EXTRACTING HEMICELLULOSES FROM SOFTWOOD AND BAGASSE AS OLIGOSACCHARIDES USING PURE WATER AND MICROWAVE HEATING

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The objective of the study was to identify conditions for hemicelluloses extraction in oligomeric form. Using microwave assisted hot water extraction (HWE), the effects of both retention time and temperature on hemicelluloses yields, as well as the degree of polymerization (DP) as analyzed by SEC-MALLS, were investigated using both softwood (sawmill shavings) and sugarcane bagasse. The results are discussed in the light of the unavoidable yield-DP compromise resulting from the application of batch mode operations. Nevertheless, significant differences between the two raw materials could be observed, as expected. For softwood shavings, data interpolation indicated that about 50% of the hemicelluloses could be obtained as oligomers at an average DP of 30 when extracted at 183 °C for 5 minutes. For bagasse, longer extraction times seemed optimal. After hot water extraction at 183 °C for 12 minutes, about 62% of the bagasse hemicelluloses were extracted as oligomers at an average DP of about 100.

Keywords: hemicelluloses, microwave hot water extraction, softwood, sugarcane bagasse

INTRODUCTION

Wood and residue from the sugar and agricultural industry comprise a large portion of the world production of biomass, and thus represent a possibly abundant source of valuable chemicals, provided that the biomass could be manipulated in such a way as to yield high-value commodities rather than simply fuels or pulp. Hemicelluloses are poly- or oligosaccharides with a degree of polymerization (DP) of about 50-200,[1] which in terms of molecular weight corresponds to 8200-32800 g/mol.[2] The hexose sugars in hemicelluloses comprise mainly glucose, galactose and mannose, whereas the pentoses fraction is mainly composed of xylose and arabinose.

Hemicelluloses have been shown to display promising properties, as e.g. barrier materials, health-promoting agents and emulsifiers.[3,4]

Further, the extraction of hemicelluloses under mild conditions, such as hot water, is desirable, facilitating the possible integration of such an operation in a larger process, which either does not rely on hemicelluloses or that even benefits from their prior removal (e.g. fermentation process, kraft pulping).

Hot-water extraction (HWE) of hemicelluloses from Norway spruce has been previously studied, both using traditional HWE (Song *et al.*[3]) and microwave (MW) assisted extraction.[5] In a study comparing steam treatment and MW-treatment, Palm and Zacchi[5] reported a maximum yield of 70 wt% (referred to mannan). Other studies[6,7] have reported similar results in terms of yields of galactoglucomannan (GGM) (referred to mannan, 78 wt%), using NaOH as process aid. Investigating the molar mass distribution of

spruce hemicelluloses fractions after size exclusion chromatography (SEC), Jacobs *et al.*[8] found that the low molecular mass fraction contained mainly small arabinoglucuronoxylan oligosaccharides (DP 4-20), while the fraction eluted last was dominated by *O*-acetyl galactoglucomannan (peak-average DP of 14). Further, as the DP decreased, so did the amount of acetyl side groups (DS).[8] Hemicelluloses extraction from sugarcane bagasse has been studied utilizing sequentially toluene, water and NaOH – with and without hydrogen peroxide.[9] This process gave total yields after all steps of about 90 wt% on hemicelluloses, and weight average molar mass ranging from 7400 g/mol in the water-extracted fraction to 45400 g/mol in the alkali-extracted fraction. Brienzo *et al.*[10] examined the effects of temperature and $MgSO_4$ addition on alkaline (pH 11.6) peroxide extraction, reaching a peak yield of 94.5 wt% on hemicelluloses after 4 h extraction time.

In this work, hot water extraction of long chain hemicelluloses by microwave heating was investigated, focusing on the effect of raw materials and process conditions on hemicelluloses yield and degree of polymerization.

EXPERIMENTAL

Raw materials

Two different raw materials were applied in this study: sawmill shavings ("SawSh" mix containing 90 wt% Norway spruce and 10 wt% Scots pine) and sugarcane bagasse (Brazil). The determined composition, in weight percent, is given in Table 1. The raw materials were milled and screened to 0.9-3 mm prior to treatment.

Table 1
Composition of raw materials

	Cellulose, wt%	Lignin, wt%	Gluco-mannan, wt%	Xylan, wt%	Other carbo-hydrates, wt%	Extractives, wt%	Ash, wt%	Sum
SawSh	40.7	31.6	17.7	5.2	1.3	2.7	0.6	*99.8*
Bagasse	40.4	25.1	0.9	20.8	1.6	0.7	10.1[a]	*99.6*

[a] The high ash content in the bagasse is not unexpected, being a waste product from the sugar industry (with dirt and sand). Ash contents ranging from 2.3wt%[9] to 20.9wt%[11] have been reported by others

Heating

A laboratory microwave oven (Anton Paar Multiwave 3000) equipped with a rotating carousel and an internal temperature probe was used. The unit was also equipped with software that allowed for automatic control of time-temperature profiles. The experiments were undertaken using a 4x4 factorial setup (Temp = 175-180-185-190 °C, time = 2-6-10-20 min). Distilled water was added to the raw material to give a solid-to-liquid ratio of 1:10. To ensure uniform liquid distribution and soaking of the sample, the mixture was allowed to settle overnight prior to extraction. Trials were performed using a heating ramp of 1.5 minutes. After the given extraction time, the vessels were cooled in an ice bath (5 min). The pH of the pressate was measured (RL060P Portable pH Meter, Russell), and the pressate was further filtered on a GF/A-filter (Whatman, 1.6 µm) and stored at -18 °C until further analysis.

Analyses

Sugar analyses

The carbohydrate analyses were performed according to the standard procedures of NREL.[12] Total carbohydrate contents were determined in the GF/A-filtered extracts. Samples were hydrolyzed using sulfuric acid (4 wt% H_2SO_4 at 124 °C for 1 hour). Hydrolyzates were neutralized with $CaCO_3$ (0.5 g). The resulting supernatant was filtered (0.2 µm) and the filtrates were analyzed by High Performance Anion Exchange Chromatography (HPAEC, ICS-5000, Dionex, CarboPac PA1 4x250 mm column, 30 °C). The eluent used was 1.5 mM NaOH under isocratic conditions. Carbohydrates were detected on a Pulsed Amperometric Detector (PAD). All carbohydrate contents are reported as anhydrosugar species. Monomeric carbohydrate analysis was performed in the same manner, but without hydrolysis with sulfuric acid and subsequent neutralization with $CaCO_3$.

Molar mass analysis

Samples were further analyzed by size-exclusion chromatography multi-angle laser light scattering (SEC-MALLS). Prior to analysis, the samples were diluted to approximately 2 mg/mL sugar concentration and filtered through a membrane filter (0.45 µm). The molar masses of extracted carbohydrates were determined by means of a High Performance-SEC instrument (Agilent 1100 Series, Agilent Tech.) with a Synergi Hydro-RP 80R HPLC column (250 mm x 4.6 mm, 4 µm, Phenomenex®) coupled with a MALLS detector (miniDAWN, Wyatt Technology) and a refractive index detector (RID-10A, Shimadzu). The eluent used was $NaNO_3$ (0.1M). Injected sample volume was 200 µL. Total run time was 55 min/sample at a speed of 0.5 mL/min, and the column operating

pressure applied was 24 bar. A refractive index increment value (dn/dc) of 0.15 mL/g was used in the molar mass calculations.[13] All the data were generated using ASTRA software (Wyatt Technology).

Optimization analysis

The data were analyzed by Minitab statistical software (Minitab Inc.). The optimization was based on desirability functions, which were elaborated for each response parameter and had a value between 0 (the lowest allowable value) and 1 (the highest needed value). The desirability functions for each response, which can be weighted according to the importance of the parameters, were combined in a *response optimizer* for each process variable. Then the response optimizer function was maximized for each process variable. For the analyses performed here, the upper boundary for the desirability function was set higher than the highest values for DP and at 100% for HC-yield, whereas the lower boundary was set to zero. Both responses were weighted equally in the analyses.

RESULTS AND DISCUSSION

In order to optimise the extraction of oligomeric hemicelluloses from biomass, we studied the effect of the raw material source and processing conditions on the yield and DP of hemicelluloses using only water as an auxiliary process aid. Initial experiments performed with sawmill shavings undermined the most suitable process conditions, and also demonstrated comparable extraction yields for MW and conventional heated extractions (data not shown here). Although no clear differences were observed in terms of different heating sources (i.e. microwave frequency irradiative vs. conventional conductive/convective heating mode), the MW heating provided a convenient way of performing test trials in a safe way. In short, using both sawmill shavings and sugarcane bagasse, the influence of extraction time and temperature on the yield of hemicelluloses and DP were studied by means of a 4x4 factorial design, in the temperature region ranging from175-190 °C and at time frames of 2 to 20 min.

Microwave hot water extraction of sugarcane bagasse

Following extractions at different temperatures and retention times, the soluble fractions were quantified by HPAEC for monosaccharide contents (arabinose, galactose, glucose, mannose and xylose), as well as with regard to the total sugar content after hydrolysis of the whole sample. The total hemicelluloses extraction yields (total sugars) from sugarcane bagasse at the different temperatures and time scales are shown in Figure 1 (left), whereas the monomer content is shown in Figure 1 (right). It can be seen that yields increased with increasing extraction time and temperature, except at 190 °C, where the yield dropped upon extending the reaction time to 20 minutes. The hemicelluloses yield peaked at approx. 70 wt% of available hemicelluloses (185 °C, 20 min). The amounts of sugar monomers demonstrated a natural increase with temperature and extraction time (Figure 1, right), which go hand-in-hand with an observed pH change from 4.6 (low temperatures/short time) to 3.6 (high temperatures/long time) (Figure 11). The high monomeric content of hemicellulose sugars under the more acidic conditions explains why hemicelluloses yields level off at approx. 70 wt%: evidently, the arabinoxylan is hydrolysed to arabinose and xylan followed by further decomposition to furfural.

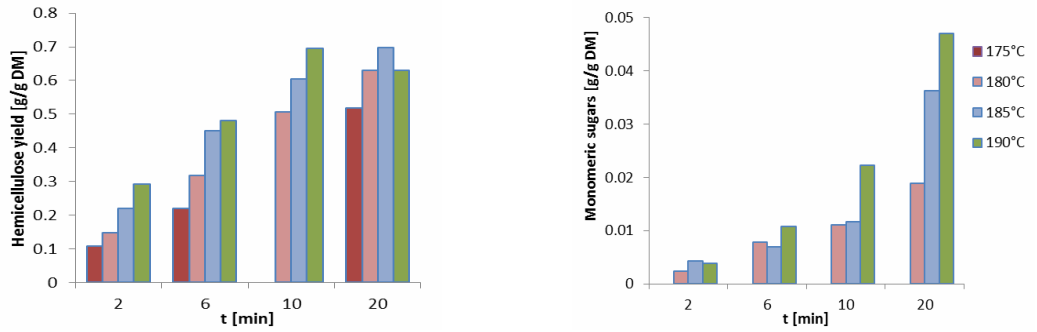


Figure 1: Total hemicelluloses yields (left) and total monomeric sugars released during hot water microwave assisted extraction of bagasse (right)

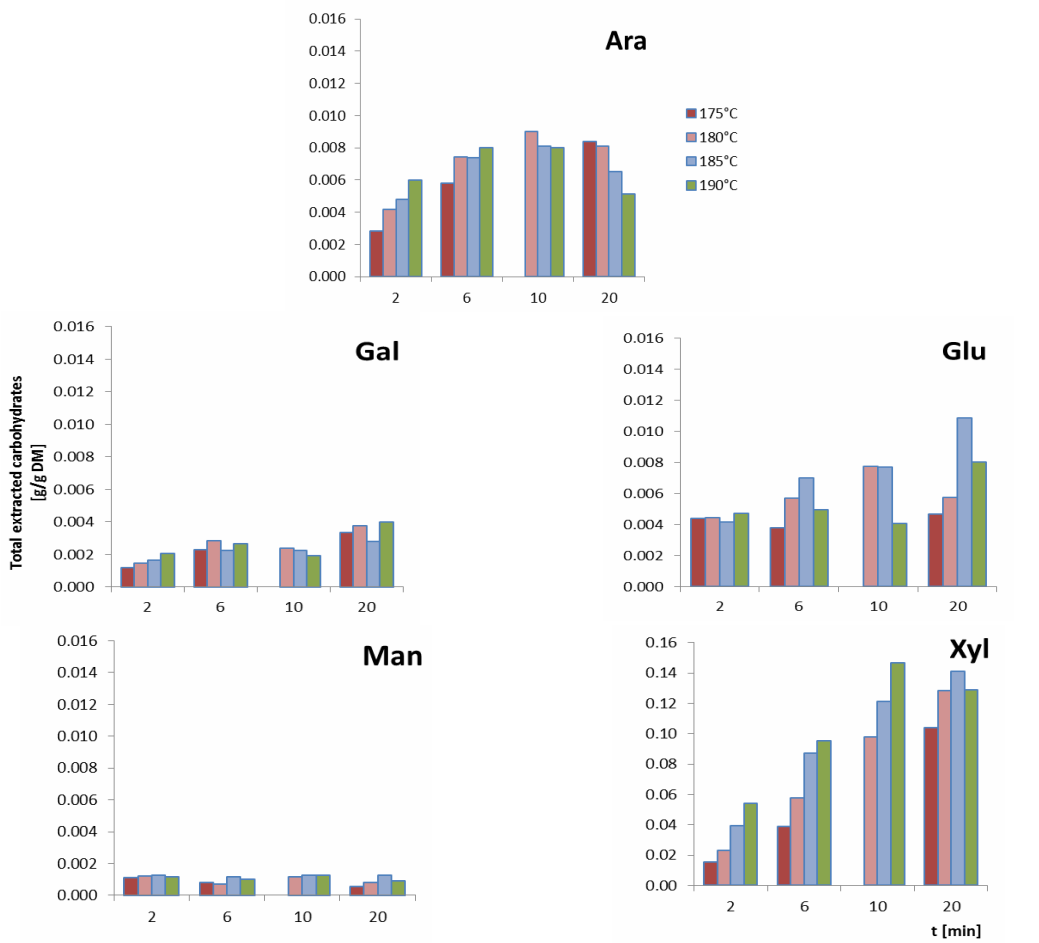


Figure 2: Extraction yields by total monomers for extraction of bagasse as function of time at different temperatures. Note: Scale for xylose is 10 times that of other monomers

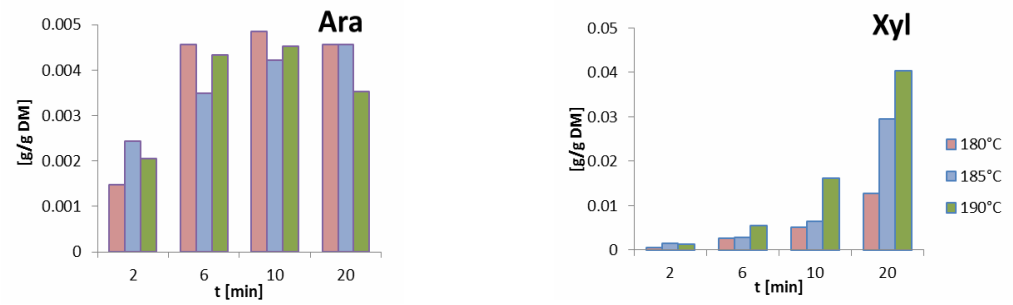


Figure 3: Content of free, monomeric arabinose and xylose sugars in bagasse extracts as a function of time at different temperatures. The results refer to unhydrolyzed samples
Note: Scale for xylose is 10 times that of arabinose

Valuable information about the process can also be obtained by inspection of how the levels of the individual carbohydrate species vary with the extraction conditions. Figure 2 displays the monomer distribution of the hemicelluloses extract (after hydrolysis), while Figure 3 shows the actual monomer content at the end of the extraction cycle for arabinose and xylan. Arabinoxylan is the main hemicellulose in bagasse with xylose being the main monosaccharide observed in the extracted material, amounting to more than 10 times the level of any of the other monomers. Xylose was extracted continuously, and a reduction in

concentration was only observed at 190 °C (treatment time of 20 min) indicating that degradation of xylan occurs at a higher rate than the release of arabinoxylan from biomass under these experimental conditions. Arabinose was extracted early and experienced degradation at all temperatures, as also reported by others.[14]

As shown in Figure 3, the extract content of monomeric arabinose peaks earlier than the content of monomeric xylose. Further, comparing the monomeric arabinose yield of the unhydrolysed extracts with the total content of arabinose in the extracts (Figure 2), we can conclude that more than half of the total extracted arabinose is extracted in the monomeric form. This could be explained by the arabinose side chains being more prone to and available for degradation than the xylose backbone where the cleavage of the intra-molecular bonds will not necessarily involve release of monomeric xylose.

The molar mass of the extracted samples was further analysed by means of SEC-MALLS, and the observed effect of processing conditions on DP is visualized in the contour plot seen in Figure 4. The plot illustrates how high temperature and time (upper and right part of the plot) lead to a relatively low DP. Thus, although yields for bagasse extraction were highest when extracting at 185 °C for 20 minutes, the degree of polymerization was very low at these conditions. Furthermore, it is evident that the desired conditions yielding the highest degree of polymerization are in the range of 180-185 °C and 2-6 minutes treatment time, respectively.

Sun *et al.*[9] reported peak average molar mass values of 7400 g/mol from water extraction and 45400 g/mol from alkali extraction. The peak DP values in Figure 4 at 180 °C, 2 min, and 185 °C, 6 min, correspond to M_w values of 29700 g/mol and 38000 g/mol, respectively.

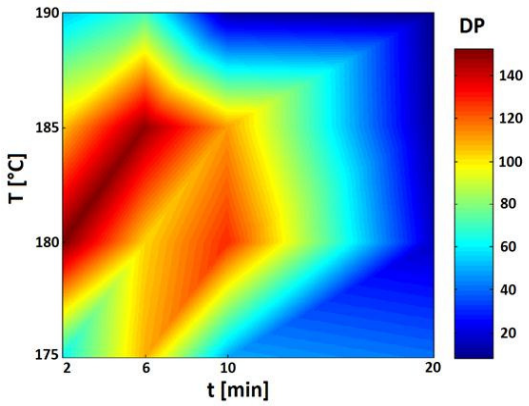


Figure 4: Hot water extraction of bagasse – Contour plot of degree of polymerization (DP) as a function of temperature and time

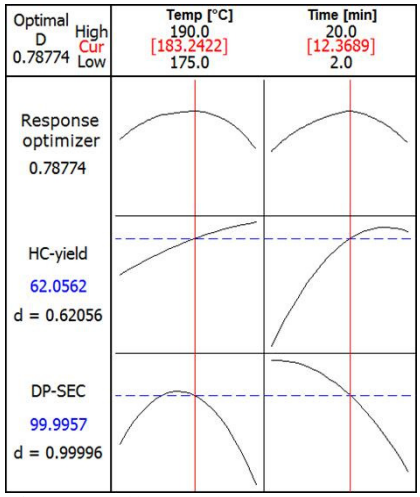


Figure 5: Trade-off analysis for hemicellulose yield and degree of polymerization for hot water extraction of bagasse. *High* and *Low* indicate boundary values for the variables, *Cur* indicates optimal variable settings; blue values represent predicted response values under optimal conditions

Yield vs. DP of hemicelluloses derived from bagasse

The yields obtained in this work were slightly lower than for a few studies performed previously.[9,10] However, the method applied herein does not involve multiple extractions or added auxiliary chemicals, and might therefore have a beneficial environmental and cost profile. Moreover, the species obtained are likely to prevail in more native form when not exposed to any chemicals potentially leading to derivatized species. As evident from Figures 1 and 4, respectively, high yields can only be obtained at the expense of the chain length of the oligomer obtained after treatment. The ideal DP will vary from application to application, but often a high DP is targeted. Trade-off analysis focusing on maximizing both yield and DP by equal weighting gave the optimization plots presented in Figure 5. These show the optimal temperature

and time to be around 183 °C and 12 min, respectively, giving an estimated hemicelluloses yield of 62 wt% and a DP of 100.

Microwave hot water extraction of sawmill shavings

As in the case of bagasse, hemicelluloses extraction of sawmill shavings was studied at extraction times ranging from 2 to 20 minutes and temperatures from 175 to 190 °C, respectively.

The yield of extracted hemicelluloses from the sawmill shavings (Figure 6, left) ranged from 17 wt% (175 °C, 2 min) to 77 wt% (190 °C, 10 min). The yield increased with temperature, most prominently from 175 °C to 180 °C, as well as with time up to 10 minutes. Beyond 10 minutes, the yield increased slightly at lower temperatures (175-180 °C), while decreased slightly at higher temperatures (185-190 °C). Evidently, except for the apparent stagnation of the yield beyond 10 minutes extraction time, these trends mimic those found for bagasse extraction. Although, the extraction yields of hemicelluloses were found to depend on temperature, interestingly, the relative increase in carbohydrate yield with extraction time was found to be constant at the different temperatures. This suggests that the higher yields experienced (77 wt% on total hemicelluloses content, or 82 wt% on mannan content) at high extraction temperatures were due to favourable reaction conditions prevailing at the very beginning of the extraction cycle.

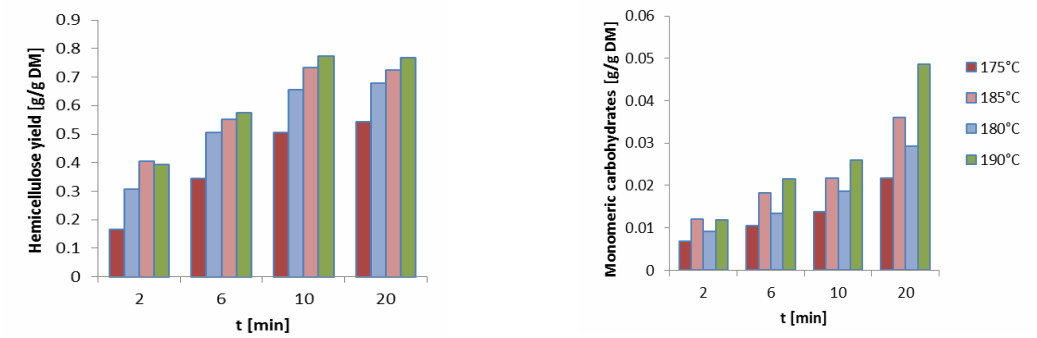
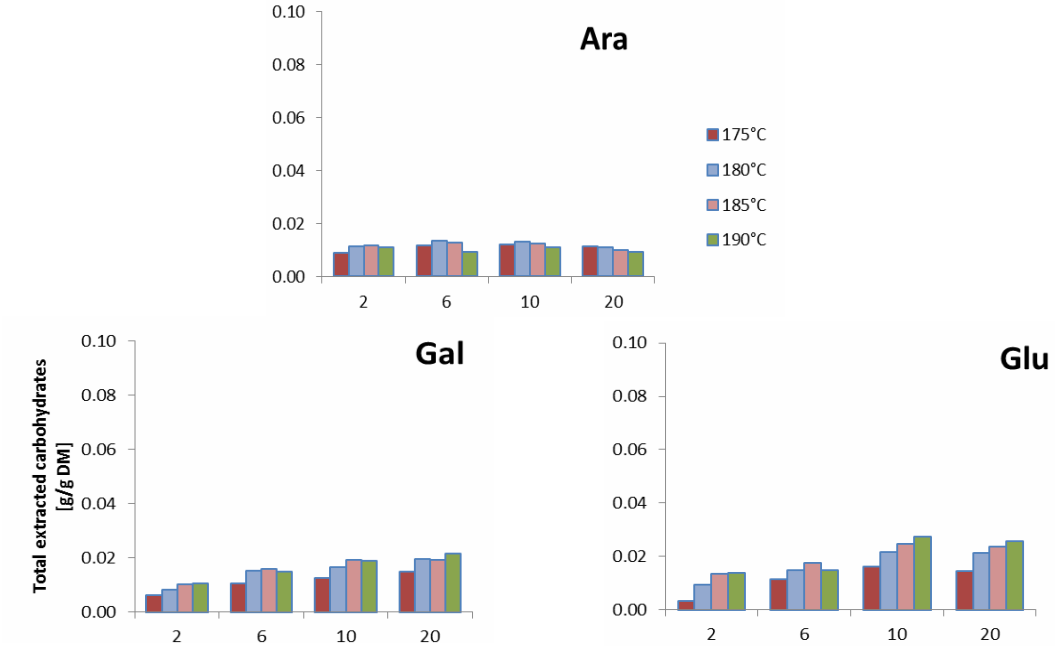


Figure 6: Total hemicelluloses yields (left) and total monomeric sugars released (right) during hot water microwave assisted extraction of sawmill shavings



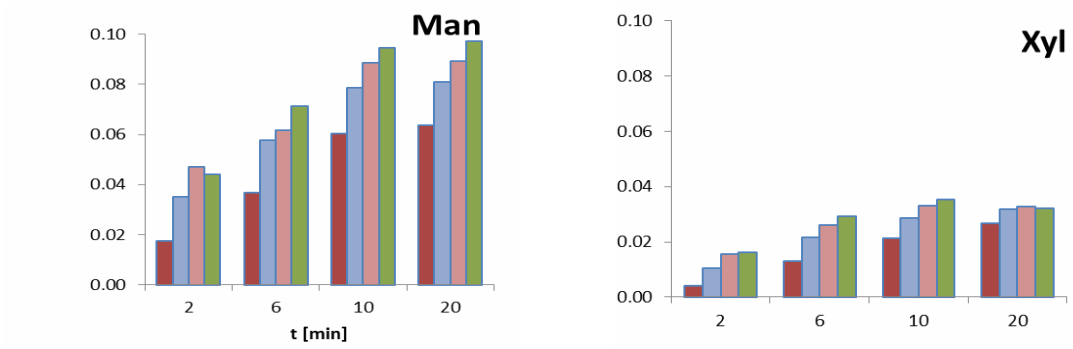


Figure 7: Extraction yields by total monomer species for extraction of softwood sawmill shavings as a function of time at different temperatures

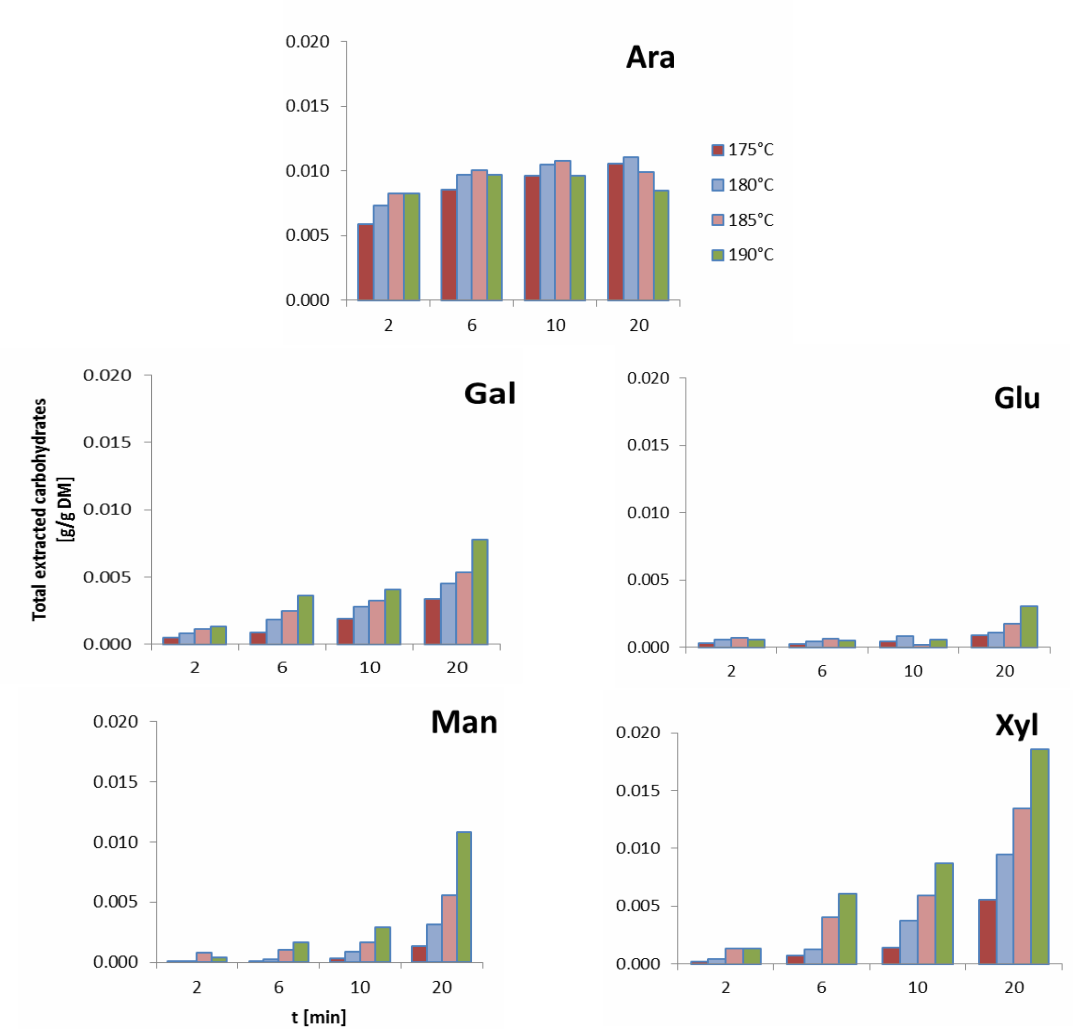


Figure 8: Content of free, monomeric sugars in extracts of softwood sawmill shavings as a function of time at different temperatures (unhydrolysed samples)

The yield stagnation observed beyond 10 min extraction time indicates that the release of hemicelluloses from the fibre occurs at a similar rate as the degradation. The monomeric sugar content of the extracts increased linearly with the time of extraction (Figure 6, right). Intuitively, this will also lead to more sugar degradation products and result in a lower DP.

The monomer distributions of the total extracted hemicelluloses (after hydrolysis) are

displayed as a function of time in Figure 7, while the monosaccharide content in the extracts is shown in Figure 8. Mannose is the most abundant monomer species, the yields of which amounted to over twice the yields of any other monomer. As seen, mannose and galactose appear more stable that the other observed sugars.

It is noteworthy that the content of arabinose in the extracts was almost equal at all temperatures and all treatment times. When looking at the plots of monomeric carbohydrate content (Figure 8), it is evident that almost all arabinose is rapidly dissolved in its monomeric form. Thus, the arabinose found in the sawmill shavings is easily available and, consequently, also experiences a higher degree of degradation at longer treatment times, similar to that observed in the case of bagasse extraction.

The effect of extraction time and temperature on hemicelluloses DP from sawmill shavings is shown in Figure 9. The plot reveals a pattern quite different from that observed in the case of bagasse (Figure 4). In the case of the softwood hemicelluloses, the chain length of the carbohydrates was retained only at short extraction times. At temperatures above 180 °C, degradation to lower molecular weight oligomers appeared to be rapid. Nevertheless, the peak DP of 48 (M_w = 11400 g/mol) at 185 °C, 2 min corresponds well to the maximum molar weight reported by e.g. Palm and Zacchi.[5]

Yield vs. DP for hemicelluloses from softwood

The yields achieved (77 wt% on total hemicelluloses or 82 wt% on mannan) are higher than the yields reported by some authors[5] (70 wt% on mannan), but lower than the yields reported by others applying longer extraction times[3] (80-90 wt% of GGM obtained). However, the yield-DP compromise to be made here represents a more difficult dilemma than in the case of bagasse – while the DP decreased already upon short treatment times, the yields obtained were rather modest. The optimization analysis presented in Figure 10 reflects this observation, considering that the value of the response optimizer function is lower than that obtained in bagasse analysis. This may be related to deacetylation of the GGM in the softwoods, thus demonstrating a lower apparent DP due to invisibility of deacetylated compounds in the analysis. The optimum values in terms of time and temperature of the extraction cycle were estimated to be 5 minutes and 183 °C, respectively. This agrees well with the rapid decline in DP at times longer than 5 minutes seen in Figure 9.

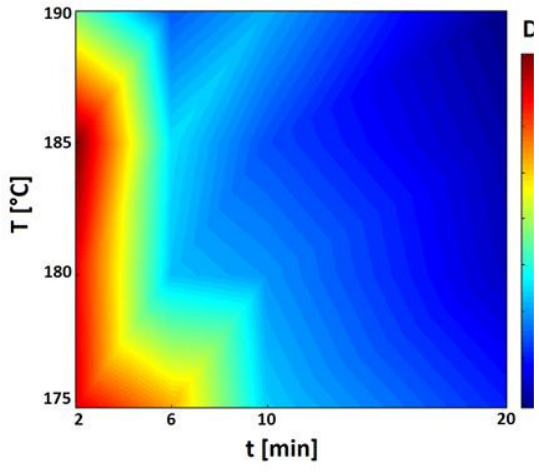


Figure 9: Contour plot of DP as a function of time and temperature (softwood sawmill shawings)

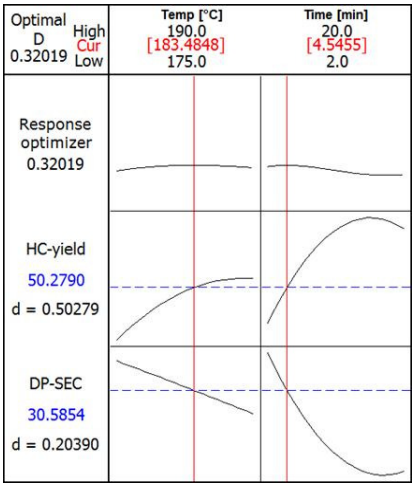


Figure 10: Optimization plot for yield and DP of hemicelluloses extracted from softwood sawmill shavings. *High* and *Low* indicate boundary values of the variables. *Cur* indicates optimal variable settings. Blue values represent predicted response values under optimal conditions

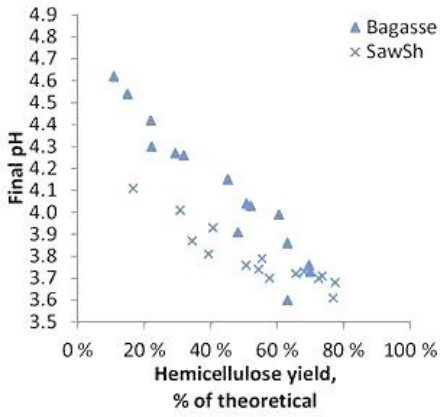


Figure 11: Final pH of hot water extracts as a function of hemicellulose yield

The pH of the extracts

The pH of the extraction liquid showed increasing acidity with increasing hemicelluloses yield. For bagasse, the pH at a given yield was consistently higher than at the same yield for sawmill shavings (Figure 11).

The slightly higher acetyl group content in softwood (2.1-2.7 wt%) as compared to bagasse (2 wt%) could be an explanation for the higher acidity of the sawmill shaving extracts. However, the higher acidity could also be an indication that more severe deacetylation took place during extraction of sawmill shavings than in the case of bagasse. A further explanation could be the degradation of the carbohydrates into acidic compounds. Lastly, the content and release of uronic acids could also affect the pH of the extraction liquids. However, as the uronic acid content of sawmill shavings was similar to that of bagasse, it is unlikely that this can explain the pH-trend difference between the two raw materials. Based on this, we consider acetyl content as the primary explanation of the higher pH of bagasse extracts than that of softwood extracts, possibly in combination with the higher degree of deacetylation of the softwoods during extraction.

already after a few minutes of extraction time. Furthermore, the final pH in the extraction liquid was consistently lower for the shavings than for bagasse at equal yields. This is possibly due to a higher initial acetyl content in the softwoods, but could also be an indication of more pronounced deacetylation in the softwood raw material compared to bagasse.

CONCLUSION

The influence of hot water extraction temperature and time on yields and on the degree of polymerization of extracted hemicelluloses using microwave heating have been investigated using sugarcane bagasse and sawmill shavings (Norway spruce and Scots pine) as raw materials.

Extraction time and temperature proved to have great influence on both the yield obtained and the degree of polymerization of the extracted samples. Both in the case of sugarcane bagasse, as well as in that of softwood sawmill shavings, the yields increased with time up to 10 minutes extraction time. At longer treatment times, the oligomers began to decompose. Similarly, the observed increase in yield was most pronounced when the treatment temperature was increased from 175 °C to 180-185 °C, for both raw materials. The effect of time and temperature on DP, however, differed markedly between the two raw material species. Whereas the hemicelluloses extracted from bagasse peaked in terms of DP at around 5 minutes, the hemicelluloses from sawmill shavings had a pronounced lower DP

Optimization analyses of the responses in terms of the percentual hemicelluloses yield and DP indicated that the best trade-off between the two experimental parameters, in the given temperature-time region, is found at the extraction temperature of 183 °C and 12 minutes treatment time for bagasse and at 183 °C and 5 minutes for sawmill shavings. Under these processing conditions, the yield and DP predicted by the optimization model were 62 wt% and 100, respectively, for bagasse and 50 wt% and 31 for the sawmill shavings. Analyses of the closest corresponding experimental conditions (T = 185 °C, t = 10 min and T = 185 °C, t = 6 min, respectively) resulted in a hemicelluloses yield of 60 wt% and DP = 111 (M_w = 38400 g/mol) for

sugarcane bagasse and in a 55 wt% yield and DP = 23 (M_w = 5700 g/mol) for sawmill shavings.

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