex in nature and the most-pronounced effects are observed with light in the lower wavelengths of the visible spectrum and in the UV spectrum [50]. The damage caused by light exposure on food may be summarized as the oxidation of fats and oils, the formation of unpleasant off-flavors, losses of vitamins A, B, C and the discoloration of pigments [50]. Fig. 6 shows that hemicellulose-based films block the light transmission mostly in UV region (190-400 nm). In accordance with the lignin contents and the colors of the films, WPS- films are almost transparent in the visible area of spectrum in contrast to films produced from hemicelluloses extracted in basic medium (11.3, 4.1 and 2 % for STEX-SPS, MAE-SPS and HVED-SPS hemicelluloses respectively). Film from starch did not affect the light transmittance significantly in the UV

region. All GGM containing films showed a drop in the UV region (278 nm). Films rich with ARX and lignin are opaque in the UV region of the spectra.

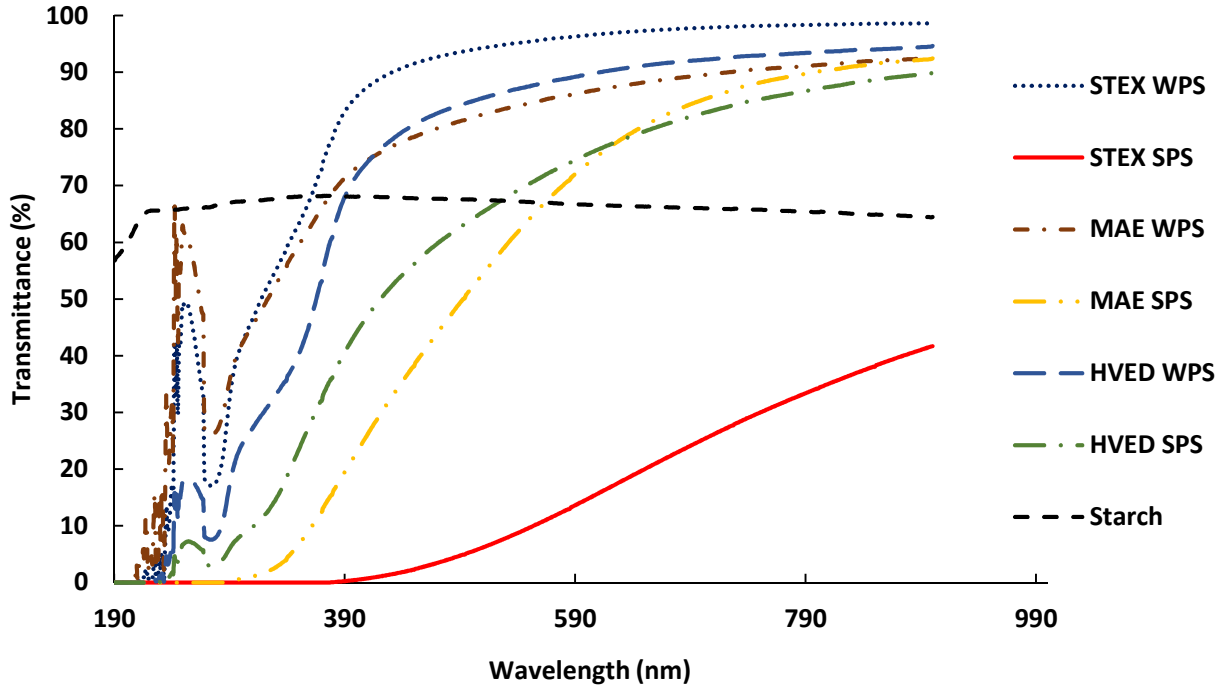


Fig. 6. Light transmittance of films

Conclusion

The extraction of polymeric hemicelluloses by steam explosion, high voltage electrical discharges and microwave assisted extraction pretreatments of impregnated spruce sawdust was investigated. The study has shown that the impregnation in water have promoted the solubilization of GGM with low lignin content (% ASL < 3.12 %) while the impregnation in basic solution has promoted the solubilization of ARX with a higher lignin contamination (2 < ASL % < 11.5). The results have shown that the operating conditions of pretreatment especially temperature and pH, were the main reason behind the differences of yield and molar mass observed between pretreatments. STEX was found to be more efficient for the extraction of high amounts of low molecular mass hemicellulose chains followed by MAE and HVED. Films prepared from hemicelluloses with high content of lignin (STEX SPS) present a good barrier property and a very low light transmittance, but weaker mechanical strength. Films from HVED pretreatments also present a good barrier to oxygen and have a good mechanical characteristic compared to MAE and STEX films.

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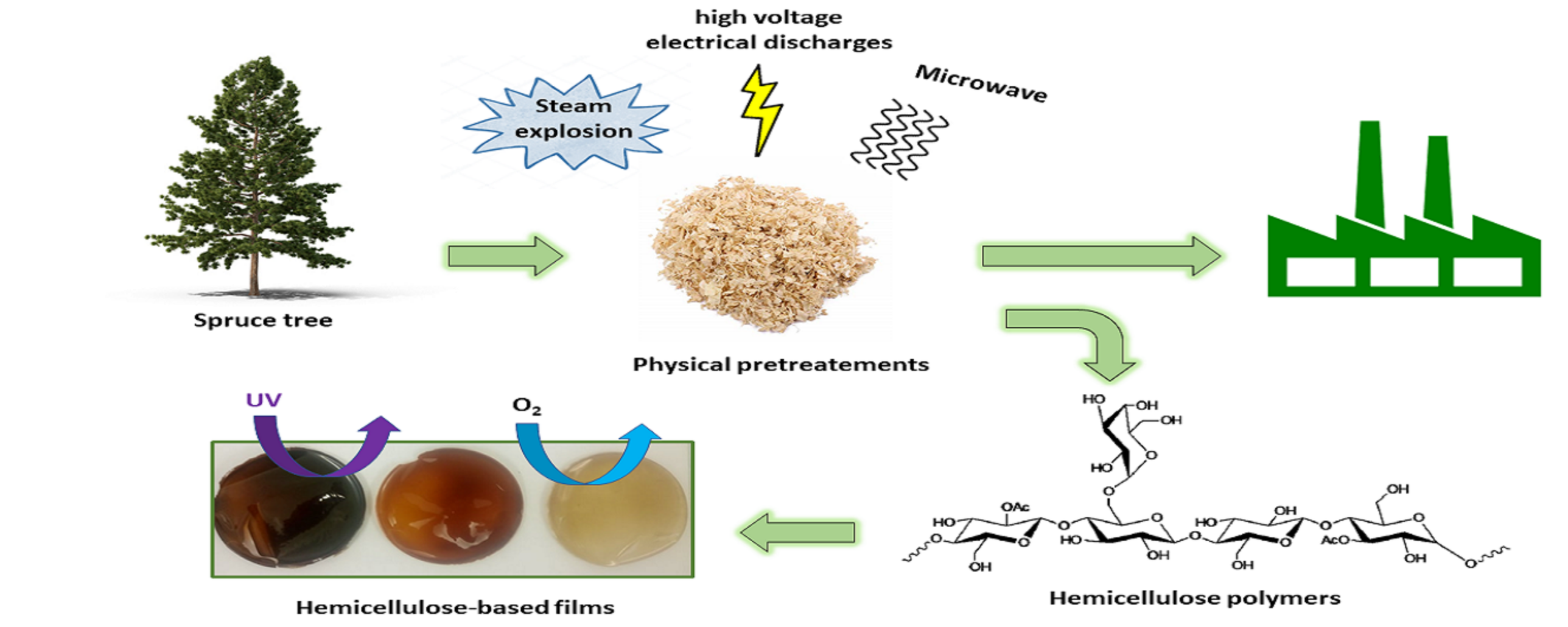
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Microwave
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Physical pretreatements
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Hemicellulose-based films
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