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Antisolvent precipitation of water-soluble hemicelluloses from TMP process water

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ABSTRACT

During the thermomechanical pulping (TMP) of spruce, hemicelluloses (mainly galactoglucomannans, GGMs) are released into the process water at relatively low concentrations that are currently impossible to efficiently recover. This paper examines the recovery of hemicelluloses precipitated from TMP process water via solubility reduction by adding antisolvents such as methanol, ethanol, and acetone. The phase separation was monitored by turbidity measurements. Gravimetric analysis, FTIR, GC–MS, UV spectroscopy, and ICP-OES were used to determine the yield, purity, and composition of the precipitates. Gel permeation chromatography and pulsed field-gradient self-diffusion NMR were used to measure the molecular mass distribution of the precipitates. Acetone was found to be the most efficient antisolvent, giving the highest yield at the lowest addition. The contents of lipophilic extractives and lignin impurities were below 0.5% and 1.6%, respectively, and the metal content was approximately 2% in the precipitates obtained with acetone.

1. Introduction

The demand for sustainable solutions to worldwide climate change and environmental problems is motivating the replacement of petroleum-based products and is the main driver of increasing research interest in biopolymers from renewable sources. Cellulose has naturally been emphasized, as it is the most abundant biopolymer on earth. However, hemicelluloses and their potential applications have recently also attracted considerable attention from scientists in universities, research institutions, and industry. Galactoglucomannans (GGMs) are the main hemicelluloses in spruce, located primarily in the secondary cell wall layer of fibers and accounting for 10–20% of the wood material (Willför, Sundberg, Hemming, & Holmbom, 2005). The exploitation of GGMs from wood is currently low, but future utilization in a wide range of applications can be foreseen. Hydrogels, food packaging films, and emulsion stabilizers for beverages are but a few products that could be manufactured from GGMs (Hartman, Albertsson, Lindblad, & Sjöberg, 2006; Hartman, Albertsson, & Sjöberg, 2006; Mikkonen et al., 2009). The backbone of GGMs comprises (1→4)-linked β-D-mannopyranosyl and (1→4)-linked β-D-glucopyranosyl units in a ratio of approximately 10:1.9–2.6, with side units of α-(1→6)-D-galactopyranosyl (Timell, 1967). The mannopyranosyl units contain acetyl groups at the C-2 and C-3 positions, giving a degree of acetylation of approximately 0.5 in spruce wood GGMs (Capek, Alföldi, & Lišková, 2002) and of 0.28–0.37 for GGMs released into spruce TMP waters (Hannuksela & Du Penhoat, 2004).

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Extraction of GGMs from spruce wood using hot water (Örså, Holmbom, & Thornton, 1997), microwave heat-fractionation (Lundqvist et al., 2003), alkaline treatment (Capek et al., 2000), and pressurized hot water (Song, Pranovich, & Holmbom, 2012; Song, Pranovich, Sumerskiy, & Holmbom, 2008) has been extensively investigated.

During the thermomechanical pulping (TMP) of spruce, GGMs are released into the process water at relatively low concentrations that are currently impossible to efficiently recover. Based on previous studies, the valuable raw materials wasted in process water by a mill producing 500,000 tons of pulp per year can be as follows: GGMs, 5880–7810 t year^{-1}; lignans, 840–910 t year^{-1}; resin acids, 77–225 t year^{-1}; and fatty acids 40–100 t year^{-1} (Strand et al., 2012; Zasadowski, Strand, Sundberg, Edlund, & Norgren, 2014). Membrane filtration techniques have been proposed for recovering hemicelluloses from TMP process waters. By means of ultrafiltration, GGMs have been concentrated to over 60 g L^{-1} (Al Manasrah, Kallioinen, Ilvesniemi, & Mänttäri, 2012; Krawczyk & Jönsson, 2011; Persson, Nordin, Zacchi, & Jönsson, 2007; Persson, Ren, Joelsson, & Jönsson, 2009). However, as the molecular mass of the hemicelluloses is relatively low, membrane filtration requires fairly low cutoffs, implying relatively low flux and overall efficiency.

Precipitation by adding antisolvents such as ethanol is an interesting approach to recovering GGMs from various waters. Peng et al. (2009) investigated the use of graded ethanol precipitation to recover hemicelluloses from sugarcane bagasse. They observed that increasing the ethanol concentration from 15% to 60% increased the recovered yield and weight-average molecular mass (M_w) of hemicelluloses, the latter increasing from 42,430 to 85,510 g mol^{-1}. Investigation of the precipitation and fractionation of hemicelluloses from *Caragana korshinskii* with ethanol confirms that hemicellulose recovery is higher at higher ethanol contents (Bian, Peng, Peng, Xu, & Sun, 2010). Increasing the ethanol content from 10% to 30% increased the M_w of hemicelluloses from 28,950 to 58,900 g mol^{-1}, while a further increase from 45% to 80% reduced the M_w from 44,000 to 15,000 g mol^{-1}. The recovery of hemicelluloses from various water streams using combined separation techniques, such as ultrafiltration and precipitation, has been examined in several studies. Xu, Willför, Sundberg, Petterson, and Holmbom (2008) used ultrafiltration to concentrate the water and then investigated the properties of ethanol-precipitated and spray-dried spruce GGMs. Hemicelluloses precipitated with ethanol reportedly had a higher GGM content and higher average molar mass than did GGMs that were only spray-dried, i.e., 46,000 g mol^{-1} versus 39,000 g mol^{-1}, respectively. A procedure for recovering hemicelluloses from TMP waters based on ultrafiltration, ethanol precipitation, and vacuum evaporation concentration has also been proposed (Willför, Rehn, Sundberg, Sundberg, & Holmbom, 2003), GGMs with an M_w of 29,000 g mol^{-1} reported being the main hemicellulose obtained.

This paper examines the separation of hemicelluloses from spruce TMP process waters by antisolvent precipitation. The process water was first pre-purified by induced air flotation to remove hydrophobic wood substances; then the influence of three antisolvents (i.e., methanol, ethanol, and acetone), pH, and temperature on the precipitation efficiency was investigated. The precipitation testing was followed by turbidity and gravimetric analysis. Moreover, the composition and content of carbohydrates in the obtained precipitates were characterized by gas chromatography (GC) and Fourier transform infrared spectroscopy (FTIR). The molecular size distributions of redissolved hemicellulose precipitates were determined by gel permeation chromatography (GPC) and ^{1}H pulsed field-gradient self-diffusion NMR (PFG NMR).

2. Materials

2.1. Chemicals

Dodecyltrimethylammonium chloride (DoTAC, purity >99%; China Innovation Group Co., Wuhan, China) was used as a foaming agent in the experiments. Hydrochloric acid (HCl, 37%, AnalaR Normapur; VMR International, Radnor, PA, USA) was used to acidify the water. Analytical grade methanol with a purity of 99.8% and technical grade acetone were obtained from VWR International. Analytical grade ethanol with a purity of 99.5% was obtained from Solveco (Solveco Group, Rosersberg, Sweden). Pullulans (Shodex, New York, NY, USA) and dextrans (Fluka, Buchs, Swiss) were used as internal standards in the GPC and PFG NMR determinations, respectively. Deuterium oxide (Cambridge Isotope Laboratories, Tewksbury, MA, USA) was used to dissolve the samples in the PFG NMR measurements.

2.2. GGM containing unbleached TMP process water

Samples of the TMP process water were taken from the wire press section before the bleaching tower at a mill in central Sweden. The pulp consistency after the wire press was 35% and the pH of the water was 5.1. Water samples not used immediately were stored at 6 °C for no longer than 4 days before the experiments.

3. Methods

3.1. Turbidity measurements

Turbidity was measured using a Ratio/XR turbidimeter, model 43,900 (Hach, Loveland, CO, USA). The hemicellulose precipitation samples were analyzed directly after vigorous tube shaking. The turbidity of the waters before hemicellulose precipitation was measured after 1 h of sedimentation to avoid errors induced by remaining fibers and fines.

3.2. Removal of lipophilic substances by induced air flotation and concentration of purified TMP process water

Flotations were performed in a Voith flotation cell (J.M. Voith GmbH, Heidenheim, Germany), consisting of a Plexiglas cube with a side length of 30 cm, at an impeller rotational speed of 1340 rpm. More detailed descriptions of induced air flotation for process water in general, and of the Voith cell setup specifically, have been presented in previous studies (Strand et al., 2012; Zasadowski, Hedenström, Edlund, & Norgren, 2012a, Zasadowski, Hedenström, Edlund, & Norgren, 2012b). Six liters of 50 °C process water was poured into a glass beaker and stirred. The pH of the water was adjusted to 3.5 with HCl, after which 80 ppm of DoTAC (foaming agent) was added. The process water was transferred into the flotation cell and flotation without forced air flow was performed for 60 min. The generated foam fraction was collected using a suction flask, and the fiber and fines fraction was thereafter removed by filtration through a fiber filter. A fraction of the purified water was collected and concentrated approximately 8.5 times using a vacuum evaporator. All the water samples were stored in a freezer for further chemical analysis and investigation.

Table 1 presents data from the various analyses of the water fractions.

3.3. Hemicellulose precipitation

Hemicelluloses were precipitated from the purified water samples, before and after concentration, at different weight fractions of methanol, ethanol, and acetone. The antisolvents were added

Table 1
Characteristics of the TMP process water before and after flotation, after filtration, and after concentration.

Analysis	Original water	Flotated water	Flotated and filtered water	Concentrated water
pH	3.5	3.7	3.8	3.3
Turbidity (NTU)	3350	458	290	4200[a]
Extractives ($mg\,L^{-1}$)				
Lignin	1280	611	380	2730
Fatty and resin acids	66.9	1.64	8.19	64.6
Lignans	330	317	202	1710
Sterols	20.9	12.3	6.92	44.6
Steryl esters	45	2.9	17.2	128
Triglycerides	61.5	0.5	2.48	10.3
Carbohydrates ($mg\,L^{-1}$)				
Mannose	1270	1300	940	7700
Glucose	355	356	249	2120
Galactose	554	410	282	2370
Arabinose	119	107	67.9	571
Xylose	38.8	37.0	27.6	224
Rhamnose	80.6	62.2	40.0	380
Galacturonic acid	97.7	86.0	46.8	390
Glucuronic acid	60.9	51.7	29.7	285
Metals (ppm)				
Calcium	13	13	14	96
Iron	0.2	0.1	0.1	0.8
Copper	0.2	0.2	0.2	1.6
Manganese	11	12	12	79

[a] Based on measurements of diluted samples.

at pH values of 3.8 and 5.1, and precipitation was carried out at 7 °C, 20 °C, and 50 °C. After 4 h of sedimentation at each temperature, the samples were shaken vigorously and the turbidity was measured. Turbidity was measured only in the antisolvent-treated samples from unconcentrated process water, as the concentrated process water samples displayed values outside the measuring range. The samples were centrifuged at $500 \times g$ for 15 min and the supernatants were carefully separated. The precipitates were transferred into 25-mL beakers, freeze-dried overnight, and then weighed. For further analyses, solutions were prepared by dissolving 25 mg of the freeze-dried precipitate in 25 mL of distilled water.

3.4. Chemical analysis of carbohydrates

The carbohydrate content was determined by GC after acid hydrolysis (Sundberg, Sundberg, Lillandt, & Holmbom, 1996; Willför et al., 2009). Sugar units were analyzed using a long-column gas chromatograph (HP-1, 30 m × 0.25 mm) with split injection and equipped with a flame ionization detector (FID).

FTIR spectroscopy was used to characterize the main functional groups of antisolvent-precipitated hemicelluloses. The FTIR spectra were recorded in the wavelength range of 4000–400 cm^{-1} on a Nicolet 6700 FTIR (Thermo Fisher Scientific, Waltham, MA, USA) equipped with OMNIC software.

3.5. Analysis of lipophilic extractives

The purified TMP process water samples were centrifuged at $500 \times g$ to remove fibers and fines. The antisolvent-precipitated hemicelluloses were analyzed without further preparation. The content of lipophilic extractives was investigated using a method described by Örså and Holmbom (1994). The samples were analyzed using a short-column gas chromatograph (HP-1, 15 m × 0.53 mm) with on-column injection and equipped with an FID.

3.6. Lignin analysis

The water samples and hemicellulose solutions were analyzed for lignin after methyl tert-butyl ether (MTBE) extraction. The ultraviolet (UV) absorption at 280 nm was measured using a Shimadzu UV-1800 spectrophotometer (Shimadzu, Kyoto, Japan). Matched QS cuvettes were used for UV-range measurements; an extinction coefficient of 0.0145 $L\,mg^{-1}\,cm^{-1}$ was used for lignin quantification according to the SCA-F W17:81 method.

3.7. Molecular mass determinations by GPC and PFG NMR measurements

GPC measurements were made using OHpak SB-800 HQ columns (Shodex) and an Ultimate 3000 UNPLC system (Dionex, Sunnyvale, CA, USA) equipped with a pulsed amperometric detection detector. Pullulan standards were used for the molecular mass calibration. Samples of 10 mg were transferred to 10 mL of water and ultrasonicated twice for 30 min. Before injection, the samples were filtered through a 0.45-μm filter. PFG NMR measurements were made using a Bruker Avance DPX 250 MHz spectrometer equipped with a Bruker self-diffusion probe capable of providing 18 $T\,m^{-1}$ at 60 A (Bruker Biospin AG, Karlsruhe, Germany). Samples of freeze-dried polysaccharides were dissolved in deuterium oxide to a concentration of 1 wt% and mixed overnight. Typically, the gradient strength was varied from 0.4 to 1.8 $T\,m^{-1}$ at a gradient pulse duration of $\delta = 1.5$ ms. The diffusion time was set to $\Delta = 40$ ms and 128 scans were acquired at 15 gradient strengths with a relaxation time of 3.0 s between successive scans, using the stimulated echo pulse sequence. The resulting self-diffusion coefficients for the polysaccharides were obtained after fitting the echo decays to a log-normal distribution function as described elsewhere (Andersson, Pranovich, Norgren, Eriksson, & Holmbom, 2008; Fleischer, 1985; Håkansson, Nydén, & Söderman, 2000). Dextran standards were used to obtain the scaling parameters (K and α) needed for calculating the approximate molecular mass distribution of hemicelluloses from the Mark–Houwink relationship between the self-diffusion coefficient (D) and the molar mass (M), $D = KM^{\alpha}$.

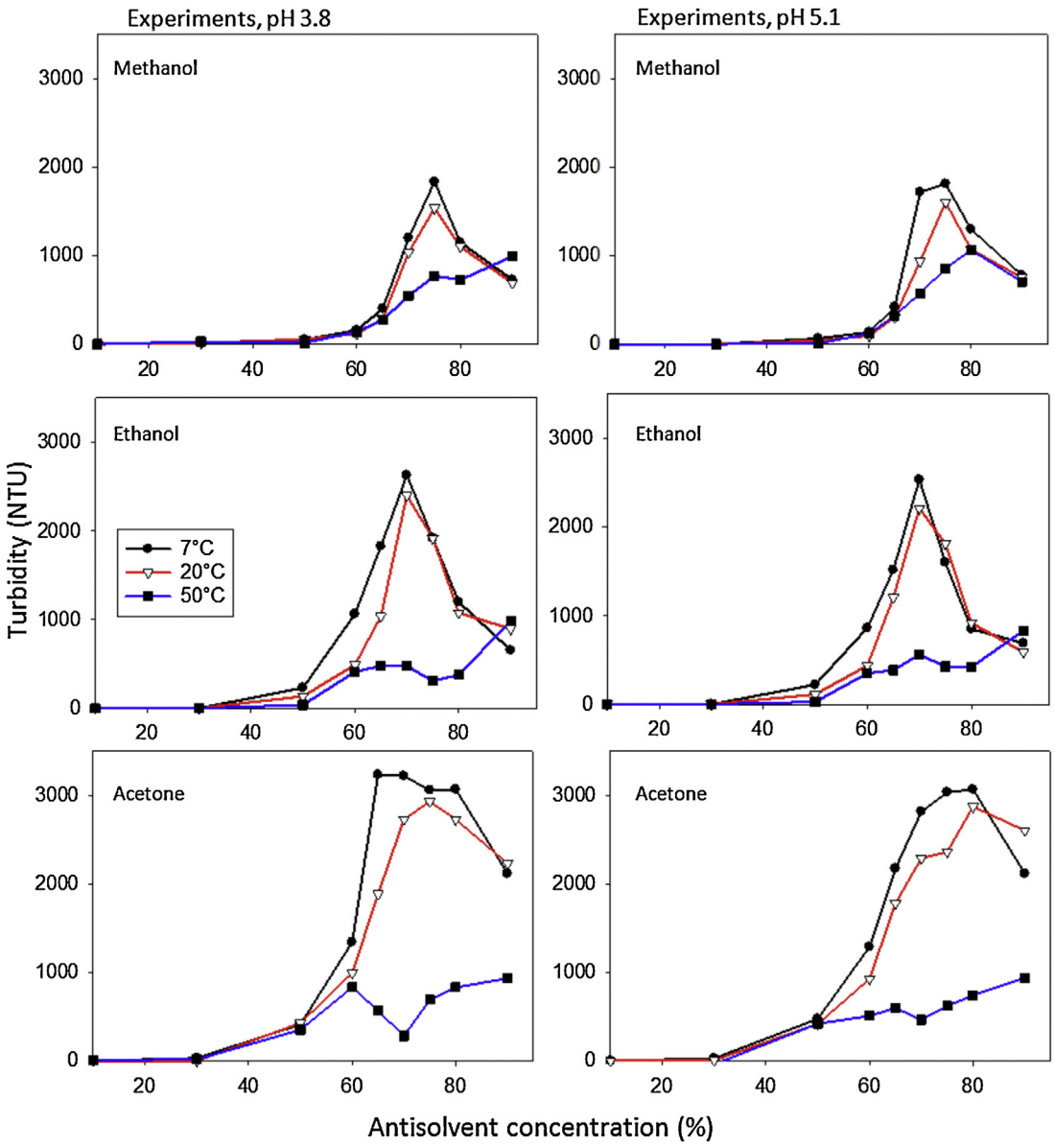

Fig. 1. Turbidity (NTU) change during antisolvent-induced phase separation of hemicelluloses from unconcentrated TMP process water at various temperatures.

The relationship between the logarithmic weight-averaged median self-diffusion coefficient and the logarithmic weight-averaged median molecular mass of the dextran standards indicated a linear correlation ($R^2 = 0.998$).

3.8. Metal analysis

A 10 mL purified TMP process water sample was refluxed for 5 min with 2.5 mL of concentrated nitric acid and 2 mL of 30% hydrogen peroxide to digest the fiber fraction. The solution was filtered through a 00 H paper filter (Munktell, Bärenstein, Germany) and adjusted to 25 mL. For the redissolved hemicellulose precipitates, 200 μL of concentrated nitric acid was added to 10 mL of the aqueous solutions. The metal ion contents were analyzed according to SCAN standard method CM 38:96 on a 720 series ICP-OES inductively coupled plasma spectrometer (Agilent, Santa Clara, CA, USA) equipped with an optical emission detector.

4. Results and discussion

4.1. Precipitation yield under different solution conditions

4.1.1. Turbidity measurements

Fig. 1 shows the influence of solution conditions, such as the antisolvent weight fraction, pH, and temperature, on the phase separation of hemicelluloses monitored by turbidity measurements. The pH value had only minor effects on the phase separation for all studied antisolvents.

At low methanol weight fractions (up to 60%), small turbidity changes were observed at all temperatures (Fig. 1). When increasing the methanol fraction, a relatively high increase in the turbidity occurred at 7 °C and 20 °C, whereas at 50 °C the increase in turbidity was lower. The highest turbidity value, approximately 2000 NTU, was observed at a methanol weight fraction of 75% at 7 °C and 20 °C. When further increasing the methanol weight fraction to 90% at 7 °C and 20 °C, the turbidity decreased to 750 NTU. At 50 °C, the highest

turbidity, approximately 1000 NTU, was observed at a methanol weight fraction of 90%.

It should be noted that hemicellulose precipitation is more efficient with ethanol than methanol (Fig. 1). The turbidity started to increase significantly above 50% ethanol at all temperatures. The highest turbidity values at pH 3.8, approximately 2600 NTU and 2400 NTU, were observed at ethanol concentrations of 70% at 7 °C and 20 °C. When the ethanol concentration exceeded 75%, a considerable decrease in the turbidity was observed at both temperatures, not due to decreasing precipitation but to a change in the particle size and structure. At 50 °C, a low increase in turbidity was observed at all ethanol weight fractions, peaking at approximately 1000 NTU at 90% ethanol.

The results presented in Fig. 1 clearly indicate that, of the studied antisolvents, acetone is the most efficient at precipitating hemicelluloses. The highest turbidity value, obtained at pH 3.8 and 7 °C, was approximately 3200 NTU. At 20 °C, the highest turbidity was 2750 NTU, which remained unchanged in the acetone weight fraction range of 70–80%.

The reasons why hemicelluloses start to precipitate under the investigated conditions can be qualitatively described using the Flory–Huggins approach (Hiemenz, 1984). A large difference in the interaction energy between segments of the polymer and solvent molecules, compared with the interaction energy between segment–segment and solvent–solvent molecules, leads to polymer precipitation (i.e., phase separation) from the solution. For entropy reasons, with lower antisolvent additions, the higher-molecular-weight species will likely separate out first, leaving the lower-molecular-weight species in solution. As more antisolvent is added, the lower-molecular-weight species start separating as well (Holmberg, Jönsson, Kronberg, & Lindman, 2002). Moreover, as ethanol is slightly more hydrophobic than methanol due to the additional methylene group, ethanol increases the hemicellulose phase separation more than methanol does. A similar carbon chain dependency has also been reported for the phase separation of salt-free ethyl(hydroxyethyl)cellulose solutions (Malmsten & Lindman, 1990).

He, Smeds, Friman, and Rosenholm (2013) investigated the solubility parameters of polysaccharides (i.e., polydextrose and spruce galactoglucomannan) for various solvents (i.e., ethanol, acetone, and DMSO). They observed that increasing the solvent weight fraction reduced the solubility parameter and increased the hydrophobicity of the polymer–solvent system. Moreover, the solubility parameters for water–acetone mixtures are lower than for water–ethanol mixtures. Furthermore, acetone is an aprotic solvent, which means that acetone may weaken or even break down hydrogen bonds between water and hemicellulose. This may contribute to a lower solubility of the species in solution and may accelerate the phase separation. Ethanol and methanol are protic solvents that reduce the solubility of the species in solution to a lower extent, as they can form hydrogen bonds with dissolved material. A correlation can also be observed between the precipitation efficiency and the inverse dielectric constants of the antisolvents, acetone having the lowest polarity and methanol the highest. The theory and examples discussed above support what is observed from the results presented in Fig. 1, namely, that more ethanol and methanol than acetone are needed to precipitate hemicellulose from the studied process waters.

4.1.2. Gravimetric analysis

The hemicellulose precipitation procedure was repeated for unconcentrated TMP process water at methanol, ethanol, and acetone weight fractions of 50–75% at pH 3.8, in order to isolate hemicelluloses quantitatively. Precipitates could not be obtained for methanol and ethanol at a weight fraction of 50%.

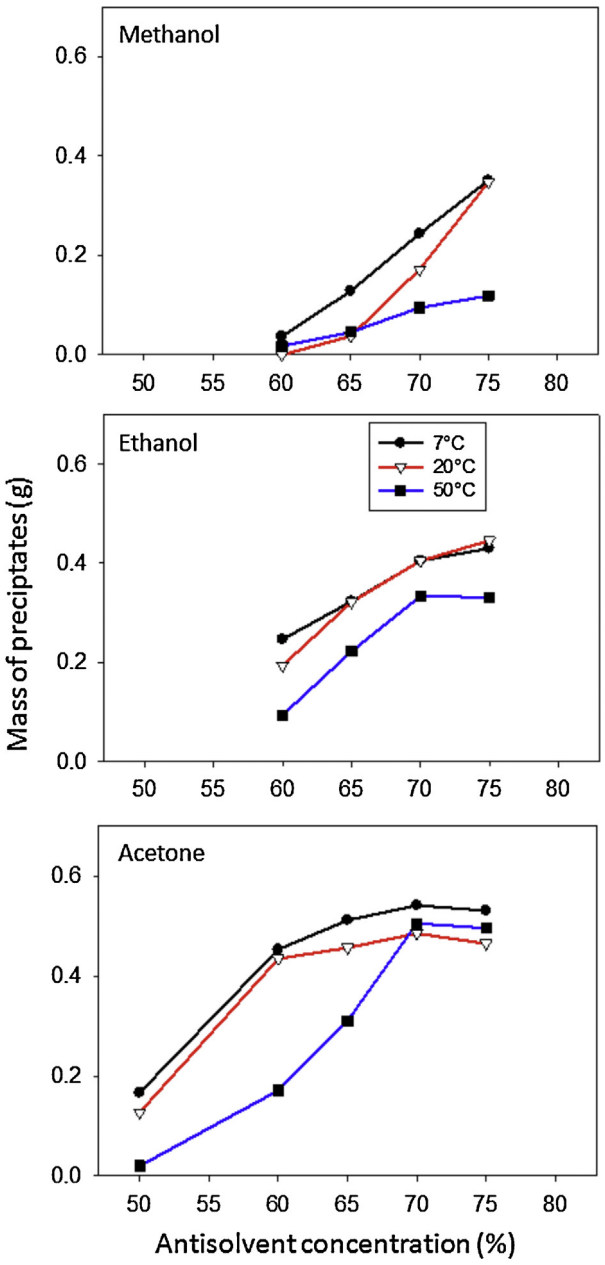

Fig. 2. Mass of hemicelluloses obtained from unconcentrated process water after precipitation with various antisolvents at various conditioning temperatures.

The hemicellulose yield increases over the whole range of methanol additions. At 7 °C, the mass of precipitated hemicelluloses is higher than at 20 °C in the range of 60–70% methanol. The highest yield, approximately 0.35 g, is obtained at 75% methanol at both 7 °C and 20 °C. At 50 °C, the amount of precipitate obtained is lower than at 7 °C and 20 °C over the whole methanol weight fraction range. When comparing the mass of obtained precipitates shown in Fig. 2 with the turbidity measurement results (Fig. 1), it can be observed that increased hemicellulose yield correlates with increased turbidity when the weight fraction of methanol increases.

Unsurprisingly, increasing the ethanol addition increased the hemicellulose yield. The precipitation was more efficient at 7 °C and 20 °C than at 50 °C, as was the case with methanol. The highest precipitate mass, approximately 0.43 g, was obtained at a weight fraction of 75% ethanol at 7 °C and 20 °C. At 7 °C and 20 °C the mass increased with increased turbidity only up to 70% ethanol (Figs. 1 and 2). At an ethanol weight fraction of 75%, the turbidity

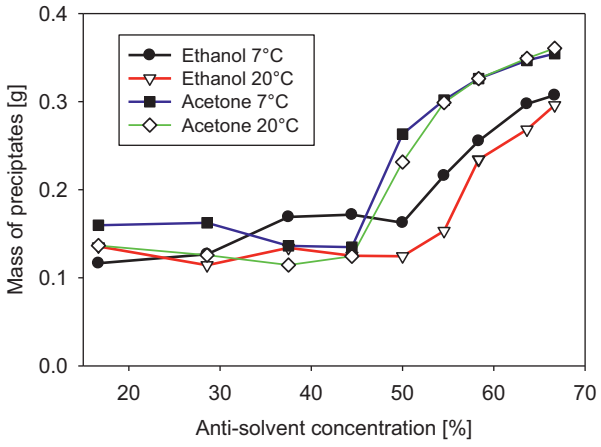

Fig. 3. Mass of hemicelluloses obtained from concentrated process water after precipitation with various antisolvents at various conditioning temperatures.

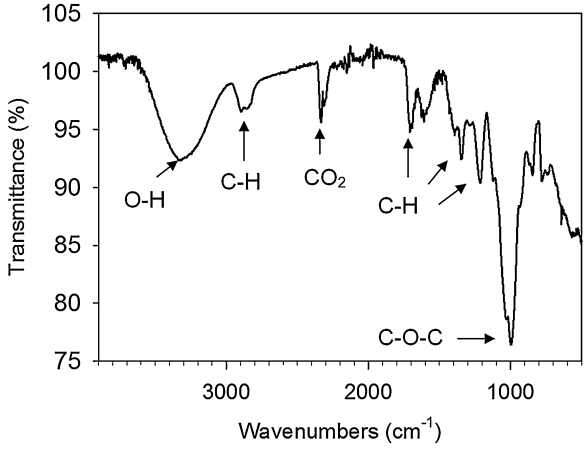

Fig. 4. FTIR spectra of hemicelluloses precipitated with 70% acetone at 7 °C.

decreased as shown in Fig. 1, whereas the mass kept increasing. At 75% ethanol, smaller amounts of aggregated flocs were observed in the water during precipitation, whereas during precipitation at below 75% ethanol, the formation of aggregates of smaller-sized particles was predominant. At 50 °C, no clear correlation between the mass of precipitates and the turbidity was observed. Fig. 2 shows that precipitation with ethanol is more efficient than with methanol, as also indicated by the turbidity measurements.

Regarding acetone, it was observed that even at a weight fraction of 60% acetone at 7 °C and 20 °C, larger amounts of hemicellulose precipitates were formed than with the other antisolvents, i.e., 0.42 g compared with 0.29 for ethanol and 0.04 g for methanol. When increasing the acetone weight fraction to 65%, the hemicellulose yield increased to 0.51 g at 7 °C and to 0.45 g at 20 °C. Further increasing the acetone weight fraction did not affect the yield. Comparing the hemicellulose yield (Fig. 2) with the turbidity measurements (Fig. 1) indicates that the increased yield corresponds to the increased turbidity only up to a weight fraction of 65%. At 70% the turbidity decreases, as shown in Fig. 1, whereas the precipitated mass increases. A similar outcome was described earlier for the precipitations with ethanol. Moreover, as with ethanol, smaller amounts of aggregate flocs were observed in the water during precipitation with acetone at weight fractions above 70%, whereas during precipitation below 70%, mostly smaller-dimension aggregates were formed.

Similar but more obvious trends were obtained when hemicelluloses were precipitated from concentrated process waters, as shown in Fig. 3, confirming that acetone is a more efficient antisolvent than ethanol.

The main difference observed between unconcentrated and concentrated process waters is that less antisolvent was needed to obtain high precipitation yields from concentrated waters. The optimum precipitation condition for unconcentrated water is found at 65–75% acetone, whereas for concentrated water the optimum is found in the 50–55% range.

4.2. Chemical analyses and yield determination

GC analysis was used to chemically characterize the obtained hemicellulose precipitated from concentrated process water. The carbohydrate composition of all the precipitates was determined as monomeric sugars and uronic acids from acidic hydrolysis. When observing the carbohydrate composition, it can be noted that mannose, galactose, and glucose are the main components, accounting for over 80% of total carbohydrate content of all precipitates regardless of precipitation conditions. The GGM content calculated from a mannose:glucose:galactose unit ratio of 4:1:0.5 (Willför et al., 2003) increased with an increase in antisolvent weight fraction. It can be observed that at lower antisolvent weight fractions for methanol up to 65% at 7 °C and 20 °C, and for ethanol and acetone up to 60% at all temperatures galactose was the dominant saccharide unit. When increasing the antisolvent weight fraction, the amount of galactose decreased, whereas the amount of mannose and glucose increased at all temperatures. With low antisolvent additions, the concentrations of arabinose and xylose were approximately 10% and 7%, respectively, at all temperatures, but decreased with increasing antisolvent additions. The rhamnose concentration was low under all conditions for all precipitates. The presented results indicate that all precipitates consist mainly of galactoglucomannans and arabino glucuronoxylans (Sjöström, 1993). It can be noted from Fig. 3 that the precipitation is most efficient in the range of 50–60% antisolvent concentration; a more detailed study of this matter is discussed below.

FTIR spectroscopy was used to identify the main functional groups of carbohydrates as shown in Fig. 4. The data were collected from 4000 cm^{-1} to 400 cm^{-1}. Strong hydrogen bond O—H stretching at 3400 cm^{-1} and C—H stretching vibration in the 2950–2850 cm^{-1} region were found. Strong signals in the 2500–2900 cm^{-1} range come from vibrations of O—H located in the carboxylic groups. The absorption at 2350–2300 cm^{-1} relates to the stretching vibration of CO_2 coming from insufficient air purification by the instrument. A band at 1740 cm^{-1} corresponds to the acetyl groups in hemicelluloses (Sun, Fang, Goodwin, Lawther, & Bolton, 1998). Bands at 1580, 1456, and 1370 cm^{-1} are assigned to the C—H vibrations of carbohydrates on the rings. The wavenumber at 1260 cm^{-1} is indicative of carboxylic acid vibrations, which are due to glucuronic acid side groups. In addition, a specific band in the 1200–1000 cm^{-1} region is dominated by ring vibrations overlapped by stretching vibration identified as coming from OH groups in uronic acids, xylose and glucose units in galactoglucomannans, and the C—O—C glycosidic bond vibration (Kačuráková & Wilson, 2001). The absorbance at 873 cm^{-1} likely comes from the pyranose rings of glucose, galactose, and mannose (Kačuráková, Capek, Sasinková, Wellner, & Ebringerová, 2000). The presented spectral assignments indicate that the hemicellulose fractions consist mainly of GGMs under all precipitation conditions.

To determine the recovery efficiency, yields based on the carbohydrate analysis of precipitates and waters obtained at antisolvent weight fractions of 50, 54.5, and 58.3% were determined (Table 2). Note that at 54.5%, a yield of 60% is obtained with ethanol, whereas the yield is 80% with acetone. When increasing the antisolvent content to 58.3%, the yields increase to approximately 70% and 90% for

Table 2
Carbohydrate content and composition of precipitates and waters after hemicellulose precipitation of concentrated process water at three weight fractions of ethanol and acetone.

Antisolvent	Conc. (%)	Fract.	Cont. (%)	Ara (%)	Rha (%)	Xyl (%)	GlcA (%)	GalA (%)	Man (%)	Gal (%)	Glc (%)	GGM[a] (%)
Ethanol	50.0	Precip.	56	4.6	0.6	0.7	2.1	1.7	46.7	27.3	16.3	64.2
		Water	41	8.3	11.2	1.5	4.0	12.9	44.5	11.9	5.7	31.4
	54.5	Precip.	60	7.0	0.7	1.7	4.9	2.8	50.0	19.7	13.3	68.8
		Water	38	5.3	1.0	2.0	3.7	6.8	64.3	10.2	6.6	36.3
	58.3	Precip.	69	5.2	0.7	0.8	2.4	2.0	53.7	20.5	14.6	73.8
		Water	34	4.4	1.4	1.8	0.6	2.3	64.1	9.5	16.0	88.1
Acetone	50.0	Precip.	56	3.8	0.4	1.2	2.3	1.6	48.4	26.1	16.2	66.5
		Water	30	5.0	1.5	1.8	0.5	3.0	63.4	8.9	16.0	87.2
	54.5	Precip.	81	2.9	0.3	1.1	1.6	1.9	56.0	20.4	15.9	77
		Water	19	7.6	2.7	2.6	0.4	4.8	55.6	9.0	17.3	76.5
	58.3	Precip.	90	2.5	0.3	1.1	1.5	1.9	55.9	20.4	16.5	76.9
		Water	15	14.3	3.3	2.9	0.4	2.9	50.1	8.8	17.4	68.9

[a] This corresponds to the GGM content estimated from a mannose:galactose:glucose unit ratio of 4:0.5:1 (Willför et al., 2003).

ethanol and acetone, respectively. GGMs are still the main hemicellulose in the precipitates.

4.3. Impurity analysis

To detect the presence of other impurities in the hemicellulose precipitates, the lignin and extractive contents were determined. Under all conditions, the precipitates obtained after methanol addition were observed to contain more impurities than did the carbohydrates precipitated with ethanol or acetone. The mean content of resin and fatty acids in precipitates obtained with methanol from unconcentrated process waters was approximately 0.2% versus 0.06% and 0.07% obtained with ethanol and acetone, respectively. In addition, the mean content of steryl esters and di- and triglycerides was much higher for hemicelluloses precipitated with methanol than with the other tested antisolvents: i.e., 0.9% and 1% for methanol, 0.2% and 0.4% for ethanol, and 0.14% and 0.2% for acetone. The lipophilic impurities in precipitates from concentrated process water were below 0.1% under all conditions. The lignan content was below 0.01% in all precipitates from unconcentrated water. For concentrated water, the lignan content was much higher, especially at lower antisolvent concentrations: i.e., approximately 4–6% at antisolvent weight fractions in the 16.7–44.4% range, decreasing to approximately 1% at higher weight fractions. The mean lignin content for methanol-induced hemicellulose precipitation was approximately 3.2%, compared with 1.3% and 1.6% for ethanol and acetone, respectively. The lignin content of precipitates originating from concentrated water was higher with lower amounts of antisolvent. With acetone and ethanol weight fractions of 37.5%, the lignin content was 7.3% and 6.9%, respectively. When increasing the antisolvent addition to 66.7%, the lignin content decreased to 2.4% for acetone and to 2.7 for ethanol, probably due to the lignin's better solubility in the less polar solvent.

The residual lignin likely originated from lignin–carbohydrate complexes (Iversen, 1985; Lawoko, Henriksson, & Gellerstedt, 2006). It must be emphasized that the water samples extracted with MTBE contained not only lignin but also dissolved hemicelluloses that may have contributed to the absorption at 280 nm, introducing an overestimation of the lignin content (Örså & Holmbom, 1994). The flotation significantly reduced the amount of lipophilic extractives, confirmed by a 90% decrease in turbidity, which contributed to small amounts of lipophilic impurities in the precipitates. The metal ion contents of the precipitates were found to be independent of antisolvent addition, being Na 0.8%, Ca 0.7%, Mn 0.2%, Cu 0.1%, and Fe 0.1% regardless of the ethanol weight fraction. As well, hemicelluloses were precipitated with 70% acetone from unflotated TMP process water. The impurities in the precipitates were: resin and fatty acids 2.2%, lignans 10%, steryl ester 9.7%, and di- and triglycerides 6.4% considerably higher extractive contents than in the pre-flotated waters. The lignin content was 3.1% and the metal content was similar to that of the precipitates from waters pre-purified by flotation.

4.4. Molecular mass distributions in hemicellulose precipitates

The molecular masses of some hemicellulose fractions obtained by antisolvent precipitation were determined by GPC and PFG NMR measurements, which give complementary information on the physical properties of the samples. GPC gives the size distribution of molecules and particles based on obstruction effects caused by the highly porous packing material in the chromatography column, which differentially affects the retention of differently sized molecules and particles. PFG NMR detects the self-diffusion of truly dissolved molecules based on differences in proton signal decay when varying a magnetic field gradient applied to the sample. Proton signals from particles in the samples are strongly suppressed due to the low freedom of molecular motion, which makes the spin–spin (T_2) relaxation for most of the protons too fast for the signals to be registered by the receiver. The data obtained by PFG NMR are based on averaging the signals from the molecules and fitting the raw data to a lognormal distribution function to extract the information used in the present investigation (Andersson et al., 2008; Fleischer, 1985; Håkansson et al., 2000).

Fig. 5 shows the results of molecular mass determinations for redissolved hemicellulose precipitates obtained by the antisolvent precipitation of flotated and concentrated process water with ethanol and acetone at 7 °C. The GPC data are shown as solid lines, whereas the PFG NMR analysis data are shown as dotted lines.

Fig. 5 shows that all the GPC measurement curves display multimodal distribution patterns. In all samples, GPC peaks indicate a fraction of molecules having very low molecular mass, in the range of approximately ten of to several hundred grams per mole. Then there is a main distribution with peak molecular mass at several tens of thousands, and finally a third distribution with a peak at several hundred thousand grams per mole. The lowest-molecular-mass distribution probably indicates mono- and disaccharides, lignans, and lignin fragments, as the lipophilic impurity content is low. Furthermore, the proportion of comparable low-molecular-mass molecules is much higher in the lower than the higher antisolvent weight fraction. The peaks of the distributions observed in the intermediate molecular mass region in all the GPC curves represent precipitated hemicelluloses. In light of previously reported values for the typical molecular masses of spruce hemicelluloses extracted using various methods (Bian et al., 2010; Peng et al., 2009), the high-molecular-mass peaks observed for all analyzed samples cannot be treated as indicating dissolved

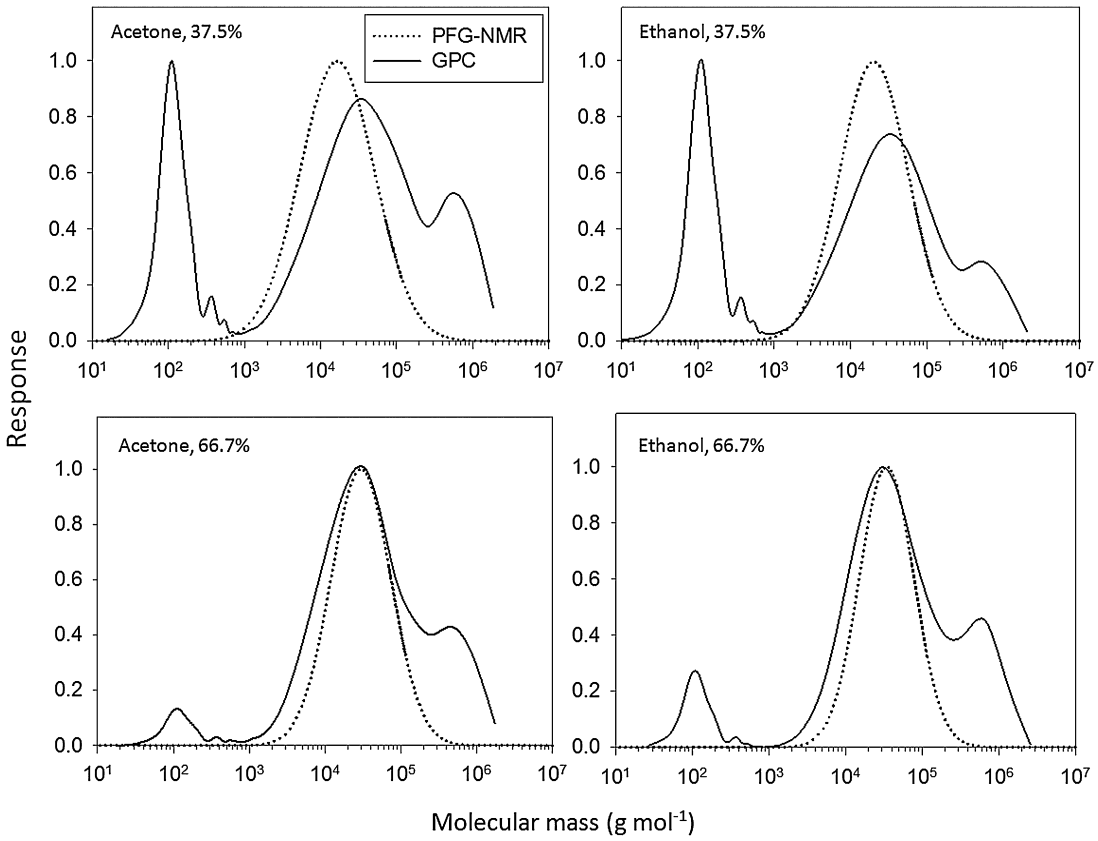

Fig. 5. Molecular mass distribution of hemicelluloses obtained after precipitating flotated and concentrated process water with one of the two antisolvents at 7 °C. The samples were redissolved in water before the analysis.

Table 3
Peak molecular mass values determined by GPC and PFG NMR measurements of redissolved hemicelluloses, previously precipitated with two antisolvent weight fractions at 7 °C.

Antisolvent	Concentration (%)	Peak molecular mass (g mol^{-1})	
		GPC	PFG NMR
Acetone	37.5	36,600	16,600
	66.7	30,400	29,800
Ethanol	37.5	33,900	20,300
	66.7	32,300	34,300

hemicellulose polymers. This is also supported by the results of PFG NMR measurements. As was mentioned briefly, PFG NMR can only detect signals from truly dissolved molecules, and the fitting procedure applied is based on the assumption that the molecules in the samples can be represented by unimodal lognormal distribution curves. On one hand, if the high-molecular-mass peaks in GPC represented dissolved hemicelluloses, the peak value and the distribution curves obtained from PFG NMR would be shifted to higher molecular mass values. This should be especially evident in the precipitates obtained at higher antisolvent concentrations, as the populations of the lowest-molecular-mass fractions determined by GPC are significantly smaller. On the other hand, the relatively large fractions of low-molecular-mass species detected by GPC in the precipitates obtained at the lowest antisolvent concentrations are indeed detected by PFG NMR and contribute to shifting the peak values of the dotted curves to lower molecular mass values, as well as slightly broadening the distributions.

Table 3 shows the median peak-molecular-mass values of hemicellulose precipitates redissolved in process water, as determined by GPC and PFG NMR measurements. The above discussion makes it clear that only the results obtained with the highest antisolvent weight fraction (66.7%) are comparable between the methods. The GPC results in Table 3 indicate that higher-molecular-mass hemicelluloses are more prone to precipitate with the lower antisolvent weight fractions than are the lower-molecular-mass hemicelluloses, confirming what was expected from theory (Holmberg et al., 2002) and some earlier investigations (e.g., Bian et al., 2010). The chemistry of the particles that give rise to the highest molecular mass peaks in the GPC analysis is still not completely outlined. However, a reasonable assumption supported by earlier studies on galactoglucomannan solubility (Holmbom, Ekman, Sjöholm, Eckerman, & Thornton, 1991; Sundberg, Sundberg, Thornton, & Holmbom, 1998) would be that the particles are comprised of aggregated deacetylated galactoglucomannans showing a very low solubility in water.

5. Conclusions

Hemicellulose precipitation by antisolvent addition is an interesting method for recovering valuable polysaccharides from process water. Under all investigated solution conditions, the precipitation was governed by the aprotic solvent and the efficiency was correlated with the inverse of the antisolvent's dielectric constant in the sequence acetone > ethanol > methanol. Moreover, acetone has the lowest boiling point and does not form azeotropes with the water, which may facilitate its recovery. It was demonstrated that higher-molecular-mass hemicelluloses are more prone to precipitating with lower antisolvent weight fractions than are lower-molecular-mass hemicelluloses. Galactoglucomannan is the main hemicellulose. To increase the overall purity of the recovered hemicelluloses, flotation of the process water before antisolvent precipitation was found to be an efficient treatment.

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