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Rapeseed straw polymeric hemicelluloses obtained by extraction methods based on severity factor

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ABSTRACT

Rapeseed straw consists of a hard epidermis that is rich in hemicellulose and lignin and a sponge-like interior that consists mainly of cellulose. The stems were subjected to water, alkali or acid as extraction medium. The effects of the extraction conditions were quantified using severity factors and by comparing the effects of different extraction pHs, temperatures and times. Extraction with alkali resulted in a higher yield, 47 g/100 g straw in, compared to water, 6 g/100 g straw in, or an acidic, 5 g/100 g straw in, extraction process. An increase in temperature improved the extraction yield; in particular, more xylan was extracted at an elevated temperature and higher alkalinity. However, at high alkalinity, increased extraction temperatures led to a reduction in the recovery of glucomannan. The highest molecular weights (~35,000 g/mol) of the extracted hemicelluloses were obtained using extraction procedures with 1.5 M NaOH at 110 °C and autohydrolysis at 150 °C. While these two parameter settings had very similar severity factors, extraction under basic conditions afforded an extract rich in xylan and low in lignin content, whereas autohydrolysis generated a glucomannan-rich extract.

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1. Introduction

Rapeseeds are a valuable agricultural resource and are used to produce vegetable oil for food and feed and for the production of a biofuel, such as rapeseed methyl ester (RME). Oil-rapeseed straw is an agro-industrial residue that has few applications. It is mainly composed of cellulose, lignin, pectin and hemicelluloses, where arabinoxylan is the primary hemicellulose followed by galactoglucomannan (Svärd et al., 2015). Conversion of agro-industrial residues into a feedstock for bioenergy has gained much interest, and different combustion techniques, steam explosion methods, organosolv, ionic liquids, autohydrolysis, alkaline pretreatments, to name a few have been used to generate monosaccharides for fermentation into bio-ethanol (Buruiana et al., 2014; López-Linares et al., 2013; Vallejos et al., 2015; Morais et al., 2014; Zhao et al., 2009; da Costa Lopes et al., 2013; Gírio et al., 2010). The presence of hemicelluloses is considered a complication in the fermentation process because hemicelluloses are typically a heterogeneous mixture of five- and six-membered monosaccharides (i.e., xylose, mannose, arabinose, galactose and glucose), while cellulose consists only of six-membered ring glucose monosaccharides. Still, polysaccharides, including hemicelluloses, are promising resources for use in bio-based materials such as renewable films, foams, and plastics. Hemicelluloses extracted from wood have been in focus for the development of such applications, but cereal straw, mainly wheat and rye, has also been shown to be viable for use in biobased materials design, especially as films for disposable products. Such applications have recently been extensively reviewed, for instance by Albertsson et al. (2011), and by Hansen and Plackett (2008). Very recently, freestanding and remarkably ductile xylan films were generated from oil-rapeseed straw and were demonstrated to have strain-to-break ratios exceeding 60%. Extraction under alkaline conditions liberated xylan fractions in good yield with number average molecular weights of approximately 16,000 g/mol (Svärd et al., 2015).

Extraction process parameters strongly influence the composition and properties of the fractions recovered from lignocellulosic feedstock and are thus of great importance for obtaining suitable raw materials for the production of functional materials. Extraction of hemicelluloses using hydrothermal methods is a complicated process that involves carbohydrate degradation, lignin and lignin-carbohydrate bond cleavage reactions, as well as mass and heat transfer. All of these reactions are dependent on the extraction conditions and are most heavily influenced by reaction times, temperatures and pH. Reaction kinetics are important for process development, and the equations needed to describe these cat-

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alytic chemical reactions and different mass transfers are complex. Mathematical modeling is typically based on various simplified approaches: pseudo homogeneous kinetic models and severity analyses. The degradation and solubilization of hemicelluloses as functions of time and temperature during hydrothermal processes can be expressed by a 'severity factorí (R_0) to enable easy comparison of results and to facilitate process control by combining time and temperature into one variable (Garrote et al., 1999; Overend et al., 1987). The use of 'severity factorsí to determine the best set of experimental parameters necessary for the release of hemicelluloses from different biomass sources has been previously demonstrated. The main goal of these studies was to degrade hemicellulose to recover oligo or monosaccharides (Garrote et al., 2001; Kabel et al., 2007; Sun et al., 2015). Roos et al. (2009) demonstrated the use of R_0 to obtain high molecular weight hemicelluloses with high yield from barley husks using a microwave-assisted extraction method.

Our aim was to unveil the relationships between hydrothermal extraction conditions and structure, composition, and molecular weights of the obtained polymeric polysaccharide-rich extracts from the extraction of oil-rapeseed straw via severity factor modeling. The extraction is evaluated using kinetic modeling, severity factor calculations, and mass flows to quantify the influence of the extraction conditions as a basis for utilization of rapeseed straw hemicellulose-based materials.

2. Experimental methods

2.1. Materials and chemicals

Rapeseed straw (hybrid Compass) was collected from farms in July 2014 in Grillby, Sweden. The collected straw was dried at 40 °C for three days, resulting in a dryness of approximately 95%, and was stored in the dark until use. Before extraction, the rapeseed straw was cut into approximately 5 cm long pieces. A sodium hydroxide solution of 1 M (1 L, 40 g/1 L H_2O Chemsolute®, Th. Geyer) was used as a stock solution to prepare a 0.25 M NaOH extraction liquid. A 10.25 M stock solution was prepared by dissolving sodium hydroxide pellets (99.7%, CAS nr: 1310-73-2, VWR International), and the resulting stock solution was used to prepare the 1.5 M NaOH extraction liquid. The 1 mM HCl extraction liquid was prepare by dilution 37% Hydrochloric acid (Sigma Aldrich, CAS: 7647-01-0). Deuterium oxide (99.9%, CAS nr: 7789-20-0, Cambridge Isotope laboratories, Inc., USA) and dry dimethyl sulfoxide-d_6 (D, 99.9%, CAS nr: 2206-27-1, Cambridge Isotope laboratories, Inc., USA) from ampoules were used for NMR analyses. For acid hydrolysis sulfuric acid (72%, LabService AB, Sweden) was used. L-(+)-Arabinose (99.9%, CAS nr: 5328-37-0, Sigma), D-(+)-galactose (99.9%, CAS nr: 59-23-4, Sigma-Aldrich), D-(+)-glucose (99%, CAS nr: 50–99-7, Sigma), D-(+)-xylose (99%, CAS nr: 58–86-6, Sigma), D-(+)-mannose (99%, CAS nr: 3458-28-4, Sigma), and L-rhamnose monohydrate (99%, CAS nr: 6155-35-7, Sigma) were used as standards in the HPLC-PAD analyses. Acetyl chloride (99%, CAS nr: 75-36-5, Acros Organics), methanol (100.0%, CAS nr: 67-56-1, VWR Chemicals), and acetic anhydride (99%, CAS nr: 108-24-7, Sigma Aldrich) were used to quantify methylglucuronic acid contents and Xylan from beech wood (90%, CAS nr: 9014-63-5, Sigma) was used as a reference. Ethanol (96% vol, CAS nr: 64-17-5, VWR Prolabo Chemical) was used for precipitation. By diluting 1 M NaOH (Chem solute, Th Geyer, Germany) a 10 mM NaOH(aq) solution was prepared.

2.2. Extraction procedure

Hemicellulose was extracted from rapeseed straw using water, base and acid as liquid extraction media. For water and alkaline extractions, 2.5 L steel autoclaves were used; for acidic extraction, 2 L Teflon-covered autoclaves were used due to the corrosive nature of the extraction medium. For each extraction, 80 g (dry weight) of rapeseed straw was placed in the appropriate autoclave depending on extraction medium. The extraction protocol was previously described by Svärd et al. (2015). Air was evacuated for 30 min before adding the extraction liquid (deionized water, 0.25 M NaOH(aq), 1.5 M NaOH or 1 mM HCl(aq)) by vacuum suction to reach a liquid-to-straw ratio of 10:1. The autoclaves were subsequently immersed in a steam-heated ethylene glycol bath with the autoclaves set slightly inclined to induce mixing by rotation. The extraction time was 60 min for all the samples, and 10 min was added to the extraction time to allow the autoclaves to reach the extraction temperature. The extraction was terminated by removing the autoclaves from the ethylene glycol bath and cooling them in a water bath for 20 min. After cooling the autoclaves, the liquid was separated from the straw by filtering the sample and pressing it by hand. The collected samples were then stored in a refrigerator for further analysis. The extraction liquid was freeze-dried for 48 h, and the powder was collected and weighed. To preserve the material as much as possible for accurate determination of the yields of hemicellulose that can be directly recovered, the extracted straw was not washed after extraction but was dried at 40 °C for 72 h and weighed.

The 'severity factor', R_0, which is expressed in Eq. (1), combines the effect of time and temperature and was used in this study to compare the different extraction temperatures chosen for this study.

$$R_0 = t \times e^{\frac{T-100}{14.75}} \quad (1)$$

where t is the time (in min), and T is the extraction temperature (in °C) (Overend et al., 1987). The reference temperature is 100 °C. The value 14.75 is an empirical parameter related to temperature and activation energy assuming first order kinetics (Carvalheiro et al., 2009). However, the way this equation is expressed by Overend et al. (1987) only considers pH levels that are close to neutral; thus, if the pH of the hydrothermal liquid medium is changed, the equation would no longer be representative. For acid catalyzed reactions, the extension of the severity factor by $R'_0 = [H^+]R_0$ has been proposed (Abatzoglou et al., 1992; Chum et al., 1990). The severity factor in this study was calculated taking this into account, according to Eq. (2), and was used to compare the effect of the different pH on the extraction media in this study.

$$R'_0 = 10^{-pH} \times t \times e^{\frac{T-100}{14.75}} \quad (2)$$

where the pH used in Eq. (2) was calculated from theoretical pH values of the extraction media, and the value is based on the type of extraction liquid and extraction temperature; the value was determined using the ionization constant of water temperature dependence listed by Bandura and Lvov (2006) at a pressure of 0.1 MPa. Extraction conditions that were chosen in this study are listed in Table 1 along with the calculated pH and $\log\left(R'_0\right)$ values (Eq. (3)). An example of a calculation of pH and $\log\left(R'_0\right)$ is presented in the Supplementary material.

$$log\left(R'_0\right) = log\left(10^{-pH} \times t \times \frac{T-100}{14.75}\right) \quad (3)$$

This equation can be simplified to Eq. (4):

$$\log\left(R'_0\right) = \log(R_0) - pH \quad (4)$$

2.3. Purification of polysaccharides

Approximately 1 g of the freeze-dried samples, LB110 and W150, were re-dissolved in water. The samples were then precipitated with a large excess of 96% ethanol under stirring. The

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