



## Research paper

## Hydrothermolysis of pine wood

Marina Ståhl\*, Kaarlo Nieminen, Herbert Sixta

Department of Bioproducts and Biosystems, Aalto University School of Chemical Engineering, Espoo, Finland



## ARTICLE INFO

## Keywords:

Hydrothermolysis  
Softwood  
Lignin  
Mass balance  
Kinetics  
Degradation

## ABSTRACT

The objective of this research was to obtain a better fundamental understanding of the extraction of lignin and carbohydrates from pine wood during hydrothermolysis at elevated temperatures. The treatment was performed in a batch reactor at three different temperatures (200, 220 and 240 °C) and a liquid-to-wood ratio of 40:1. It was found that up to 35% of native pine lignin solubilized at 240 °C within a few minutes of reaction time. Delignification kinetics of wood during hydrothermolysis was successfully modeled by the assumption of simultaneous dissolution (depolymerization) and condensations reactions of lignin. Two distinct lignin fractions, so-called soluble and insoluble lignin were found in the hydrolysates and can be considered as potential material for the production of high-value products. Complete removal of pine wood hemicellulose was achieved at a concomitant cellulose yield loss of about 12.5%. Up to 85% of pine wood mannan could be recovered from the hydrolysate as manno-oligosaccharides, in contrast to only 46% of xylo-oligosaccharides. Kinetic models fitting experimental data are proposed to explain degradation and conversion reactions of two main hemicellulosic components of pine wood, xylan and mannan. Overall, this study provides initial fundamental knowledge required for potentially efficient utilization of softwoods using wood biorefinery concept.

## 1. Introduction

The basic goal of the modern biorefinery concept is the selective separation of the three main wood components, cellulose, hemicellulose and lignin, and their versatile utilization for the production of high added-value products through the integration of clean processes [1]. Nevertheless, it has been a great challenge to design an efficient fractionation process of lignocellulosic materials which would be both technologically feasible and economically viable [2].

Bobleter, Niesner and Röhr [3] suggested to use water for the pre-treatment of lignocellulosic material to enhance its susceptibility to enzymatic hydrolysis. The processes using liquid water under high temperature and pressure are also named in literature as hydrothermal treatment, hydrothermolysis, autohydrolysis, Aquasolv® process and pressure-cooking in water [4].

Degradation of wood components during hydrothermolysis takes place via acidic hydronium ions ( $\text{H}_3\text{O}^+$ ) and basic hydroxide ions ( $\text{OH}^-$ ) generated due to water autoionization at high temperatures [4]. Hydronium ions cleave the acetyl groups linked to the hemicellulose resulting in the formation of acetic acid [5]. The dissociation of acetic acid further catalyzes the hydrolysis of glycosidic bonds in carbohydrates [6] as well as it promotes the cleavage of lignin carbohydrate linkages and the depolymerization of lignin [4].

The use of hot water for biomass fractionation received significant

attention in the recent years and was considered a promising method for the extraction and recovery of hemicellulose and lignin. The reason for this is that hydrothermolysis is envisioned as relatively inexpensive and environmentally friendly process because fractionation is achieved by use of water and heat only.

The majority of the studies of biomass hydrothermolysis deal with hardwoods [7–10] and annual plants [11–15]. Softwoods, are generally recognized as being more resistant towards hydrothermal treatment, owing to their more rigid structure [16], a lower degree of acetyl groups substitution in carbohydrates [17], higher lignin and phenolic extractives contents and their high tendency to condensation reactions [7]. Nevertheless, softwoods represent the principal lignocellulosics in the Northern hemisphere [18] and therefore their utilization is of interest.

Although the hydrothermolysis of softwoods has not gained as much attention as that of other raw materials, some studies concerning this topic have been performed. The effectiveness of hydrothermolysis on the selective solubilization of carbohydrates of softwoods was confirmed by Yoon, Kimberley and van Heiningen [19] and Leppänen, Spetz, Pranovich, Hartonen, Kitunen and Ilvesniemi [20]. A number of studies have investigated hydrothermolysis of softwoods as pretreatment process and were mainly focused on the extraction of hemicelluloses and their subsequent acid hydrolysis [16] and fermentation to ethanol [21].

\* Corresponding author.

E-mail address: [marina.stahl@aalto.fi](mailto:marina.stahl@aalto.fi) (M. Ståhl).

The effect of process conditions on the yield and structure of softwood non-cellulosic polysaccharides has been investigated. Spruce wood has been extracted with pressurized hot water at temperatures from 100 to 180 °C [22]. It was found that all hemicelluloses were partly hydrolyzed during extractions at 160–180 °C, however xylans and arabinogalactans were hydrolyzed to a higher extent than galactoglucomannan (GGM). Particular consideration was given to the extraction of polymeric GGM applying optimized process conditions [22] or using phthalate buffer for regulation of pH [23]. The authors suggested that a pH of about 4 is optimal for the extraction of high molar-mass GGM in relatively high yields [23].

The effect of temperature using the flow-through pressurized hot water extraction on the removal of hemicellulose from Norway spruce was studied by Leppänen, Spetz, Pranovich, Hartonen, Kitunen and Iivesniemi [20]. The flow-through operation mode induces less hydrolysis of glycosidic bonds as compared to that of batch extraction, resulting in higher average molar masses of the extracted carbohydrates and a lower removal rate of acetyl groups from GGM. It was shown that GGM dissolution was significantly enhanced at an extraction temperature beyond 160 °C. About 15% of lignin was dissolved at 220 °C while hemicellulose was completely removed from wood. Partial degradation of cellulose took place only at 240 °C.

Aqueous extraction kinetics of hemicellulose from spruce sapwood was investigated by Grénman, Eränen, Krogell, Willför, Salmi and Murzin [24] in the range of 150–170 °C. The extraction rate was observed to increase considerably with temperature, with the conversion after extraction ranging from about 10% to 80%. However, the extraction temperature did not influence the selectivity of dissolution significantly. Additionally, it was shown that deacetylation of hemicelluloses takes place inside the chips before they enter the liquid phase [1,24].

So far, research work on hydrothermolysis of pine wood was limited to rather moderate temperatures below 180 °C. Additionally, the majority of the studies reported about the degradation of carbohydrates while the fate of lignin during hydrothermolysis of pine was largely ignored. In this work, the effect of hydrothermolysis on the degradation and dissolution of lignin and carbohydrates from pine wood using a wide range of process conditions was studied. The target was to elucidate the degradation and dissolution mechanisms of both carbohydrates and lignin during pine wood hydrothermolysis by fitting the experimental data with the aid of comprehensive kinetic models.

## 2. Materials and methods

### 2.1. Materials

Pine wood chips used for hydrothermolysis experiments were supplied by Metsä Fiber, Finland. The chips were screened (SCAN-CM 40:01; Scandinavian Standard, 2001) and stored refrigerated before use. Pine chips were air-dried at ambient temperature to dry matter content (DMC) over 95% and then grinded in a Wiley mill with 1-mm screen to obtain a fraction with a particles size smaller than 1 mm. The chemical composition of initial pine wood is shown in Table 1. The DMC was determined by oven drying at 105 °C overnight.

### 2.2. Hydrothermolysis

Hydrothermolysis experiments were conducted in a 10 L batch reactor, equipped with a mechanical stirrer, a temperature controller, a pressure gauge and a valve for the removal of hot extraction liquors. Approximately 95 g (on dry basis) of wood was weighted and extracted at 200, 220 and 240 °C for different time periods up to 120 min in water at a liquid-to-wood ratio (L:W) of 40 g/g. Such a high L:W was selected in order to minimize the solubility limitations of wood components triggered by mass transfer of wood matrix. The degradation of wood components during preheating was taken into account by conversion of

**Table 1**  
Chemical composition of pine wood. •

Component	Amount [% on o.d. wood]
Cellulose	40.85
(Galacto)glucomannan (GGM)	15.79
Arabinoglucuronoxylan (AX)	9.08
Galactan	1.89
Arabinan	0.55
Klason lignin	26.87
Acid soluble lignin	0.56
Extractives (acetone soluble matter)	3.00
Ash	0.21
<b>Total</b>	<b>98.80</b>

heating up phase into isothermal reaction time using a previously published method [7]. After reaching the set reaction time, the hydrolysate was discharged from the autoclave. The obtained water extracts were stored at 4 °C. Here and later terms liquid/aqueous fraction refer to hydrolysate. The wood residue was recovered from the reactor, washed with hot water and air-dried before the yield was determined on a dry weight basis.

### 2.3. Methods

Klason lignin, acid soluble lignin (ASL) and carbohydrate contents of solid samples (untreated wood and wood residue after the treatment) were determined after acid hydrolysis according to NREL/TP-510-42618 [25]. Carbohydrates in liquid samples were measured after acid hydrolysis according to NREL/TP-510-42623 [26]. Subsequent analysis of the recovered neutral sugar monomers was performed by using a Dionex ICS 3000 high-performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD) equipped with a CarboPacPA20 column (Dionex, Sunnyvale, CA, USA). Water was used as the eluent at a flow rate of 0.4 mL/min at 30 °C. Monosaccharides in the liquid samples were quantified by HPAEC directly from the raw hydrolysates. The amount of oligosaccharides in the liquid samples was calculated by the subtraction of the monosaccharide content from the total polysaccharide content. A minimum of two parallel lignin and carbohydrate determinations were performed, with an additional determination if a noticeable differences between the two measurements were observed. The amount of carbohydrates and lignin in the non-treated pine wood mill is an average of 4 determinations.

The insoluble lignin fraction from the hydrolysates was recovered by centrifugation at 4500 rpm for 15 min and the yield was determined gravimetrically. The soluble lignin in the liquid phase (hydrolysates) was measured by a Shimadzu UV-2550 spectrometer at a wavelength of 205 nm, using an absorptivity constant of 110 g/L [27]. Determination of soluble and insoluble lignin fractions in the hydrolysates was carried out at least in duplicate.

The carbohydrate composition in solid samples was calculated according to a previously published method [27]. As carbohydrates content was calculated according to Janson [27] formula, glucose units incorporated in hemicellulose side chains were taken into account when hemicellulose content was considered; therefore the term “cellulose content” used here is entirely related to cellulose.

Furfural and 5-hydroxymethylfurfural (HMF) content in the water extracts were determined according to the NREL/TP-510-42623 [26] analytical method. Furfural and HMF were determined by High Performance Liquid Chromatography (HPLC) in a Dionex Ultimate 3000 column. All samples were prepared in duplicates, and each duplicate was analyzed by double injection. The carbohydrates were determined as an hydrosugars, and furfural and HMF were determined as C<sub>5</sub>-sugars and C<sub>6</sub>-sugars-equivalents, respectively.

Download English Version:

<https://daneshyari.com/en/article/7063019>

Download Persian Version:

<https://daneshyari.com/article/7063019>

[Daneshyari.com](https://daneshyari.com)