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Extraction of hemicelluloses from fiberized spruce wood

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ABSTRACT

A novel mechanical pre-treatment method was used to separate the wood chips into fiber bundles in order to extract high molecular weight wood polymers. The mechanical pre-treatment involved chip compression in a conical plug-screw followed by defibration in a fiberizer. The fiberized wood was treated with hot water at various combinations of time and temperature in order to analyze the extraction yield of hemicelluloses at different conditions. Nearly 6 mg/g wood of galactoglucomannan was obtained at 90 °C/120 min which was about three times more than what could be extracted from wood chips. The extracted carbohydrates had molecular weight ranging up to 60 kDa. About 10% of each of the extracted material had a molecular weight above 30 kDa. The extraction liquor could also be reused for consecutive extractions with successive increase in the extraction yield of hemicelluloses.

1. Introduction

Norway Spruce (*Picea abies*) contains 25–30% hemicelluloses, of which about 18% is present in the compound middle lamella, 19% in the S1 layer and 63% in the S2 and S3 layers of the secondary cell wall (Fengel & Wegener, 1983; Sjöström, 1993). The extractability of hemicelluloses from wood is limited, probably due to that lignin crosslink the different polysaccharides which decreases their solubility (Lawoko, Henriksson, & Gellerstedt, 2006), but a portion of these hemicelluloses is soluble in hot water or even water at room temperature (Casebier, Hamilton, & Hergert, 1969; Örså, Holmbom, & Thornton, 1997; Willför & Holmbom, 2004). The amount of water soluble hemicelluloses is large at high temperatures and long treatment times, however, hydrolytic cleavage degrades the polysaccharides at elevated conditions (Lundqvist et al., 2002; Song, Pranovich, Sumerskiy, & Holmbom, 2008). A considerably large amount of hemicelluloses can be extracted from ground wood compared to wood chips (Song et al., 2008) on the cost of low molecular weight hemicelluloses and a wet solid residue having a value corresponding to the fuel value. The dissolution is even more extensive from thermomechanical pulp (Thornton, Ekman, Holmbom, & Örså, 1994; Willför, Sjöholm, et al., 2003). The refining process in thermomechanical pulping (TMP) vigorously cracks S1/S2 fiber walls, which prompts the dissolution of hemicelluloses from cell walls into process water. Hemicellulose from TMP process water can be fractionated with high purity by combining different techniques; for example, ultrafiltration and chromatography (Westerberg et al., 2012; Willför, Rehn, et al., 2003). Water soluble polysaccharides mainly consists of O-acetyl-galactoglucomannans (AcGGM) (Lundqvist et al., 2003; Thornton et al., 1994) with molecular weight ranging up to as high as 60 kDa (Lundqvist et al., 2002; Willför, Sjöholm, et al., 2003). Other water soluble substances include mainly acidic arabinogalactans, some xylans and lignin (Lundqvist et al., 2002; Willför & Holmbom, 2004).

Potential applications of hemicelluloses are still exploring. To date hemicelluloses have been tested for making films to be used as gas barriers with promising mechanical properties (Edlund, Ryberg, & Albertsson, 2010; Höije, Gröndahl, Tømmeraas, & Gatenholm, 2005; Mikkonen, Heikkilä, Willför, & Tenkanen, 2012), as an additive in paper making to improve paper strength properties (Hannuksela, Fardim, & Holmbom, 2003; Hartmans et al., 2009) and as hydrogels (Gabrielii, Gatenholm, Glasser, Jain, & Kenne, 2000; Lindblad, Ranucci, & Albertsson, 2001).

TMP is an energy intensive process and most of the energy is converted to heat while refining. This is a large economical and environmental problem both when TMP is used for classical pulping for paper properties and also for the method as a pre-treatment stage in biorefinery concepts. However, in recent years much work has been done to understand the mechanism of mechanical pulping on the wood structure in order to reduce the energy demand

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during refining. Mechanical pre-treatment of chips combined with increased refining intensity has been demonstrated to considerably reduce the energy demand in a novel process called advanced thermomechanical pulping (ATMP) (Johansson, Hill, Gorski, & Axelsson, 2011). The pre-treatment stage in ATMP consists of an impressafiner and a fiberizer. The impressafiner is a screw-press where chips are compressed at a high strain in a pressurized environment. A fiberizer is essentially a small moderately pressurized refiner which defibrates the wood chips into fiber bundles called as fiberized wood (Hill, Johansson, Sabourin, & Aichinger, 2009; Hill et al., 2010). The compressive pre-treatment separates the wood fibers and creates cracks in S1 and S2 fiber walls which increases the surface area and decrease the mass transport length (Kure, Dahlqvist, Sabourin, & Helle, 1999). Compressive pre-treatment prior to mainline refining saves up to 20% energy compared to conventionally produced TMP pulps (Sabourin, Aichinger, & Wiseman, 2003). Integrating a hot water extraction system together with mechanical pre-treatment in the primary stages of either mechanical or chemical pulping processes will, in addition to saving energy, produce valuable products from isolated hemicelluloses which otherwise are degraded and/or dissolved in the processing liquors (Heiningen, 2006; Lisboa, Evtuguin, Neto, & Goodfellow, 2005).

In this study, fiberized spruce wood has been subjected to hot water extractions with the goal to investigate its possible role in a biorefinery context by extracting high molecular weight galactoglucomannan (GGM) and that the solid residue could be used as a raw material in the pulping processes. Different extraction conditions of time and temperature were used in order to investigate the effect on the amount and molar mass of isolated polysaccharides. Since the aim was to isolate relatively native hemicelluloses therefore elevated treatment conditions were not studied due to the risk of polymer degradation. The extracted material was investigated for lignocellulosic composition, molar mass distribution and acetyl content. An attempt to reuse the extraction liquor containing dissolved solids from the wood has also been made in order to foresee the potential in a mill application to increase the concentration of hemicelluloses in the extraction liquor.

2. Experimental

2.1. Material and mechanical pre-treatment

Chips of Norway spruce (*P. abies*) were obtained directly after the impressafiner from Braviken paper mill, Holmen Paper AB in Norrköping, Sweden. Impressafined chips were steamed for 5 min with atmospheric steam and fiberized using a pilot scale 12″ disc refiner (Sprout-Waldron) at Chalmers University of Technology, Sweden. The net energy input of the refiner was adjusted to 300 kWh/odt wood by adjusting the speed of the conveyer belt delivering wood to the refiner in a single pass mode. Fiberized wood was stored in the dark at −24 °C and thawed overnight at room temperature prior to further use.

2.2. Extractions

Distinct batches of fiberized wood were extracted with water at 30, 60 and 90 °C for different times ranging from 5 to 120 min. For comparison, frozen spruce wood chips were thawed overnight and subjected to hot water extraction at 90 °C for different times. For each batch of extraction, 500 ml of deionized water was first heated in a beaker to the target temperature followed by the addition of 10 g (dry weight) of fiberized wood or wood chips. The temperature drop due to the addition of wood, was recovered in 2–3 min, however a variation of ±2 °C was noted throughout the treatment. The water–wood mixture was stirred with a mechanical stirrer using an axial flow impeller rotating at ≈400 rpm. Subsequently, the liquid was separated from the wood using a fiber cloth sieve (Monodur PA-71, Mesh opening 71 μm) under vacuum, followed by washing the wood with 100 ml deionized water. The liquid was again vacuum-filtered through a glass fiber filter (Whatman GF/A, 1.6 μm) to remove any particles or colloids. The filtrate was allowed to cool and the pH was recorded at room temperature. Filtrate containing dissolved solids from wood was concentrated by vacuum evaporation using a water bath at 50 °C and lyophilized.

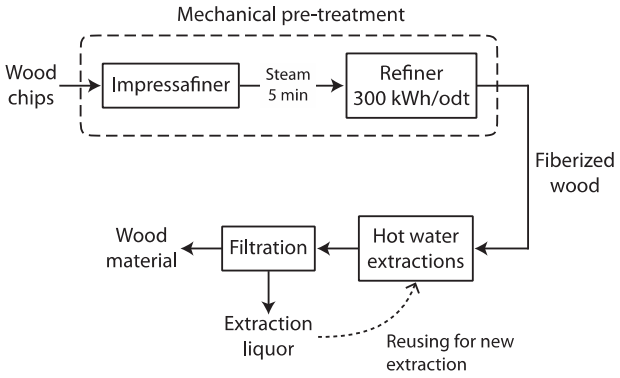

Fig. 1. Schematic diagram depicting the mechanical pre-treatment of spruce wood chips followed by hot water extraction. The extraction liquor was reused multiple times with new atch of fiberized wood.

For reusing the extraction liquor, six consecutive extractions were performed at 90 °C for 120 min. The liquid containing dissolved solids from the first extraction was reused for extraction with a new batch of fiberized wood and was further used to carry four more batch-wise extractions. A 10 g (dry weight) of fiberized wood was used in each batch. Extraction liquid in each stage was filtered the above-mentioned way before subjecting to the following extraction (Fig. 1).

2.3. Analysis

2.3.1. Gravimetric analysis

The total amount of material dissolved from the fiberized wood was calculated gravimetrically by lyophilizing the extracted aliquots.

Lignin content in the extracts was determined by subtracting the amount of Klason lignin in the remaining wood after extraction, from the lignin present in the starting fiberized wood. For lignin analysis, wood samples were dried at 105 °C and ground to pass a 40-mesh screen. 200 mg of ground wood was hydrolysed employing conditions described in a standard method (SCAN, 2009). The hydrolysates were filtered and the insoluble part on the filter paper was dried and weighed giving the amount of Klason lignin.

2.3.2. Carbohydrate composition

Carbohydrate composition of the lyophilized extracts was determined after acid hydrolysis (SCAN, 2009). Monosaccharide content of the hydrolysate was analyzed with high-performance anion-exchange chromatography (Dionex, Sunnyvale, CA, USA) equipped with pulsed amperometric detector (HPAEC-PAD) using a CarboPac PA-1 column (4 × 250 mm). The system was equilibrated for 7 min with 260 mM sodium hydroxide and 170 mM sodium acetate followed by Milli-Q water for 6 min. Only Milli-Q water was used as eluent at a flow rate of 1 ml/min. A solution of 300 mM NaOH was added to the column effluent before the PAD cell at a flow rate of 0.5 ml/min. Data was processed with Chromeleon 7.1 software.

2.3.3. Molar mass analysis

Molar mass distribution of lyophilized extracts was estimated by size exclusion chromatography (SEC) carried out on a Dionex Ultimate-3000 HPLC system (Dionex, Sunnyvale, CA, USA) maintained at 40 °C with 10 mM NaOH as mobile phase flowing at a rate of 1 ml/min. The system consisted of three PSS suprema columns in series (300 × 8 mm, 10 μm particle size) with 30 Å, 1000 Å and 1000 Å pore sizes, together with a guard column (50 × 8 mm, 10 μm particle size). The system was equipped with an LPG-3400SD gradient pump, a WPS-3000SL autosampler and a DAD-3000 UV/vis detector (Dionex, Sunnyvale, CA, USA) in addition to a Waters-410 refractive index (RI) detector (Waters, Milford, MA, USA). Pollulan standards ranging from Mp = 342 to 708,000 Da (PSS, Germany) were used for calibration. The sample was dissolved in 10 mM NaOH at a concentration of 5–6 mg/mL and 20 μL of the solution was injected in the system.

2.3.4. Acetyl content

Acetyl content in the extract was estimated from the integral responses of acetyl relative to internal standard from the spectra obtained using ^{1}HNMR. Trimesic acid was used as an internal standard. About 3 mg of the dried sample was dissolved in 0.7 ml of Deuterated dimethyl sulfoxide (DMSO-d_6) together with a known amount of the internal standard. ^{1}HNMR spectra were recorded at room temperature on a Bruker Avance 400 MHz instrument.

2.3.5. Scanning electron microscopy (SEM)

Dried samples of wood chips and fiberized wood were cut transverse to the fiber direction using Cold Laser ablation. SEM images of the cross sections were taken using a table-top Hitachi TM-1000 SEM with an acceleration voltage of 15 kV.

3. Results and discussion

3.1. Effects of mechanical pre-treatment

Mechanical pre-treatment stage was comprised of macerating the wood chips in an impressafiner followed by defibration in a fiberizer. In the impressafiner (a plug screw-press), chips were compressed at high strain in a pressurized environment that squeezed out water, extractives and entrained air. Defibration was performed in the refiner at a net energy input of 300 kWh/odt wood, considerably lower than the energy demand of a primary refiner in a TMP mill. Impressafined chips retain the basic wood structure whereas the fiberized material consisted of fibers separated from each other to a certain degree with an average length of 10 mm (Fig. 2).

The purpose of the mechanical pre-treatment was to increase the available surface area by partly disintegrating the chips to wood fibers and induce cracks within fiber walls. Fractures were created in the middle lamellae and possibly primary layer of the cell wall as shown in Fig. 3c and d. However, the cells in wood chips were properly aligned (Fig. 3a and b) without any crumbling effect as in case of fiberized wood. The combined effect of larger surface area and shorter diffusion paths of the fiberized wood considerably increased the mass transfer from fiberized wood and facilitated the extraction of hemicelluloses. The amount of hemicelluloses dissolved from fiberized wood was almost double than what could be dissolved from wood chips (Table 1).

3.2. Extractions

Hot water extractions were performed on fiberized wood and wood chips at different combinations of temperature and time. Higher temperature and longer treatment times were avoided due to the risk of polymer degradation. In addition, the energy demand

Table 1
Amount and composition of carbohydrates (mg/g wood) extracted from fiberized wood and wood chips.

	30 °C					60 °C					90 °C					From wood chips at 90 °C				
	5 min	15 min	30 min	60 min	90 min	120 min	5 min	15 min	30 min	60 min	90 min	120 min	5 min	15 min	30 min	60 min	90 min	120 min	5 min	15 min	30 min	60 min	90 min	120 min
Anhydrous monosaccharides																								
Man	1.8	1.9	2.0	2.0	2.2	2.2	2.2	2.3	2.4	2.8	2.8	2.8	2.6	2.9	3.3	3.5	3.9	4.1	0.8	1.0	1.2	1.1	1.1	1.3
Glu	1.2	1.2	1.3	1.1	1.5	1.3	1.7	1.8	1.9	1.9	1.9	2.0	1.3	1.8	2.0	2.1	2.3	2.5	0.3	0.4	0.6	0.4	0.4	0.4
Gal	0.1	0.8	0.9	0.9	1.1	0.9	1.3	1.3	1.3	1.0	1.0	1.2	1.0	1.1	1.1	1.1	1.1	1.4	0.3	0.4	0.4	0.4	0.4	0.8
Ara	0.3	0.2	0.3	0.2	0.2	0.3	0.4	0.4	0.4	0.4	0.4	0.4	0.3	0.3	0.4	0.4	0.4	0.8	0.8	1.0	1.3	1.2	1.3	1.7
Xyl	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.3	0.2	0.1	0.1	0.2	0.2	0.2	0.2
Sum	3.5	4.2	4.5	4.2	5.1	4.7	5.5	5.7	6.1	6.3	6.3	6.6	5.2	6.2	6.9	7.2	7.9	8.9	2.3	2.8	3.7	3.3	3.4	4.5
Dissolved GGM[a]																								
Total	3.0	2.9	3.2	3.1	3.4	3.4	3.7	3.8	3.9	4.2	4.1	4.4	3.9	4.3	4.9	5.0	5.4	5.9	1.2	1.5	1.8	1.6	1.6	2.2
Yield[b]	1.8	1.8	2.0	1.9	2.1	2.1	2.3	2.3	2.4	2.6	2.5	2.7	2.4	2.6	3.0	3.1	3.3	3.6	0.7	0.9	1.1	1.0	1.0	1.3

[a] GGM = (Gal + (1 + 1/3.5) × Man) × 0.9.
[b] AcGGM in spruce = 163 mg/g wood (Sjöström, 1993).

Fig. 2. Fiberized wood.

of the extraction stage was also thought to keep low. The collected extracts were cooled to room temperature and the pH of all the extracts was observed to be in the range of 5.7–6.8. The slight drop in the pH was probably due to the release of small amounts of acetic acid when treated at high temperatures for longer times. The aliquots were later lyophilized and analyzed for composition, molar mass distribution and acetyl groups.

3.2.1. Amount of extracted carbohydrates

The amount and composition of carbohydrates extracted from fiberized wood and wood chips, analyzed by HPAEC after acid hydrolysis, are presented in Table 1. Total amount of carbohydrates extracted from fiberized wood increased with temperature and time. The upsurge in the extraction yield was believed to be due to the softening of fibers at high temperatures that enabled the dissolution of hemicelluloses through the cracks in the cell wall created by defibration. A maximum amount of 8.9 mg/g of carbohydrates was obtained at 90 °C and 120 min, whereas only 4.5 mg/g of carbohydrates were possible to extract from wood chips at similar conditions. The significant difference in the amounts of extracted carbohydrates indicated an increased available surface area of fiberized wood as compared to wood chips.

At 90 °C/120 min the extraction yield of GGM was more than 3.6%, which comprised about 66% of the total extracted carbohydrates from fiberized wood. The relative high proportions of arabinose units in the extracts were probably derived from water-soluble arabinogalactan, which is a minor polysaccharide present in spruce wood (Willför, Sjöholm, Laine, & Holmbom, 2002). The amount of xylan present in the extracts was insignificant and did not noticeably increase at elevated conditions. The glucose in GGM was calculated based on the ratio of glucose to mannose (1:3.5) (Meier, 1958). The surplus of glucose present in the extracts was probably derived from xyloglucan and/or other glucans, which are present in minor amounts in spruce.

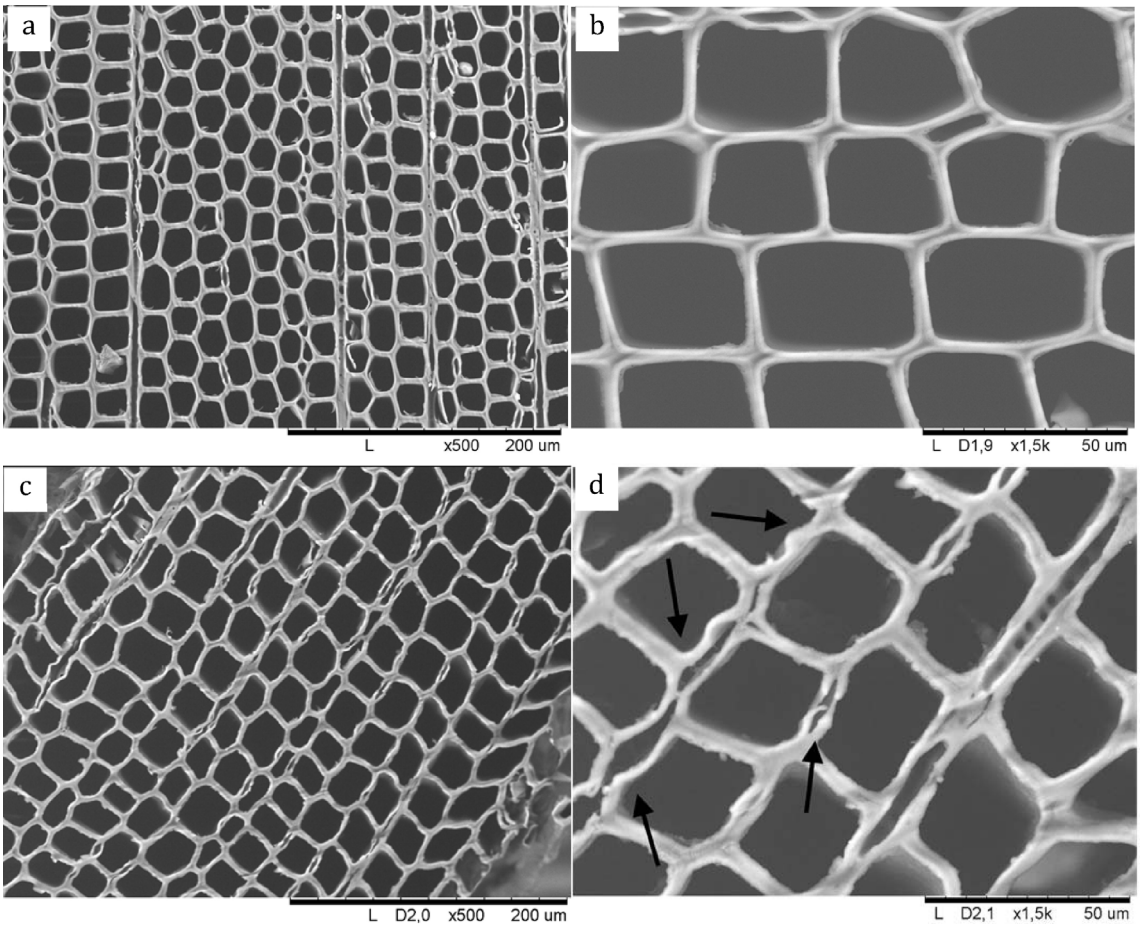

Fig. 3. Cross-sectional SEM micrographs of wood chips (a and b) and fiberized wood (c and d).

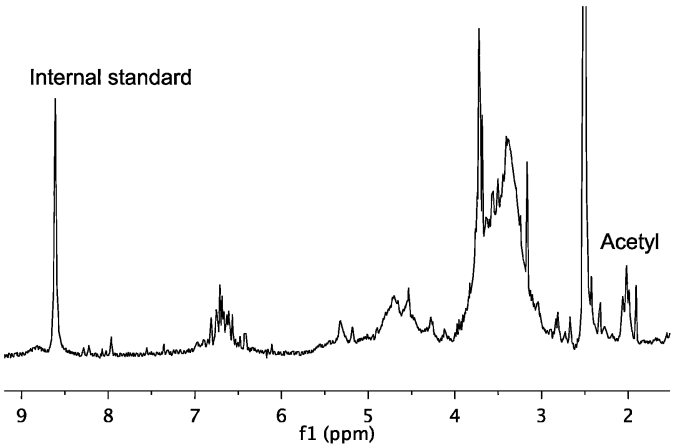

Fig. 4. ^{1}HNMR spectra of acetyl-GGM extracted from fiberized wood with water at 90 °C/15 min.

3.2.2. Degree of deacetylation

The samples extracted at 90 °C were analyzed for degree of acetyl substitution using ^{1}HNMR. The spectra of sample extracted at 90 °C/15 min is shown in Fig. 4. The peak at 2.2 ppm was assigned to acetyl groups among several strong signals in the spectra. The signal at 2.5 was from DMSO whereas the anomeric protons of the GGM caused the signals between 4.5 and 5.2. Other protons from GGM mostly appeared from 3.2 to 4.2. The peak between 6.5 and 7 ppm was from double bonds from GGM or aromatic compounds which might be the lignin present in the extracts.

It was found that the GGM backbone of glucosyl and mannosyl units was acetylated in the range of 25–40%, assuming that all the acetyl groups were linked to glucomannan. This is in accordance with the previous observation: according to Capek, Alföldi, and Lišková (2002), the degree of substitution of acetyl groups is about 50% whereas Lundqvist et al. (2002) reported that about one third of the mannose units are O-acetylated. However, the O-acetyl side groups seemed to reduce with longer treatment times.

3.2.3. Extracted lignin

The amount of lignin extracted from fiberized wood increased with increasing time and temperature ranging from 2 mg/g wood (30 °C, 5 min) to 5.3 mg/g wood (90 °C, 120 min). The maximum extraction yield of lignin was up to 2%, whereas this value was less than 1% in case of wood chips. The increased surface area of fiberized wood also facilitated the dissolution of lignin.

3.2.4. Molar mass of extracts

The RI- and UV-detector responses of the dried extracts obtained using SEC are plotted against time in Fig. 5. It was observed that each extracted sample showed the same molecular weight distribution trend as presented in Fig. 5. The RI response (with no UV response) between 21 and 23 min indicated the presence of pure hemicelluloses with non-detectable amounts of lignin. The cumulative weight distribution curve showed that more than 10% of the material had a molecular weight above 30 kDa. Since GGM was the main carbohydrate in the extract; therefore, it was anticipated that the hot water extracts from fiberized wood contained a pure fraction of GGM with a molecular weight of up to more

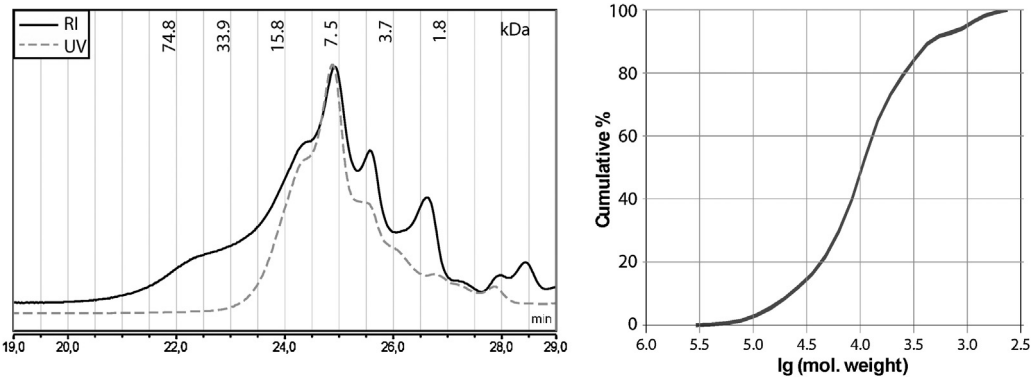

Fig. 5. SEC chromatogram of freeze-dried material extracted at 60 °C for 60 min showing RI and UV signals along with cumulative weight distribution curve obtained by integrating the RI signal peak.

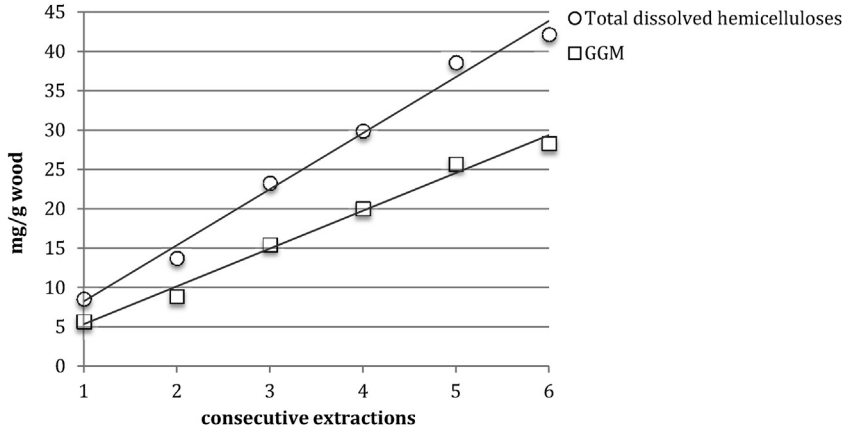

Fig. 6. Linear plot for the cumulative amount of total dissolved hemicelluloses from fiberized wood when extracted at 90 °C for 120 min for six consecutive extractions with respect to the total amount of dissolved GGM.

than 30 kDa, corresponding to a degree of polymerization of 160. The lignin present in the extract could be covalently cross-linked with low molecular weight hemicelluloses or present in oligomeric or monomeric form.

3.3. Reusing extraction liquor

By recycling the extraction liquor to perform multiple extractions, it was observed that the extraction liquid could be reused several times until it was saturated with the dissolved components from fiberized wood, which is an important factor at commercialization of biorefineries. The amount of total extracted carbohydrates increased in each extraction stage and the cumulative amount after six recirculation reached up to 43 mg/g as shown in Fig. 6. The GGM fraction of the extract also increased in each case and reached a total of more than 28 mg/g after sixth cycle. The molar mass of each dried extract was analyzed and it was observed that the extract from each stage showed the same trend as presented in Fig. 5. This shows the potential in a mill application to increase the concentration of hemicelluloses in the extraction liquor, the maximum concentration remains, however, to be investigated. An increased concentration in the extraction liquor will lower the cost in the following stages to obtain a hemicellulose product.

4. Conclusions

This study showed that

- The fiberizer, with a considerably low energy input of 300 kWh/odt wood, cracked the fiber walls to the extent which enabled a partial dissolution of the wood polymers into water.
- A fraction of hemicelluloses was readily dissolved in water from the fiberized wood at all temperatures. However, the extraction yield increased with the increase in temperature and time reaching to the maximum at 90 °C and 120 min.
- The extract obtained at 90 °C/120 min contained about 6 mg/g wood of galactoglucomannan with high degree of acetyl substitution and molecular weight ranging up to 60 kDa.
- About 10% of the material in each extract was composed of an almost pure fraction of GGM with an average molecular weight of more than 30 kDa.
- The extraction liquor could be reused multiple times without any significant decrease in the extraction yield.

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