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Hemicellulose degradation upon hydrothermal treatment of black liquor

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Abstract

Black liquor from Kraft pulping is a very promising feedstock for isolation of bio-based platform chemicals. As a pre-treatment step before fractionation and isolation processes, hydrothermal treatment of black liquor can be beneficial to improve the processability of the liquor and fine-tune its composition. In the present study, we present the results of black liquor heat treatment experiments and show that the hemicelluloses can be completely degraded upon treatment at 220 °C for 2 h.

Introduction

The Kraft process is the most important chemical pulping process worldwide. About 60 % of the total pulp production can be attributed to Kraft pulp mills [1]. In consequence, the vast amounts of biomass that are processed in the course of Kraft pulping need to be used as efficient as possible. During pulping, lignin and part of the hemicelluloses contained in wood are partially degraded and thereupon dissolved in the spent pulping liquor. The organic constituents of this so called black liquor (BL) are mainly lignin, aliphatic carboxylic acids, and hemicelluloses. The rest is inorganic pulping chemicals like sulphur compounds and sodium. The weak black liquor after separation of the cellulose has a solids content between 15 and 20 %. In the evaporators, the BL is concentrated to a final solids content of 65-85 %. Thereafter it is burned in the recovery boiler to recover heat in the form of steam and to regenerate the inorganic pulping chemicals. [2]–[6] With the BL, many potential bio-based raw materials are burned, too. Especially lignin and carboxylic acids are valuable side products from pulping and could be isolated from BL prior to incineration. The hemicellulose concentration is typically lower than that of the other organics [7]. Nevertheless, also hemicelluloses are valuable precursors. Another option is to degrade the hemicelluloses to e.g. aliphatic carboxylic acids. By that, the aliphatic carboxylic acid concentration is increased and furthermore, the viscosity of the BL decreases, which significantly facilitates further processing [8], [9]. The degradation of hemicellulose can be achieved by hydrothermal treatment of the BL [9], [10]. Besides the formation of carboxylic acids and the decrease of viscosity, heat treatment influences the chemical structure of the lignin by changing the molecular weight and increasing the content of active groups. This increases the range of possible applications for the lignin after a potential isolation step.

This study aims to investigate the effect of hydrothermal treatment on the BL constituents, especially on the hemicellulose degradation and the change in BL pH value. A short summary of the reactions taking place during hydrothermal treatment of BL explains the underlying mechanism. Heat treatment experiments with BL for up to 2 h at 150-220 °C were carried out and evaluated.

Hydrothermal Treatment of Black Liquor

The degradation reactions during digestion and heat treatment are often similar. The heat treatment can be seen as an extended digestion, but without any influence of the cellulose fibres, which have been separated from the black liquor used for heat treatment.

The degradation of the organic liquor constituents, namely carbohydrates and lignin, depends on the treatment temperature as well as on the concentration of inorganic pulping chemicals. Lignin degradation is enforced by high concentration of sulphide as well as alkali, while carbohydrate degradation mainly depends on the alkali concentration.

During Kraft cooking, various carbohydrate degradation reactions occur. Cellulose, but mainly hemicellulose is degraded due to the high alkalinity and temperature. Above 70 °C, the acetyl moieties of softwood galactoglucomannans and hardwood glucuronoxylans are deacetylated, leading to formation of acetic acid during the initial stages of the cook. Subsequently a major portion of the deacetylated hemicelluloses dissolve in the pulping liquor. These molecules are partially precipitated on the cellulose fibres, increasing the fibre strength.

The further degradation and depolymerisation of wood carbohydrates is governed by three different reaction types: end-wise peeling, oxidative peeling and alkaline hydrolysis. The degree to which these reactions occur depends on the carbohydrate structure and the pulping conditions like temperature and hydroxyl ion concentration.

The end-wise peeling reaction cleaves off one monosaccharide unit after the other from the reducing end of a polysaccharide chain. In parallel, a competitive stopping reaction can take place, leading to formation of a stable terminal saccharinic acid group that is inaccessible to further peeling. Both reactions can occur in alkaline media at temperatures above 80 °C. For cellulose, it was estimated that on average 50-60 glucose units are peeled off, before the degradation of a polymer molecule is terminated by a stopping reaction. However, the ratio strongly depends on the reaction conditions, the estimated activation energy of the peeling and stopping reaction are stated to be 103 kJ/mol and 135 kJ/mol, respectively. This indicates that at increased temperatures the peeling reaction becomes less pronounced. Alkaline hydrolysis occurs at temperatures above 140 °C. The polysaccharide chains are cleaved randomly, creating again new reducing ends accessible to so-called secondary peeling. [7]

Experiments and methods

The hardwood black liquor used for all experiments was received from a local Kraft pulp and paper mill and had been concentrated to 43 % dry solids before sampling. This liquor was not further treated and stored at -18 °C until the heat treatment experiments.

The heat treatment was carried out in a 1-L stainless steel reactor vessel, equipped with temperature and pressure sensors, shown in **Error! Reference source not found.** Liquid as well as gas samples could be taken throughout the experiments with the installed stainless steel sampling lines. The reactor was heated and mixed by a magnetic stirrer and heating plate. Approximately 1 kg of BL was weighted into the reactor and heating was started after the reactor had been sealed. After the target temperature had been reached, it was held for 2 h, before the BL samples were taken, cooled to room temperature and then frozen until analysis. The treatment temperatures were 150, 185 and 220 °C.



Figure 1. Heat treatment reactor.

For analysis of the samples, first the pH was measured at room temperature with an SI Analytics A164 1M-DIN-ID pH electrode. The hemicellulose content was measured based on the method described by Sluiter and coworkers [11], which was adapted for the special requirements that come with the use of a difficult sample like BL. In a first step, the samples were diluted 1:4 with purified water. The dilute samples were filled into a weighted temperature resistant bottle and acidified with 72 % H₂SO₄ to a pH<1. Then the samples were further diluted with water and put into an autoclave. They were heated to the target temperature of 120 °C, which took 2.5 h. After a holding time of 30 min the autoclave was switched off and slowly cooled to room temperature. The samples were then weighted to attribute for any loss of evaporated water. The liquid supernatant was decanted off and diluted with ultrapure water prior to chromatography. The measurement was carried out with a Dionex Integrion high-performance anion exchange system (ThermoFisher Scientific) with pulsed amperometric detection. The elution method is summarized in the following points:

- Column: CarboPac PA20
- Eluent: 2 mM KOH (aqu)
- Eluent – regeneration 100 mM KOH (aqu)
- Flow rate: 0.4 ml/min
- Pressure: 2300 psi
- Time: 45 min
- Column temperature: 30 °C
- Detector temperature: 20 °C
- Detector: pulsed amperometric detection, reference electrode (pH-Ag/AgCl)
- Injection volume: 10 µl

Results

The degradation of hemicelluloses from BL showed a strong dependency on the temperature maintained during hydrothermal treatment. In the tested temperature range, a higher temperature generally led to a higher degree of hemicellulose degradation, as can be seen in Figure 3. While after treatment at 150 °C still 53 % of the original hemicellulose content can be found in the BL sample, the

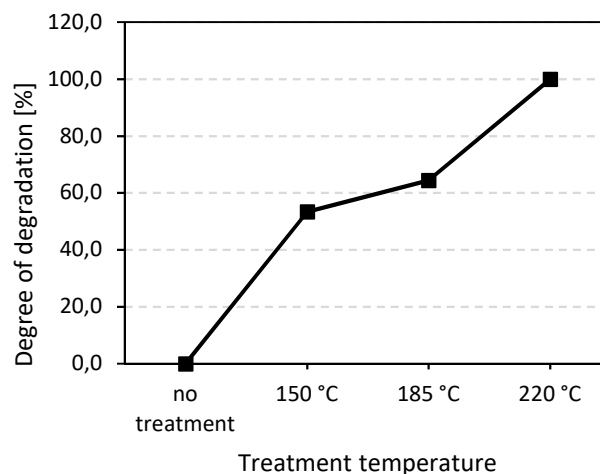


Figure 2. Change of concentration of total hemicellulose from hardwood BL upon heat treatment. The liquor used had a solids content of 43 % and was treated for 2 h at the target temperature. Analysis was performed by acid hydrolysis followed by high-performance anion exchange chromatography with pulsed amperometric detection.

hemicelluloses had been completely degraded after treatment for 2 h at 220 °C. Clearly, the effect of a temperature rise from 185 to 220 °C is more significant for the change of total hemicellulose concentration compared to 150 to 185 °C. This effect is clarified by the behaviour of the single monosaccharide units that make up the hemicelluloses from the tested BL. Hardwood BL contains mainly xylose from glucuronoxyylan and smaller amounts of galactoglucomannans [7]. The liquor tested for this study contains mainly the xylose from xylan, glucose and galactose from other hemicellulose types like galactoglucomannan, and arabinose which can also be found in e.g. xylans and galactoglucomannans. Figure 3 shows the different degrees of degradation for the single monosaccharide units. The content of xylose – and thus xylan – decreases linearly with increasing treatment temperature. In contrast to that, the hexose content is lower after treatment at 150 °C compared to treatment at 185 °C. The stabilizing stopping reaction that protects the polysaccharides' reducing ends from further degradation thus plays a significant role during degradation of galactoglucomannans at temperatures above 150 °C. This is in accordance with the activation energies for the peeling and the stopping reaction, the stopping reaction has a higher activation energy and thus is more dominant at higher temperatures, slowing down the degradation of galactoglucomannan at 185 °C which leads to an increase in the measured concentration after heat treatment. These results fit to the experiments of Nieminen and coworkers, who found that the effect of temperature on the degradation rate is more pronounced for xylan than for galactoglucomannan [12].

After treatment at 220 °C all the hemicelluloses are degraded, regardless of the type. This shows that at even higher temperature the hydrolysis and degradation reaction are again faster than the stabilizing stopping reaction. For example, Louhelainen and Alén found that more than 90 % of the hemicelluloses from softwood BL were degraded upon heat treatment for 30 min at 190 °C [13].

The development of the BL pH value corresponds to the chemical reactions that take place in the sample during heat treatment (see Figure 4). The degradation reactions of hemicelluloses and also lignin consume alkali and sulphide ions. This in turn decreases the initially very high BL pH value.

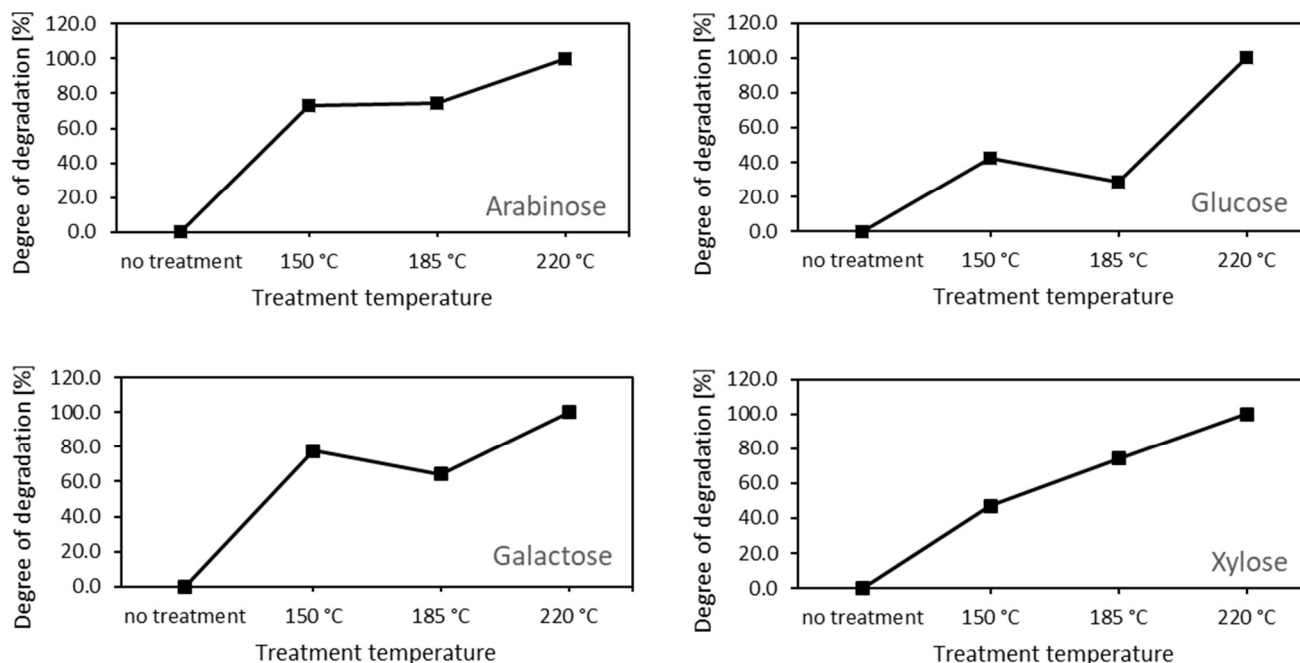


Figure 3. Change of concentration of the single monosaccharides from degraded hemicelluloses upon heat treatment. The BL used had a solids content of 43 % and was treated for 2 h at the target temperature. Analysis was performed by acid hydrolysis followed by high-performance anion exchange chromatography with pulsed amperometric detection.

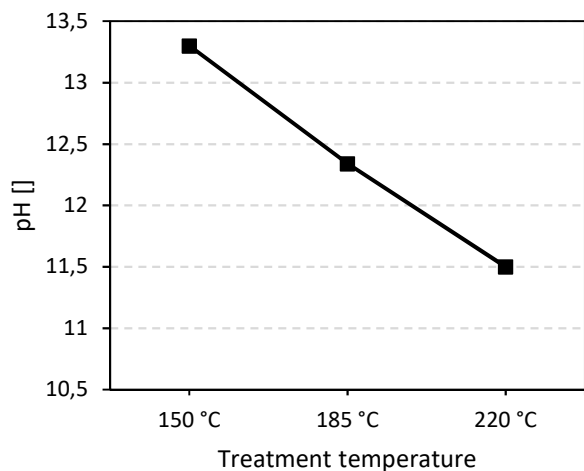


Figure 4. Development of BL pH upon heat treatment. The liquor used had a solids content of 43 % and was treated for 2 h at the target temperature

Aliphatic carboxylic acids are formed that further decrease the pH value. These reactions lead to an overall decrease of pH from originally 13.5 to 11.5 after treatment at 220 °C. In this pH range the properties of BL start to change due to precipitation of lignin [14], [15]. This needs to be considered for further processing of the BL.

Conclusion

Heat treatment of hardwood BL was shown to significantly influence the properties of the liquor. Depending on the treatment temperature, the residual hemicelluloses in the BL could be partially or even completely degraded. This degradation happened together with a distinct decrease in BL

pH value which was lowered up to two pH units. Upon heat treatment at 185 °C, the different types of hemicellulose showed significantly different behaviour. While xylan was degraded faster compared to lower treatment temperatures, the degradation of galactoglucomannan was hindered, possibly due to the stopping reaction protecting the reducing end groups from further peeling. After treatment at 220 °C, all the hemicelluloses were completely degraded.

Acknowledgement

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References

- [1] P. Bajpai, "Alternative Chemical Recovery Processes," in *Biermann's Handbook of Pulp and Paper*, 3rd ed., Elsevier, 2018, pp. 453–464.
- [2] M. Ragnar, G. Henriksson, M. E. Lindström, M. Wimby, J. Blechschmidt, and S. Heinemann, "Pulp," *Ullmann's Encyclopedia of Industrial Chemistry*. Wiley-VCH Verlag GmbH & Co. KGaA, 2014.
- [3] New Zealand Institute of Chemistry, "The pulp and paper industry," *Chem. Process. New Zeal.*, 1998.
- [4] United States Environmental Protection Agency, "Chemical Wood Pulping," *AP-42 Compil. Air Emiss. Factors*, 1990.
- [5] J. Kuenen, M. Deslauriers, C. Trozzi, and M. Woodfield, "Pulp and paper," in *EMEP/EEA emission inventory guidebook 2009*, 2009, pp. 1–21.
- [6] P. Bajpai, "Evaporation of Black Liquor," in *Pulp and Paper Industry*, Elsevier, 2017, pp. 39–66.

- [7] H. Sixta, A. Potthast, and A. W. Krottschek, *Chemical Pulping Processes*. Wiley, 2006.
- [8] L. Söderhjelm, P.-E. Sagfors, and E. Kiiskilä, "Factors influencing heat treatment of black liquor," in *International Chemical Recovery Conference*, 1998.
- [9] J. D. Small and A. L. Fricke, "Thermal Stability of Kraft Black Liquor Viscosity at Elevated Temperatures," *Ind. Eng. Chem. Prod. Res. Dev.*, vol. 24, no. 4, pp. 608–614, 1985.
- [10] P. Wong, "Improving Black Liquor Processability and Combustibility," in *Steam & Steam Power Fall Meeting*, 2007.
- [11] A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, and D. Templeton, "Determination of Sugars , Byproducts , and Degradation Products in Liquid Fraction Process Samples Laboratory Analytical Procedure (LAP) Issue Date : 12 / 08 / 2006 Determination of Sugars , Byproducts , and Degradation Products in Liquid Fraction Proce," *Lab. Anal. Proced. NREL/TP-510-42623*, no. January, pp. 1–14, 2008.
- [12] K. Nieminen, M. Paananen, and H. Sixta, "Kinetic model for carbohydrate degradation and dissolution during kraft pulping," *Ind. Eng. Chem. Res.*, vol. 53, no. 28, pp. 11292–11302, 2014.
- [13] J. Louhelainen and R. Alén, "Changes in the Carbohydrate-Derived Materials of Wood and Nonwood Black Liquors During Heat Treatment," in *Fall Technical Conference*, 2003.
- [14] H. Loutfi, B. Blackwell, and V. Uloth, "Lignin recovery from kraft black liquor: preliminary process design," *Tappi J.*, vol. 74, no. 1, 1991.
- [15] B. Saake and R. Lehnen, "Lignin," *Ullmann's Encyclopedia of Industrial Chemistry*. Wiley-VCH Verlag GmbH & Co. KGaA, pp. 21–36, 2012.