

Microwave heat treatment of black liquor for the degradation of hemicellulose

by

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Preface

After five years of studies at the Faculty of Engineering at the University of Lund, I am happy to finish my education by presenting this Master Thesis. It has been inspiring to work with this project that has the potential to contribute to the development of a process for the production of sustainable fuel.

I would like to thank my supervisors Mats Galbe, Linnéa Kollberg and Caroline Ottosson for their guidance and for always taking time to answer my questions. I would also like to thank Henrik Almqvist and Herje Schagerlöf for the help with equipment and analysis.

Abstract

The largest use of fossil petroleum is the production of fuels. Hence, finding sustainable alternatives is an important step to reduce the emissions of greenhouse gases. One such alternative is to produce fuel from biomass, such as waste products from agriculture and the forest industry. In Sweden, the forest industry is an important part of the economy. The pulp mills produce an excessive amount of a by-product called black liquor, which has a high content of the biopolymer lignin. The company SunCarbon is developing a process to separate the lignin from the black liquor, purify it and recycle the remaining chemicals to the pulp mill. The purified lignin is to be mixed with a carrier oil to a lignin-rich oil that can be used in refineries to produce fuel such as gasoline and diesel.

One of the steps in the process is the heat treatment, which has the purpose to degrade especially hemicellulose, but also lignin, into smaller molecule fractions. A problem with the heat treatment is the corrosion of steel in the reactor vessel, causing the release of metals that pollute the product oil and that are difficult to remove. To solve this problem, the idea to use microwave heating has been introduced. Traditional heating methods require high temperature of the reactor vessel to heat up the medium by conduction and convection. Microwaves heat the material directly and thus the prior heating of the reactor vessel is not required. This means that the temperature of the reactor vessel should be lower and enable for the use of Teflon vessels that do not leach metals to the liquor. The direct heating of the material should also enable faster heating rate. In this Master Thesis, microwave heat treatment was investigated and compared to traditional heat treatment in a steel autoclave. Evaluation was made by analysing the degradation of hemicellulose and lignin with chromatographical methods and lignin yield in the subsequent separation by acidulation in the SunCarbon process.

The microwave treatment resulted in degradation of lignin of the same degree as the heating in the autoclave, at temperatures up to 200°C. The microwave had a faster heating rate than the autoclave. When varying the heating time and the time at the target working temperature, the results indicated equal degradation of lignin independent of treatment time. Analysis of sugar content after treating with acid hydrolysis indicates that the degradation of hemicellulose was greater in the autoclave for treatment at 200°C. This could be explained by the shorter heating rate or the instability of the pressure in the microwave vessels. The sugar concentrations were very similar in material treated with the two heat-treatment methods at lower temperatures, where no leakage had occurred, and the treatment time was equal. Neither of the two heat-treatment methods degraded hemicellulose as much as expected, based on previous studies by SunCarbon. This might be due to insufficient temperatures or treatment times, as temperatures above 200°C could not be investigated with the current laboratory microwave equipment. Conclusively, only a short heating time is sufficient to degrade lignin, but to degrade hemicellulose longer treatment times or higher temperatures are required. The degradation of both lignin and hemicellulose seem to be independent of heat treatment method, indicating that the use of microwaves can be as efficient as other heating methods. This was also confirmed by the nearly equal yields of lignin in the subsequent separation process.

When treating black liquor retentate with acid hydrolysis in a pH range of pH 1-3, a substance is formed that precipitate and form crystals when dissolving the mixture with 50% acetonitrile/water. Analysis indicates that the crystals are composed of oligomers of five monomers, each with the molecular weight 142 Da. Further investigation is required to identify the composition of the crystals, for example using NMR analysis.

Abbreviations

AHT	Autoclave Heat Treatment
BLR	Black Liquor Retentate
DI-MS	Direct Infusion Mass Spectrometry
FTIR	Fourier Transform Infrared Spectroscopy
GGM	Galactoglucomannan
HPLC	High Performance Liquid Chromatography
HT	Heat Treatment
LAP	Laboratory Analytical Procedure
MWT	Microwave Treatment
Mw	Molecular Weight
NREL	National Renewable Energy Laboratory of the U.S Department of Energy
PEG	Polyethylene glycol
PSS	Polystyrene sulfate
RI	Refractive Index
SEC	Size Exclusion Chromatography
TFM	Modified Poly-Tetra-Fluoro-Ethylene
UFLC	Ultra Fast Liquid Chromatography
UPLC	Ultra Performance Liquid Chromatography

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1 Introduction

The issue of global warming, caused primarily by the combustion of fossil fuels (National Geographic, 2019), calls for new alternative solutions regarding fuel production for transportation. Renewable fuel with low impact on the climate can be produced from biomass. However, a concern regarding production of biofuels is the competition for land area with food production (Love & Bryant, 2017). Fortunately, this issue can be avoided by utilizing already available waste products from agriculture and the forest industry.

In Sweden, 70% (Skogsindustrierna, 2015, a) of the land is occupied by forest plantations, and the pulp and paper industry is an important part of the economy of the country, representing approximately 10% of the national economy (Skogsindustrierna, 2015, b). The process of a pulp mill starts with the grinding and chipping of wood, usually followed by a chemical cooking process to decompose the material in order to separate the cellulose from the hemicellulose and the lignin. There are mainly two kinds of pulp mills: sulfate mills and sulfite mills. In Sweden, the most common is the sulfate process, also called the Kraft process. (Skogssverige, 2017, a)

In the Kraft process, the cooking step is performed with a so-called white liquor, which consists mainly of sodium hydroxide (NaOH) and sodium sulfide (Na₂S) dissolved in water. After cooking, the cooking chemicals are separated from the cellulose fibers. The chemical mixture now contains high amounts of lignin which gives the liquor a black color. This liquor is called *black liquor*. In the Kraft process, a purification process follows, that recycles chemicals to the white liquor. The remains of the black liquor that cannot be recycled are used to produce steam in a steam boiler, which is used for energy. (Skogssverige, 2017, b)

The steam boiler is often a bottleneck in the pulp mill. Decreasing the load on the steam boiler could thus potentially enable an increased production of pulp. In addition, the black liquor could be more efficiently utilized by extracting the lignin and use it to produce biofuels, which is the business idea of SunCarbon AB. The intention of SunCarbon is to develop a process that can be integrated with Kraft pulp mills to produce lignin that can be mixed to a pumpable oil, ready to be sent to a petroleum refinery for final upgrading to gasoline and diesel.

The SunCarbon process idea starts with membrane separation, which separates the major part of the cooking chemicals from the lignin. The cooking chemicals are recirculated to the pulp mill while the lignin-rich retentate is further processed by heat treatment for depolymerization of hemicellulose. After follows an acid-induced separation of lignin and a purification process. Lastly, the lignin is mixed with a carrier oil, which could be either a bio-based or a fossil oil. Other additives may also be added, such as surfactants. Finally, the SunCarbon product oil is ready to be sent to a petroleum refinery.

1.1 Problem description

The thermal treatment of black liquor retentate (BLR) in the SunCarbon process, with the purpose to degrade hemicellulose, has proven to be difficult. The high temperature causes corrosion of metals from the reactor vessel that pollute the final product. Certain metals, such as

molybdenum that is found in steel, are difficult to remove in the purification step. Such metals cause downstream problems and are not accepted in the product. Thus, it is of great interest to investigate alternative solutions for the hydrothermal treatment that can degrade hemicellulose without causing leaching of metals to the liquor. Other process ideas that are investigated as alternative solutions are the use of heat exchanging and steam injection. Another alternative that has been presented, but not yet investigated in practice by SunCarbon, is microwave treatment. The temperature profile of microwave heating is different from that of conductive and convective heating. Microwave heating works relatively uniformly throughout the material and may facilitate a lower working temperature of the reactor vessel. The prospect is that microwave treatment of BLR may enable sufficient decomposition of hemicellulose at reactor temperatures suitable for the use of Teflon coating on the reactor vessel, thus avoiding leaching of metals from the steel.

1.2 Aim and scope

The aim of this study was to investigate the possibility of using microwave treatment for the decomposition of hemicellulose. The method was evaluated in a practical laboratory study. The prospect was to gather knowledge that would provide foundation for the decision-making regarding what technique should be further tested in pilot scale.

The scope included testing of microwave treatment at different temperatures and duration times of treatment, as well as treatment with a catalyst. The degradation of hemicellulose and lignin was analyzed with HPLC, SEC, UV-Vis and pH measurements. The lignin yield in the separation process was also tested. During the working process, a discovery was made that extended the scope of the study. During the preparation of HPLC analysis, an unknown compound formed crystals in the sample vials. Thus, it was decided to extend the scope to include further investigation of the content of these crystals and the way they were formed.

1.3 Structure of the report

The report starts with a brief introduction and description of the problem that has led up to this study. Next follows a background, which starts with a description of the chemical structure of lignocellulosic biomass. In addition, a summary is presented of the present knowledge on the decomposition mechanism of hemicellulose, since the objective of the microwave heat treatment is to decompose hemicellulose.

An overview of the pulping process is presented to provide an understanding for the source of the black liquor, which is the raw material of the SunCarbon process, presented thereafter. Furthermore, an introduction to microwave technology is presented, including previous studies on the use of microwave treatment for the decomposition of biomaterial, especially hemicellulose. In order to understand the core of the issue, the next section gives a background to corrosion of steel, which is used as reactor material today by SunCarbon. Teflon, which could be an alternative coating material, is also described.

After the background, the methods and materials used in the study are described, including the analysis methods SEC, UV-Vis, HPLC, UPLC and DI-MS. The results are presented and discussed in the following section, and lastly the conclusions are summarized.

2 Background

2.1 Lignocellulosic biomass

Wood consists mainly of the three polymer structures cellulose, hemicellulose and lignin. Cellulose and hemicellulose are polysaccharides while lignin is built up by aromatic units. Cellulose is a linear polymer consisting of glucose monomers linked by covalent glycosidic bonds. The glucose ring has OH-groups attached which is why cellulose form strong intermolecular hydrogen bonds and the chains form crystalline structures. This strong structural bonding that make up cellulose fibers makes cellulose a suitable material for paper production. (Fellers & Norman, 1998)

Lignin is composed of aromatic units that form large three-dimensional structures. In the production of paper, lignin is removed by making it water-soluble through chemical modification and partial decomposition in the cooking process. (Fellers & Norman, 1998) The lignin is removed as part of the black liquor and makes up the main raw material for the SunCarbon product. The lignin content is higher in trees that are classified as softwood, such as pine and spruce, than in broadleaved deciduous trees, classified as hardwood. (Celignis Analytical, n.d.)

Hemicellulose is a group of polysaccharides consisting of monomers of pentoses and hexoses such as glucose, mannose, xylose, arabinose and galactose (see Figure 1). Hemicelluloses often have highly branched structures. (Fellers & Norman, 1998) Xylose is the main constituent of hemicellulose in hardwood; it may comprise up to 90% of the hemicellulose structure. (Sánchez, et al., 2011) The most abundant hemicellulose group, consisting of xylose, are glucuronoxylans. Glucomannan, consisting of glucose and mannose, is another group that occurs in hardwood. In softwood, such as pine and spruce, O-acetyl-galactoglucomannan is the main component, consisting mainly of mannose, glucose and galactose. (Celignis Analysis, u.d.)

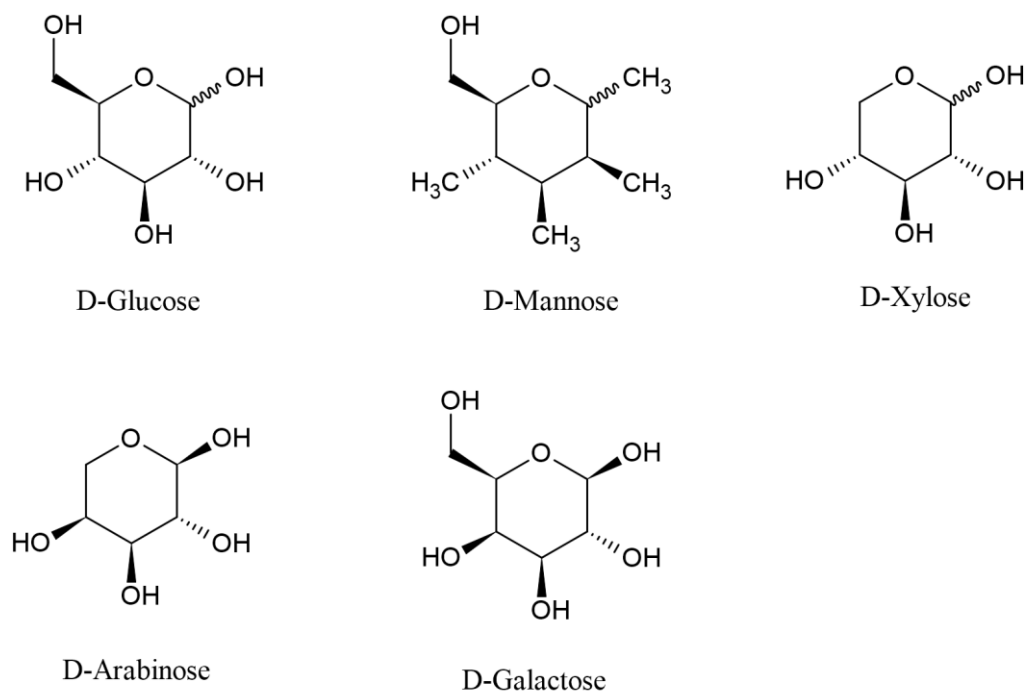


Figure 1. Structure of the five most common sugar monomers in hemicellulose.

2.1.1 Degradation of hemicellulose

The degradation of biomaterial polymers can be divided in 2 steps: first from polymers to monomers, then to smaller compounds. The degradation of hardwood hemicellulose will primarily yield oligomeric xylan, which in turn is degraded to monomeric xylose. Pentoses such as xylose and arabinose are then degraded to furfural (see Figure 2) and then to a range of other degradation products, such as phenols and organic acids. The xylosidic bonds between the xylose units are easily hydrolyzed by acids, whereas the linkages between the uronic acid groups and xylose are very resistant. (Celignis Analytical, n.d.) Hexoses such as glucose, mannose and galactose are primarily degraded to HMF (see Figure 2). Higher temperature enhances degradation of hemicellulose. Carbohydrate content generally decreases, but repolymerization and dehydration of degradation products such as furfural may also take place. (Sánchez, et al., 2011, p. 128)



Figure 2. Molecular structure of furfural and HMF, two common degradation products of hemicellulose and cellulose.

The thermal decomposition of hemicellulose has been investigated by Lv et.al (2010). The results show that hemicellulose degrades mainly in the temperature range 180-340°C. A higher heating rate, i.e. shorter time for heating up to the determined working temperature, could slightly delay the decomposition process to higher temperatures. The monosaccharides of hemicellulose degrade through ring-opening and secondary decomposition. CO₂ is formed mainly due to the cleavage of O-acetyl groups and 4-O-methylglucuronic acid. (Lv, et al., 2010)

The difficulty of isolating hemicelluloses without destroying the branched structure makes it difficult to study the degradation mechanism. A thorough study of the decomposition pathway has thus been performed at a model compound of xylose: O-acetyl-4-O-methylglucurono-xylan. It was found that the major degradation products of xylose after pyrolysis are furfural, glycolaldehyde, acetaldehyde and acetone. The decomposition products of xylan can be divided into 3 groups: (1) low molecular weight products, such as CO, CO₂, acetic acid, acetaldehyde and acetone, (2) furan or pyran ring derivatives, such as furfural, and (3) anhydrosugars. (Lv, et al., 2010)

Thermal decomposition of hemicellulose has also been investigated by Werner et al. (2014), through analyses of seven different commercial hemicelluloses using thermogravimetric analysis coupled to FTIR, differential scanning calorimetry, and pyrolysis-gas chromatography/mass spectroscopy. Their results indicate big differences between the different kinds of hemicellulose. The mass-loss rate was the highest for xylan-based hemicelluloses, meaning that these are the least stable, while those based on cellulose and glucon were the most stable. Xylan also showed a different behavior during slow heating. The heat flow rate from the decomposition of xylan was exothermal, while the other hemicelluloses showed endothermal degradation.

The exothermal behavior of xylan is probably due to the complete oxidation of carbon to CO₂. The off-gases produced during the thermal treatment were analyzed, confirming the high amounts of CO₂ and small amounts of other components produced by xylan. This is explained either by decarboxylation of COOH-groups on units of glucuronic acid, cracking and reforming of C=O and COOH-groups, or decarboxylation of O-acetyl groups linked to xylan. The other polysaccharides gave rise to substantial amounts of CO, methanol, methane, furfural, 5-hydroxymethylfurfural and anhydrosugars (correlated to the polysaccharide-type). (Werner, et al., 2014)

The presence of alkali metals (K, Na) may have a slight catalyzing effect on the thermal degradation of hemicellulose. This has been shown by K. Haddad et al. (2017) for pyrolysis in the temperature range 195-306°C. They also showed that alkaline earth metals (Mg, Ca) have the opposite effect: these inhibit the decomposition. (Haddad, et al., 2017)

2.2 The pulping process

The production of pulp and/or paper starts with debarking and chipping of wood into smaller pieces. Chemical pulping, which is more common than the alternative mechanical pulping, gives a strong, white paper due to the removal of lignin and bleaching. The two most commonly employed kinds of chemical pulping are sulfate and sulfite pulping. The use of sulfate is more common; this is also called the *Kraft process*. (Skogssverige, 2017, a) A box diagram of this process can be seen in Figure 3.

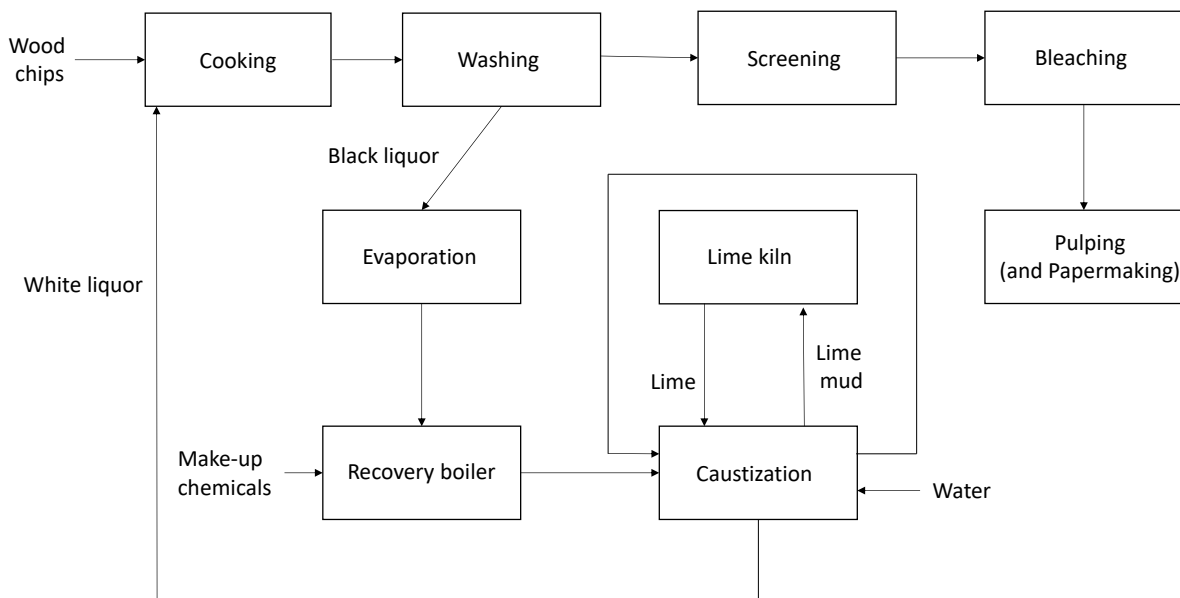


Figure 3. Box diagram of the Kraft process.

In the Kraft process, wood chips are treated with alkaline cooking chemicals. The mix of chemicals is called white liquor. It consists mainly of NaOH and Na₂S dissolved in water, along with small amounts of other substances such as sodium carbonate (Na₂CO₃) and sodium

sulfate (Na_2SO_4). The cooking, which is carried out at approximately 170°C , dissolves the wood components and enables the separation of most of the lignin from the cellulose. Lignin polymers are degraded through depolymerization reactions, in which NaOH works as a catalyst. The depolymerization happens primarily through two different mechanisms. One is the cleavage of phenolic β -ethers by hydrosulfide ions (HS^-), and the other is an epoxide mechanism in which a non-phenolic β -ether is cleaved by a hydroxyl ion (OH^-). (Rinaldi, et al., 2016) After cooking, the cooking chemicals are washed out, along with lignin and some hemicellulose, in a washing procedure of several steps. The lignin gives the mixture a dark color, which is why it is called black liquor. (Skogssverige, 2017, a)

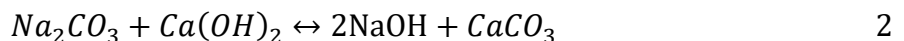
The pulp is further cleaned in the screening step with sieves. Finally, the pulp is ready to be bleached. If this is needed depends on how much lignin remains, which has a dark color and makes the pulp unsuited for some areas of application. Depending on the mill, the next and last step is either drying and papermaking or pulping. (Skogssverige, 2017, a)

The black liquor, which is first called weak black liquor, is taken care of to recycle as much as possible of the cooking chemicals and to use the remaining material, which is mostly lignin, some hemicellulose and trace metals, for energy production. The recycling starts with a series of evaporators to remove water and make the liquor combustible. Between the evaporators, rosin soap can be skimmed off the surface in its sodium form. The rosin is used for production of tall oil. (Ek, et al., 2019)

The concentrated liquor, now called heavy black liquor, is sent to the recovery boiler. Lignin and other trace elements are combusted at temperatures above 1000°C and with limited oxygen supply. This energy is used to produce steam, usually in quantities high enough to run the whole mill. Na_2SO_4 is added as a make-up chemical. It is reduced by carbon to re-form the cooking chemical Na_2S , which is then recycled. (Ek, et al., 2019)

The flue gases from the recovery boiler are collected and cleaned. These contain Na_2SO_4 and Na_2CO_3 , which are precipitated and returned to the strong black liquor to prevent loss of cooking chemicals. (Ek, et al., 2019)

In the bottom of the recovery boiler, Na_2CO_3 , Na_2S and small amounts of other salts are collected as a smelt. These are mixed with weak white liquor to form what is called green liquor. Sludge with insoluble material is removed from the green liquor through sedimentation and filtration. To reform the cooking chemical NaOH , calcium oxide (CaO) is added. It reacts with Na_2CO_3 according to the reactions described below (Ek, et al., 2019):



The precipitated calcium carbonate (CaCO_3) is treated at high temperature in the lime kiln to reform calcium oxide (CaO), according to the reaction below. (Ek, et al., 2019)



The cooking chemicals that have now been regenerated are returned to the cooking process as white liquor. (Ek, et al., 2019) (Skogssverige, 2017)

2.3 The SunCarbon process

The SunCarbon process can be divided into five parts: membrane filtration, heat treatment, separation and purification of lignin, and final after-treatment and mixing of product oil. An over-view in the form of a box diagram can be seen below in Figure 4.

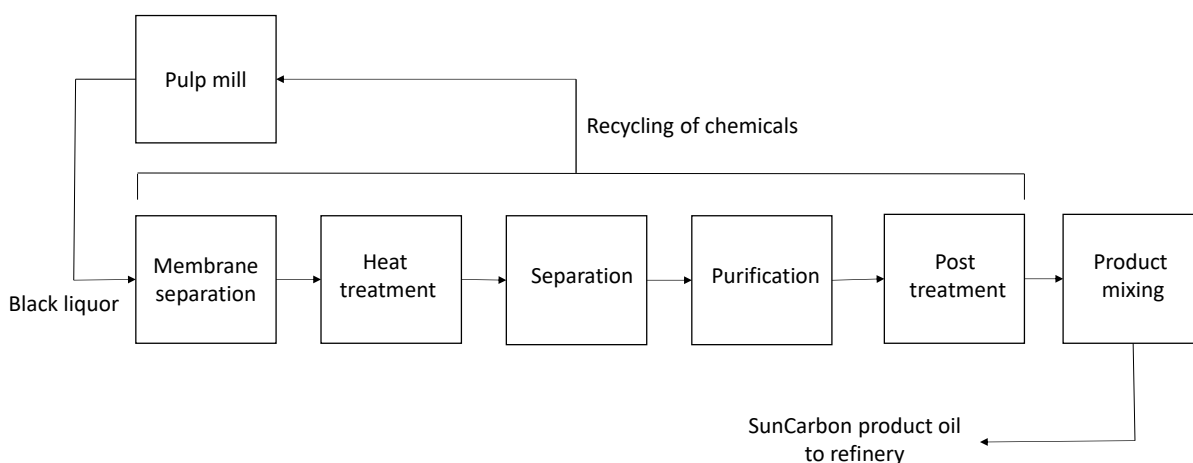


Figure 4. Box diagram of the SunCarbon process.

A major part of the cooking chemicals is separated from the black liquor in the membrane filtration. The chemicals are recycled to the pulp mill, while the concentrated black liquor is sent to the heat-treatment. The main purpose of this treatment is to break down hemicellulose, but also large lignin-molecules are depolymerized to smaller components. The reaction is similar to the base catalyzed depolymerization in the Kraft process, but the NaOH is not regenerated and thus the reaction is not catalytic. To increase degradation, elevated temperature and pressure is applied.

Depolymerization of lignin is associated with the formation of carbonaceous deposits (usually called coke). Coke is formed by re-polymerization through formation of C-C bonds. This problem is known to be reduced by the presence of NaOH (Evstigneev, 2011). However, as the concentration of NaOH decrease with reaction time when pH decreases, the risk of coke formation could increase. Sometimes capping agents such as phenol can be used to decrease the coke formation in depolymerization of lignin. (Toledano, et al., 2015)

The next step is an acid-catalyzed separation of lignin, followed by a series of purification steps that remove remaining cooking chemicals, ash and water. Lastly, the lignin is mixed with a carrier oil and possibly other additives such as surfactants to produce a pumpable liquid with the desired viscosity. It is not yet determined what carrier oil will be used; it could be either a fossil or a bio-based oil.

2.4 Microwave treatment

2.4.1 Microwave chemistry

Microwave irradiation lies in the frequency range of 0.3 to 300 GHz in the electromagnetic spectrum. Specialized chemistry microwave reactors usually operate at 2.45 GHz, similar to household microwaves. Microwaves heat up material through the “microwave dielectric heating effects”, which depend on the tendency of the material to absorb microwave energy and convert it to heat. (Lanigan, 2010, p. 23)

The heating is caused by two main mechanisms: dipolar polarization and ionic conduction. Materials that contain polar molecules are heated by dipolar polarization. When polar molecules are exposed to an electric field, they orientate opposite to the direction of the electric field. When the molecules relax and return to their original orientations, heat is dissipated. (Lanigan, 2010) The ability of a material to convert microwave energy to heat depends on the loss factor ($\tan \delta$), which is calculated as the fraction of the dielectric loss (ϵ'') and the dielectric constant (ϵ'), which represent the materials ability to be polarized by the electric field (see equation (1)). (National Institute of Standards and Technology, CEM Corporation, 1988, p. 9)

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (1)$$

In materials where free ions are present, microwaves also cause heating by inducing fast movement of the ions: ionic conduction. Due to the occurrence of chemical reactions that cannot be explained solely by the two heating mechanisms mentioned, there are also theories about a third “specific” microwave effect, caused by the accelerated rate of heating. (Lanigan, 2010, p. 23)

Microwave heating has the advantage of heating up a whole volume instead of heating through conduction from the reactor vessel. This also leads to a very fast heating since there is no need to wait for a heating source to heat up. (National Institute of Standards and Technology, CEM Corporation, 1988) However, hot or cold spots may appear due to standing waves in the microwave. Convective heating then works to even out the temperature differences. The penetration depth may also be limited and depends on the effect of the microwave, as well as properties of the material, such as salt content. (Koskiniemi, et al., 2011)

2.4.2 Microwave treating of lignocellulosic material

For macromolecules such as lignocellulosic polymers the polarizability and dielectric loss factor are low. Only parts of the macromolecules are polarized, and thus only amorphous parts of molecules can align according to the electric field. Cellulose has an intermediate loss factor ($\tan \delta \approx 0.2$), but the behavior of hemicellulose and lignin under microwave irradiation has not been much studied. However, the complex structure and lack of hydroxyl groups in lignin propose a different heating mechanism compared to cellulose and hemicellulose. (Lanigan, 2010, p. 38) According to Hollertz (2014), the dielectric properties of hemicellulose and cellulose can be assumed to be similar. Hollertz also showed that a higher lignin content in dissolving pulp increases the value of $\tan \delta$. (Hollertz, 2014)

Microwave technology has been used on lignocellulosic material for various purposes. For example, as a supplementary method in pretreatment in the production of bioethanol, where the microwave technology works to separate cellulose from lignin and xylan. (Chen & Wan, 2018) As a pretreatment method, prior to biological treatment in production of biofuels, microwave

irradiation has been used also on its own in treatment of sludge. Several studies have reported delignification as a result of microwave pretreatment, and some have also reported removal of hemicellulose. Results have shown that acid pretreatment was better for the separation and removal of hemicellulose, while alkali pretreatment was better for lignin removal. (Bundhoo, 2018) In a different study by Kuittinen et al. (2016), microwave treatment was successfully used to extract hemicellulose from spruce lignocellulose under acid conditions. As low concentrations as 0.05% of H₂SO₄ was enough to liberate hemicellulose monosaccharides without degrading much of the monosaccharides. (Kuittinen, et al., 2016)

Furthermore, liquefaction of biomass can be done with microwave technology. Compared to conventional liquefaction, this technique is more efficient and the average molecular weight after treatment is lower. (Shao, et al., 2019) Another example is microwave-assisted acidolysis as a separation technique for the isolation of lignin from softwood, without severe chemical modification of the lignin. (Zhou, et al., 2017) In addition, in the production of biodiesel, transesterification through microwave treatment has been proven to give satisfactory results with shorter treatment times. Microwave treatment can also be applied in enzymatic hydrolysis to break down cell walls and lignin, which enhances the availability for the enzymes. (Bundhoo, 2018)

2.4.3 Study of degradation mechanism in microwave assisted pyrolysis

Catalyzed microwave-assisted pyrolysis has been proven a successful method to produce bio-oil from lignocellulosic material. (Morgan Jr., et al., 2017) Microwave treatment has also been evaluated as an alternative to gasification and pyrolysis of biomaterial by Lanigan (2010). The study identified 180°C as the temperature at which the degradation of cellulose starts. At this temperature, the amorphous regions of cellulose soften and the structures begin to rearrange, which increases the efficiency of the microwave heating and result in acid-catalyzed decomposition. In the production of chars from cellulose, the temperature could be decreased by 100°C compared to conventional pyrolysis. For hemicellulose, the temperature could be decreased by 150°C. (Lanigan, 2010, p. 61) The degradation mechanism of hemicellulose could not be identified, although it could be assumed to be similar to that of cellulose; the microwave energy cause an increase in molecular freedom of movement and the presence of hydroxyl groups give rise to dipolar polarization. (Lanigan, 2010, pp. 63-64)

Fourier Transform Infrared Spectroscopy (FTIR) analysis of hemicellulose showed that the structural changes were similar for both treatment methods, but with microwave treatment they occur at lower temperatures. The FTIR analysis indicates a break down or rearrangement of ring structures at 260°C. From the FTIR analysis it can also be concluded that, with increasing temperature, the number of hydroxyl groups decrease on behalf of carbon-hydrogen bonds, indicating dehydration and rearrangement of molecules resulting in alkyl-carbonyl structures such as ketones and aldehydes. (Lanigan, 2010, p. 61) Lanigan suggests that the degradation mechanism for microwave treatment is a combination of dehydration, decarboxylation, dehydrogenation or oxidation. This would be similar to pyrolysis treatment, but the reaction pathway is suggested to be different based on an elemental analysis that was performed. (Lanigan, 2010, p. 62)

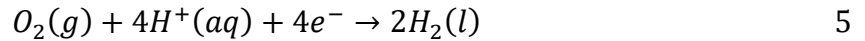
Modulated Differential Scanning Calorimetry (MDSC) was used to identify thermal transitions in xylan. A single peak was identified at 168°C, indicating a melt within the xylan. Lanigan (2010) conclude that the microwave effect should not be advantageous below this temperature. Also, pilot trials were performed with positive results indicating that the technology of microwave treatment of biomaterial is scalable. (Lanigan, 2010, p. 38)

2.5 Reactor material

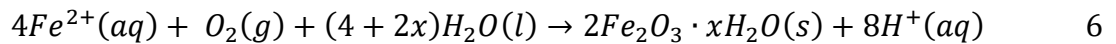
Steel is the standard reactor material in the heat treatment today. Steel is sensitive to corrosion; the formation of rust on iron. Other metals also corrode according to the same principle. During corrosion, a region of the metal's surface serves as the anode, where oxidation occurs. For iron (Fe) the mechanism is as follows:



On another region of the same material, oxygen is reduced by the two electrons released from the iron:



As indicated by the hydrogen ions, the reaction takes place in an acidic environment. The Fe^{2+} are then further oxidized to rust:



The amount of water can vary, which is why x is the number of water molecules. The electrical circuit is completed by the migration of electrons and ions. (Chang, 2008) Molybdenum (Mo) is commonly added to steel alloys to decrease the formation of rust. (Damstahl, n.d.) During the corrosion of steel, molybdenum enrich the inner rust layer and form insoluble molybdate compounds. (Haoa, et al., 2012) However, it has been confirmed that some molybdenum leaches into the black liquor retentate during the heat treatment in the SunCarbon process. Several types of species can be formed, for example $[MoO_4]^{2-}$ and/or $MoOS_3^{2-}$ and MoS_4^{2-} . Many different types of Mo(IV) ions with oxygen or sulfur exist, depending on the pH. Most of these ions are negatively charged and cannot be removed during the acid-washing step of the SunCarbon process. A further obstacle could be the size of these poly-ions as they can get "trapped" in the lignin matrix during the acid treatment. Furthermore, if Mo(IV)-sulfur ions are formed, these can form donor-acceptor bonds with parts of the lignin that contain sulfur. (IMO, n.d.)

The idea behind this study is to use Teflon coating in the reactor vessel to avoid corrosion and leaching of molybdenum. Teflon, or tetrafluoroethylene, is a homopolymer consisting of chains of CF_2 . (Chang, 2008) The C-F bonds are strong, making the material non-reactive and thus suitable for coating of containers with reacting and corrosive content. It is also hydrophobic due to the high electronegativity of fluorine. Its hydrophobicity and heat resistance explain why it is commonly used as a coating on pans and other cookware to create a non-stick surface. Pans coated with Teflon can withstand temperatures up to 260°C at atmospheric pressure. (Teflon brand, n.d.) The crystalline melting point of Teflon is 327°C. (Brydson, 1995)

3 Material and method

Black liquor retentate (BLR) from a pulp mill in Sweden, consisting of a mix of hardwood and softwood, was used as raw material for the experiments. The content of soluble lignin in the BLR was measured with UV absorption. The concentration of soluble lignin was used to determine the concentration of catalyst used in one of the tests.

3.1 Microwave treatment (MWT)

The BLR was treated in a TFM Ethos Plus laboratory microwave (Figure 5). TFM stands for Modified Poly-Tetra-Fluoro-Ethylene and has small amounts of perfluoro(propyl vinyl ether). Samples of 200 mL were put in microwave TFM Teflon vessels, which were properly sealed according to instructions of the Ethos Plus. Each vessel was put in a HTC protection shield and covered with a lid with a HTC safety spring before placing it in a holder (see Figure 6). The holder was tightened to a torque of 20 Nm with a torque wrench. Three holders with filled vessels were used in each trial. A temperature sensor was fit in one of the vessels.

The desired temperature was reached after at most 15 minutes of heating. Treatment temperatures of 100, 150, 180 and 200°C were tested. The samples were treated at this temperature for a determined treatment time (between 5 and 60 minutes). In one test run, a catalyst was added. The amount of catalyst was 3%_{weight} of the lignin content of the BLR. After treatment, the microwave beakers were put in a water bath to cool down before transferring the BLR to storage containers, to reduce the amount of hydrogen sulfide gas released. Cooling down took approximately 30 minutes. The samples were stored in a refrigerator.

The maximum working temperature of TFM Teflon, which is the material of the microwave vessels, is 260°C for extended use and 300°C for short times. The melting range is 320-340°C. (Milestone, 2000)



Figure 5. Ethos Plus Microwave and water bath.



Figure 6. TFM microwave vessel with lid and safety spring in the HTC protection shield. To the right, the vessel is placed in the holder.

3.2 Autoclave Heat Treatment (AHT)

Autoclave heat treatment (AHT) experiments were performed, according to the standard procedure of SunCarbon, in a PARR autoclave (see Figure 7) equipped with a stirrer and a heating jacket. The 500 mL reactor vessel was filled with 250 mL BLR for each experiment. The gas vent and the safety valve were connected to an expansion vessel of 200 L. To create an environment of inert gas, the system was purged with 6 bar nitrogen gas 3 times before starting the experiment. The autoclave was heated to the desired temperature with a heating jacket. The temperature was varied between 150, 180 and 200°C. Reaching the desired target temperature took between 25 and 35 minutes. Heating at the target temperature was then carried out for 15 minutes. Continuous stirring of 400 rpm was used. A PARR PID controller was used to control the temperature, and circulation of water was used for cooling of the stirrer and the pressure

transmitter. After turning of the heating, the heating jacket was removed, and a fan was used for cooling to at least 60°C. Cooling down took approximately 2 hours. The system was then purged again to clean the air from hydrogen sulfide and other toxic gases before opening the vessel. The samples were stored in a refrigerator.

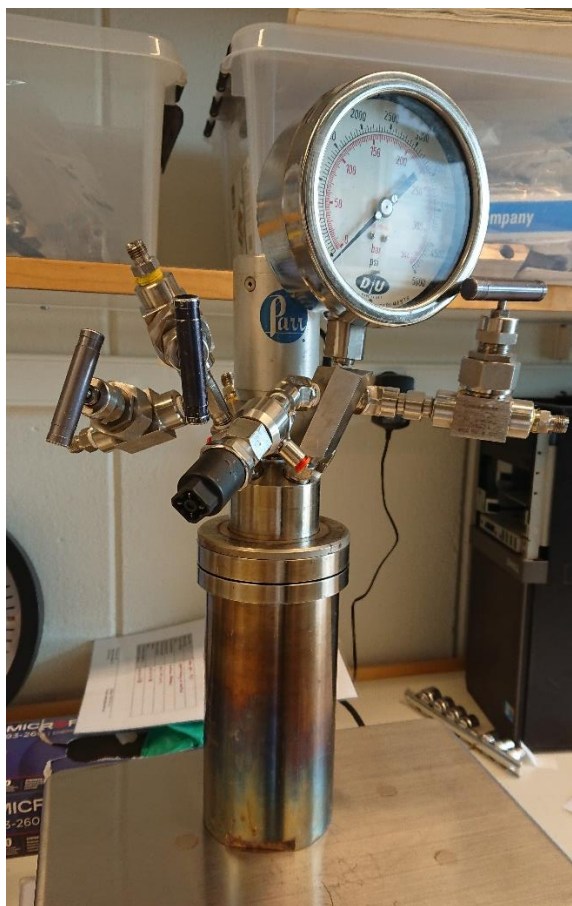


Figure 7. The PARR autoclave before monitoring and attaching tubes and connections.

3.3 Size Exclusion Chromatography (SEC)

Size Exclusion Chromatography (SEC) is a method to analyze the molecular weight distribution by separating molecules in solution based by their size. It is used primarily for large molecules such as polymers. The solution is passed through a column packed with a permeable solid. The retention time in the column is longer the smaller the molecule. The small molecules travel a longer distance since they enter the pores of the permeable solid, while the larger molecules that cannot penetrate the pores pass quicker. After the adsorption column, UV spectroscopy is used to determine the molar mass distribution, measuring at 280nm. The adsorption is plotted versus retention time. The retention time is later translated to molecular weight (Mw) through calibration with a similar compound of known molecular weight. For analysis of lignin, polystyrene sulfate (PSS) is used as standard because it has a molecular structure relatively similar to lignin. For analysis of sugar polymers or oligomers, RI detection is used, and polyethylene glycol (PEG) is used for calibration.

Samples were prepared by diluting 200 times with water. Normally, 0.1 M NaOH solution is used, but since the pH of the samples was already so high, the assumption was made that adding more NaOH was not necessary.

Two columns were used: GE Healthcare, Superdex 200 Increase 300/10 GL, and GE Healthcare, Superdex 30 Increase 300/10 GL. For detection, a refractive index (RI) detector and a UV detector measuring at 280nm were used. The mobile liquid phase used was 0.1 M NaOH, the flow was 0.5 mL/min and the injection volume was 20 μ L. The column temperature was -1°C.

3.4 UV-Visible spectroscopy

UV-Visible spectroscopy measures the absorption of electromagnetic irradiation in the ultraviolet and visible spectra, which covers wavelengths from 190 to 800 nm. The energy absorbance corresponds to the energy difference between the excited and the ground state of an electron. Aromatic compounds absorb at 168-330 nm. The absorbance varies in the interval but is rather stable around 280 nm for lignin, which is why absorbance at this wavelength is usually used as the reference point. (Lagesson, et al., 2000)

The absorption sensitivity varies between compounds, meaning that quantification by measuring UV absorption is uncertain. However, when the composition of samples is rather consistent, the method becomes more reliable. In the pulp and paper industry, the molar absorptivity constant ϵ has been empirically derived for different types of wood. The absorbance extinction factor of hardwood is 21.1 ($\text{g}^{-1} \text{cm}^{-1}$) and that of softwood is 24.6 ($\text{g}^{-1} \text{cm}^{-1}$). Accounting for the respective mass percentages of hardwood/softwood used at a pulp mill, the weighted extinction factor is 23.6 ($\text{g}^{-1} \text{cm}^{-1}$). (Sundin, 2017) The concentration of soluble lignin in the solution (C) can then be estimated from the absorptivity $A_{280\text{nm}}$ with Beer-Lamberts law (equation 2):

$$A_{280\text{nm}} = \epsilon \cdot b \cdot C \quad (2)$$

The optical path length b of the spectrophotometer is 1 cm. A ThermoFisher Scientific GENESYS 10S UV-Vis spectrophotometer was used to perform the measurements.

3.5 Acid hydrolysis for the degradation of hemicellulose to monomeric sugars

Acid hydrolysis was performed to degrade hemicellulose to sugar monomers prior to quantification of sugar content with High Performance Liquid Chromatography (HPLC) or Ultra Performance Liquid Chromatography (UPLC) refractive index detection, according to the Laboratory Analytical Procedure (LAP) of the National Renewable Energy Laboratory of the U.S Department of Energy (NREL) (2006). The LAP describes the preparation of liquid fraction process samples, different from the BLR. A quick reference guide for BLR analysis from Sun-Carbon was thus used for preparation of samples for acid hydrolysis. The guide suggested to mix 20 mL BLR solution with 1.5 mL 72% sulfuric acid (H_2SO_4). However, since the glass tubes used were suitable for bigger volumes, the volume was doubled. When adding the acid, lignin precipitates and the BLR solution turns in to a thick mass. Since it was difficult to handle and to measure pH, it was tested to dilute the BLR prior to acidification. After the first set of samples had been analyzed, it was decided to also increase the acidity.

To summarize, the following two methods of sample preparation were tested.

- (1) 40 mL samples of heat treated BLR were mixed with 3 mL 72% sulphuric acid (H_2SO_4), to a pH of approximately 3.
- (2) The BLR was diluted 4 times with water to 40 mL before acidifying to approximately pH 0.5 with 3mL sulphuric acid.

The acidified samples were treated in an autoclave at 120°C for one hour. After treatment, two phases had been formed, one solid and one liquid phase. When the samples had cooled down after treatment, samples that were going to be analyzed in the HPLC were neutralized with magnesium carbonate (MgCO_3). This is required due to the sensitivity to acidity of the HPLC instrument. Neutralization was not required prior to analysis with UPLC. The liquid was centrifuged and then passed through a 0.2 μm filter into an autosampler vial. The vials were stored in a freezer.

3.6 High Performance Liquid Chromatography (HPLC) for the quantification of sugars

HPLC is a method to separate components of a mixture and identify and quantify these. A liquid solvent act as the mobile phase, transporting the sample mixture through a column of a solid absorbent material. The compounds are separated due to variances in how strongly these interact with the absorbent. It is commonly used to measure the concentration of monomeric sugars by refractive index detection (RI). The method described in the LAP of NREL was used (Sluiter, et al., 2006).

A series of standard solutions with different concentrations were used for calibration. For quantification of sugar, samples are pumped through a column that contains small polymer granulates of polystyrene coated with ionic lead (Pb^{2+}). Ionic bonds are formed with the OH groups of sugar molecules. Thus, how tight a molecule is bonded depends on its structure, allowing to distinguish between different sugars. The analysis is presented as a plot over the absorbance through time. The sugars that have the least interactions with the ionic lead show up first. Each sugar is shown as a peak, which size corresponds to its abundance.

Three HPLC instruments were used, with the following specifications and settings:

- (1) A Waters HPLC with a Bio-rad, Aminex HPX-87P 9 μm column, with the measures 7.8 x 300 mm, and an RI detector. HPLC grade water was used as the mobile liquid phase, the flow was 0.6 mL/min and the injection volume 20 μL . The column temperature was 80°C.
- (2) A Shimadzu HPLC with an Aminex HPX-87H column, an RI detector and 5mM H_2SO_4 as mobile liquid phase. The flow was 0.5 mL/min, the injection volume 20 μL and the column temperature 50°C.
- (3) A Shimadzu Prominence UFLC (Ultra Fast Liquid Chromatography), which is a kind of HPLC, with a Concise CHO782 column and an RI detector. Deionized water was

used as mobile liquid phase, the flow was 0.5 mL/min and the injection volume 20 μ L. The column temperature was 80°C.

3.6.1 Ultra Performance Liquid Chromatography (UPLC) for the quantification of sugars

UPLC is a version of HPLC with a smaller, finer column. The column contains particles of silica-carbon chain complexes with hydrophilic groups. Water dissolving compounds are retained in the column, while hydrophobic compounds pass through. Due to the smaller particles, the UPLC needs to operate at much higher pressure than the HPLC. The analysis is also faster. The polar aprotic solvent acetonitrile is used to dissolve and carry the hydrophobic compounds. The following column and settings were used:

Two columns in series were used of the type Acquity UPLC BEH Amide, of the measures 130Å, 1.7 μ m, 2.1 mm x 100 mm. An Acquity UPLC Evaporative Light Scattering (ELS) Detector was used for detection. The mobile liquid phase used was 80% acetone and 20% H₂O + NH₄OAc. A flow of 0.1 mL/min was used and the injection volume was 1 μ L. The column temperature was 60°C.

3.7 Direct Infusion Mass Spectrometry (DI-MS)

Direct Infusion Mass Spectrometry (DI-MS) is a form of mass spectrometry in which the sample is injected directly into the spectrophotometer from a syringe with a syringe pump. Direct infusion is compatible with electrospray ionization. The molecules are fragmented and then the mass of the smaller fragments is measured with liquid chromatography, to aid in determining the molecular structure and identification of the molecule of interest. (JBL Science, n.d.) .

The sample was analysed using HPLC-MS (1260 Infinity II HPLC and 6545 QTOF, Agilent, Santa Clara, CA, USA). The QTOF was operated in MS mode using positive electrospray ionization under the following conditions: drying gas temperature 200 °C, drying gas flow 5 L min⁻¹, sheath gas temperature 225 °C, sheath gas flow 8 L min⁻¹, nebulizer pressure 25 psig, capillary voltage 2500 V, nozzle voltage 0 V, fragmentor voltage 175 V, skimmer voltage 65 V, octopole RF voltage 750 Vpp. Data was collected in the range 50-1600 m z⁻¹ at a rate of 10 spectra s⁻¹. To stabilize the ionisation the LC system provided a flow of 0.1 mL min⁻¹ of 0.1% formic acid which was combined (using a T-cross) with the sample flow (5 μ L min⁻¹) provided by a syringe pump.

3.8 Separation of Lignin by Acidulation with CO₂

Separation of lignin by acidulation was performed in the PARR autoclave according to the SunCarbon standard procedure, to test the lignin yield. Two trials were made, one with MWT material, and one with material from standard autoclave heat treatment, both treated at 200°C for 15 minutes, to compare the yield of two methods.

A pressure of 6 bar was applied with nitrogen gas, to keep water in its liquid state during heating. Heating was set to 100°C and a stirring of 400 rpm was used. In the case of heating liquid that had been treated in the microwave, the starting temperature was approximately room temperature. Reaching the target temperature then took 12 minutes. When the material had been

treated with AHT, acidulation with CO₂ was performed subsequently, thus starting at a temperature higher than the target temperature. Cooling down from 200°C to 100°C took approximately 30 minutes. When the target temperature had been reached, stirring was turned off and CO₂ was added to create an over-pressure. Stirring was started again at 300 rpm. The lower speed was set to allow a heavier liquid phase with lignin to settle, while still avoiding scorching at the reactor walls. A stable pressure had to be reached, which was defined as keeping the pressure constant within one decimal for 15 minutes. This took approximately 3 hours. The stirring was then turned off but the heating was kept on for 30 minutes. Subsequently, the heating jacket was removed and a fan was used for cooling to at least 60°C, which took approximately 30 minutes. The gas was purged with nitrogen gas to remove hydrogen sulfide gas before opening the reactor vessel.

The separation process results in one light phase and one heavy phase with higher concentration of lignin. The heavy phase turns solid during cooling. The liquid phase was collected and stored in refrigerator. The solid phase, which was stuck in the bottom of the reactor vessel, was removed with scraping tools and dried with paper before weighing.

4 Results and discussion

4.1 Method development of the microwave treatment

While performing the MWT runs, some problems were addressed. Weight measurements of samples before and after the MWT indicated leakage of the vessels at 200°C. It is probable that the high pressure caused leakage of gases; mainly water vapor and hydrogen sulfide (H₂S). The material in the vessel where the temperature sensor was situated, had the greatest mass reduction (up to 56% for 200°C MWT for 30+20 minutes). The BLR turned solid when treating at 200°C for 20 or 30 minutes, but after 15 min treatment at 200°C the BLR was still liquid. However, in a different trial the BLR in the vessel with the temperature sensor became solid after only 10 minutes of treatment. The clear variances between runs and between vessels in the same run indicates varying leakage, perhaps due to varying properties of the HTC safety springs or the TFM lids of the vessels, depending on how worn out they were.

Sometimes, the solid material in the vessel with the temperature sensor became porous, indicating that gas had been dissolved in the liquid during the solidification process. It is possible that the leakage was greater due to the temperature sensor. The amount of leakage did not show any correlation with the length of treatment time. When the BLR changed phase to solid or highly viscous at high temperature MWT, it is probable that the temperature sensor was unable to detect the temperature properly, which may have led to that the microwave continued to increase the effect, building up higher temperature than intended.

The material turned into highly viscous or solid material, although it was treated at the same temperature and time as with the AHT. The question arose why the material reacts so differently in the microwave, and if the change in viscosity and phase was caused solely by evaporation or if some other chemical reaction took place. One aspect that could be of importance is that the temperature profile in the microwave vessels is different from that in the autoclave, especially due to the lack of mixing in the microwave. The solid material was soluble in NaOH solution, which proves that it is not coke. The material was investigated with SEC by dissolving it in water (result presented in section 4.4, Figure 18).

When the material turned solid, it was very difficult to clean the vessels and there was a risk of damaging the temperature sensor. Furthermore, the temperature sensor cannot detect the temperature in solid, meaning that the feedback control of the temperature was not working. Conclusively, temperatures and times above the threshold where the material turned solid could not be investigated.

To tackle the issue of leakage, the following methods were tested:

- A different BLR starting material was tested. In standard heat treatment, it has previously been seen that the material changes viscosity. BLR of higher concentration of water and NaOH has not become as viscous. The concentration of NaOH solution in BLR depends on how much has been removed in the membrane filtration. The BLR initially used in this study had been membrane filtered to a reduction of 80%_{volume} from the initial black liquor in the process. An addition of NaOH solution was added to imitate a BLR that has only been reduced 70%_{volume}. However, this attempt was not

successful. The percentage of leakage was higher for the diluted samples (54-70%_{weight} instead of 36-56%_{weight}). The material was solidified in the vessel with the temperature sensor and one other vessel, while the material in the third vessel became highly viscous. Conclusively, this did not solve the problem.

- A smaller volume of sample was tested. Samples of 100 mL instead of 200 mL were used in the same vessels to test if a bigger head space would solve the problem. However, the weight percentage of leakage was similar.
- Another microwave vessel with a bigger volume was tested, to confirm if the problem could be solved by using other vessels. The leakage from this vessel was even greater than from the smaller ones previously used.
- The alternative to add an anti-coke agent, such as phenol or boric acid was considered. However, it was determined that this idea was not safe to try due to the risk of leakage of hazardous chemicals.
- Water was added after MWT. The vessels were weighed before and after MWT, and the decrease in weight was compensated for by adding water. The assumption was made that the loss of other gases would not affect further analyses. However, this was not a possible solution to the samples that were solidified. This could affect the analysis of sugar, where the concentration is measured. The SEC analysis should however not be affected.
- An investigation was carried out to find the maximum temperature that could be used without causing leakage. Water was used in the vessels to avoid damage on the MW equipment and to save BLR. The maximum temperature was determined to be 180°C, for 15 minutes of MWT. Subsequently, this temperature was used to investigate varying lengths of treatment time, as well as for the trial with catalyst. However, some leakage still occurred from the vessel with the temperature sensor when treating for longer times. As long as the BLR remained liquid, water was added to compensate for the loss of vapor, assuming that water accounted for the major part of the losses. However, some other gases were probably also lost, such as CO, CO₂ and H₂S. This may affect the analysis of concentration further on, but this effect was assumed to be small.

4.2 pH measurements of the BLR

The starting material had a pH of approximately 13.4. The pH decreases during heat treatment because hydroxyl ions (OH⁻) are consumed in the cleavage of non-phenolic β-O-4 bonds in lignin. Subsequently, carboxylic acids are protonated, resulting in decreased polarity and lower solubility of lignin.

It can be seen in Figure 8 that pH decreases with higher treatment temperature, as expected. In accordance with the results of the SEC analysis (see section 4.4 and appendix sections 7.1-7.2), no significant effect can be seen of 100°C treatment. For 150°C, pH drops with approximately 0.5 units, for 180°C the decrease is approximately 1.4 pH units, and for 200°C it drops about 1.9 pH units. No significant difference can be seen between heat treatment in the PARR autoclave and the MWT. The pH drops more in the test sample where a catalyst was added compared

to treatment at the same temperature without catalyst, indicating an effect on depolymerization of the catalyst.

For those tests that have at least three replicates, an average value is presented with an error bar for the standard deviation. One microwave treatment run generates three samples (from the three vessels), while the autoclave only generates one. The catalyst was only added to one sample. Untreated BLR in different storage containers were also measured and presented the same way. The difference between equal samples is believed to be caused by uncertainties of the pH measurements for such strong bases, as well as non-homogeneous properties of the retentate due to insufficient mixing.

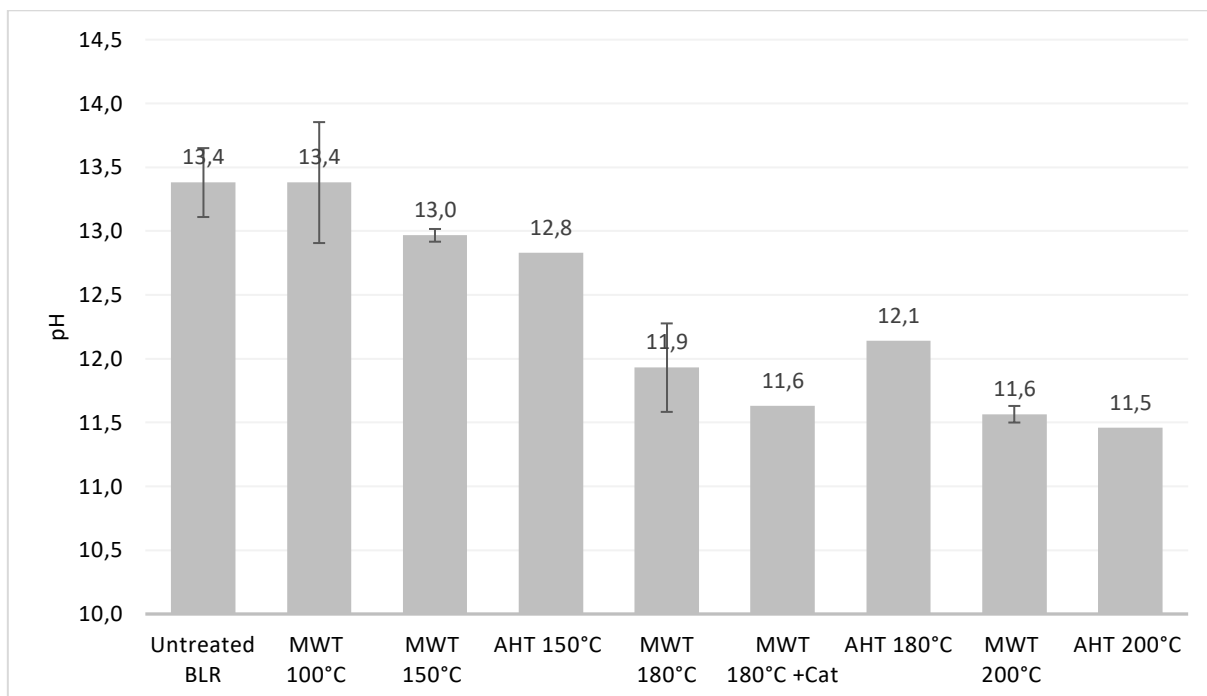


Figure 8. pH of untreated BLR as well as material treated at 100, 150, 180 and 200°C, MWT or AHT. Error bars are based on a mean of at least 3 measurements.

4.3 Method development and calibration of SEC

Initially, a dilution test was made to establish a suitable concentration for analysis. Samples diluted 100, 200 and 500 times were tested. The resulting conclusion was that 200 times was a suitable dilution. A stability test was made to see if samples could be prepared and analyzed in batch. Two equal samples were prepared; one was analyzed immediately and the other one after 24 hours. A slight shift in the molecular weight distribution curve could be observed, indicating that the later sample had more large molecules, which suggest that some repolymerization had occurred. Conclusively, the rest of the samples were prepared one at a time and analyzed immediately.

Calibration for the analysis of lignin was performed by running a series of polystyrene sulfate (PSS) standards of molecular mass ranging from 1.000 to 67.000 Da, measuring with UV280 detection. Since the absorbance at 280nm depends on the number of carbon double bonds, other compounds that are not lignin may also affect the results. However, the content of other

disturbing components is expected to be low and does not differ much between the samples. Conclusively, the UV absorbance does not provide a precise measure of the lignin concentration, but it is a good estimate and enables the comparison between samples.

For the analysis of sugar, polyethylene glycol (PEG) standards were used, measured with RI detection. The retention time of the standard samples were then used to estimate the molecular mass as a function of the retention time for test samples of large molecules such as lignin. The calibration curves can be seen in Figure 9 and Figure 10.

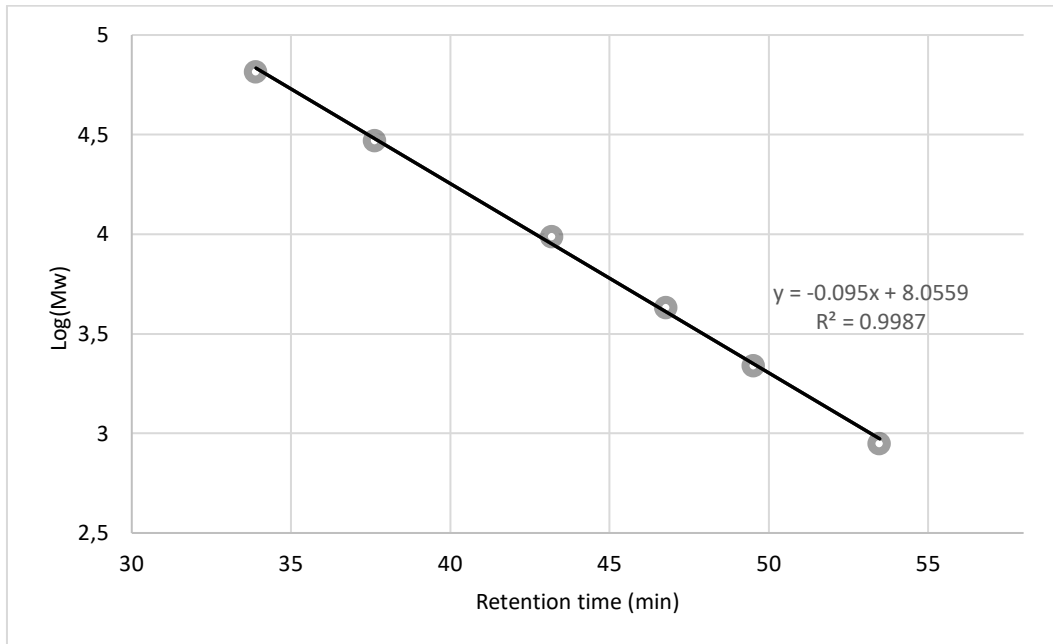


Figure 9. Calibration curve for SEC with UV280 detection, based on PSS. This was used for the analysis of lignin.

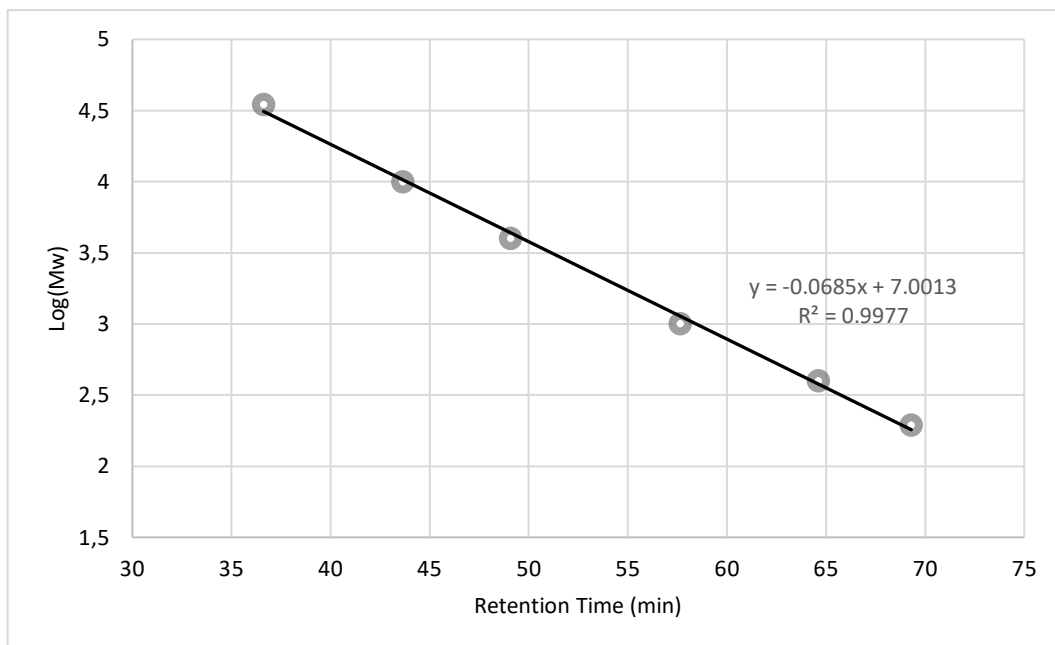


Figure 10. Calibration curve for SEC RI detection, based on PEG. This was used for the analysis of sugar oligomers.

4.4 Molecular weight distribution of lignin measured with SEC

The results of the SEC analysis are presented in the graphs below in figures Figure 11 to Figure 20. The peaks of maximum absorption for all tests have been set to 1 for normalization of the curves and to facilitate the comparison between them. Normalization based on the integral area is not suitable because the absorbance of different compounds differs. This causes variances in the integral area although the samples contain the same amount of material, as they all originate from the same amount of starting material. Conclusively, the height of the absorbance curve should not be correlated to the abundance of a molecular weight (Mw), but rather its' sole presence. A comparison of the molecular weights where the absorption peak appears can be seen in Figure 11. This demonstrates the trend of decreased molecular weight with increased heat treatment.

Two outliers were identified with the SEC analysis: 180°C 15+30 min MWT and 100°C 10+30 minutes. Repeated analysis with SEC yield similar results. Thus, the unexpected result must be caused by a mistake in the microwave treatment. These two microwave runs were performed just before the thermocouple was confirmed to be broken and was exchanged for a new one. Conclusively, this has been accepted as an explanation for the outliers and these have consequently been removed from the figures presented here.

An estimation of the highest molecular weight present has been made (see Figure 12). These values are rough approximations, as some of the samples did not reach an actual max. However, the estimation has been made based on when the absorption is close to zero. The maximum molecular weight observed differs more between the treatment temperatures than the molecular weight for maximum absorption. This indicates that the degradation is more efficient for the largest lignin molecules, above 20 kDa. Moreover, there is no indication that either AHT or MWT is degrades more than the other.

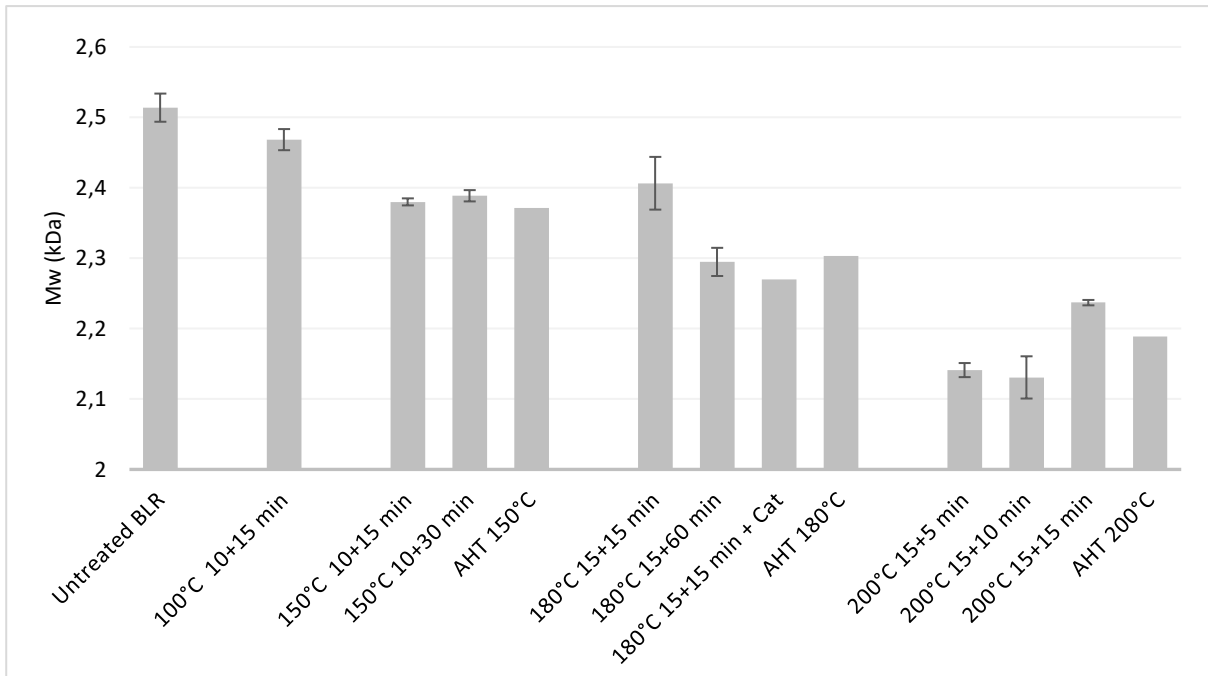


Figure 11. The molecular weight for which maximum absorption occurs. The treatment time is presented as “heating time to reach treatment temperature + treatment time at the set temperature”. The values of MWT tests and untreated BLR are a mean of three samples.

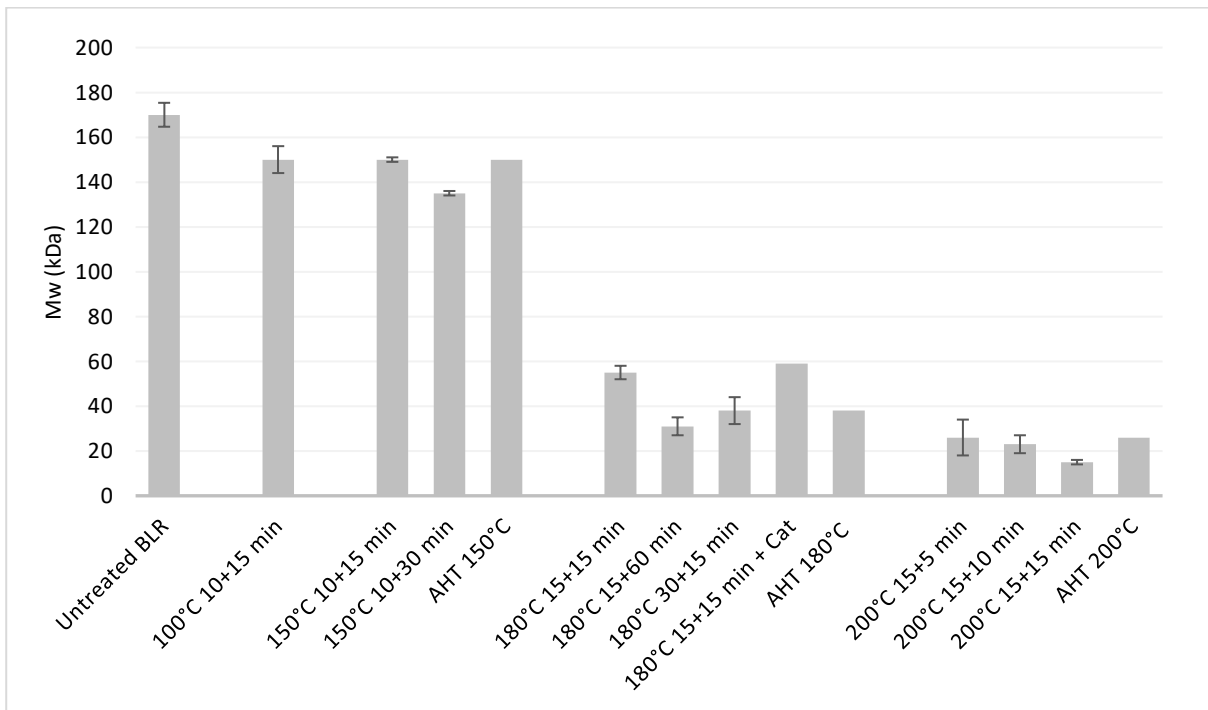


Figure 12. The highest molecular weight at which a significant absorption can be observed. The treatment time is presented as “heating time to reach treatment temperature + treatment time at the set temperature”. The values of MWT tests and untreated BLR are a mean of three samples.

SEC analysis was used to check stability between the three microwave vessels (see appendix section 7.1). The results indicate high stability, which supports that it is enough to present the data of one of the vessels. Furthermore, the stability between microwave runs of equal conditions was also evaluated (see appendix section 7.2). Again, the results indicate high stability. Thus, data from only one microwave run is presented in the graphs below.

Initially, MWT at 100°C was investigated. However, as the result indicate no significant degradation, these graphs are only presented in appendix, section 7.1 and 7.2. MWT at 150°C was performed for 15 and 30 minutes, with 10 minutes heating time, as well as with 25 minutes heating time and 15 minutes treatment, to imitate the conditions of the heat treatment in the PARR autoclave. The results, presented in Figure 13, indicate that heating for a longer time only increases degradation very little. Neither of the tests show any significant decrease in molecular mass compared to untreated BLR.

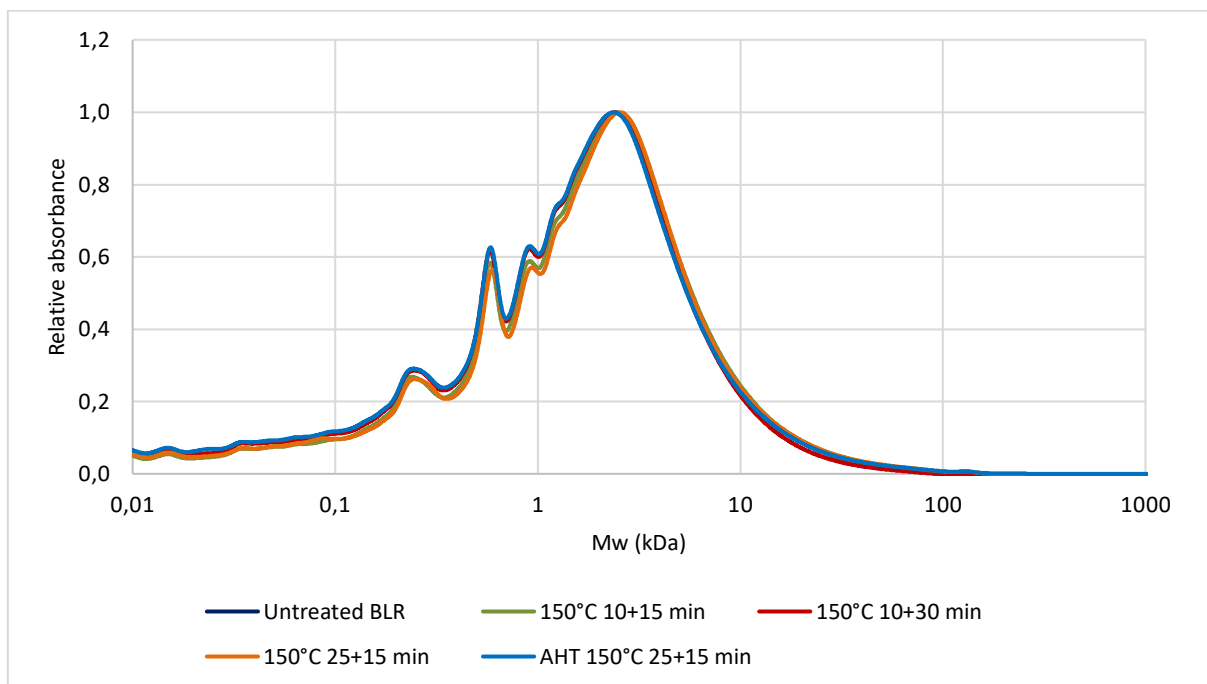


Figure 13. Molecular weight distribution of untreated BLR and material treated at 150°C with varying treatment times.

MWT at 180°C was performed for 15, 30 and 60 minutes, with 15 minutes heating time (see Figure 14), as well as with 25 minutes heating time and 15 minutes treatment, to imitate the conditions of the heat treatment in the PARR autoclave (see Figure 15). The results indicate that heating for a longer time only increases degradation very little. It also shows that, when heating for the same length of time as in the PARR autoclave, degradation with MWT has the same effect on decrease in molecular weight. The highest molecular weight decreases from approximately 170 kDa, in untreated BLR, to around 38 kDa (see Figure 12).

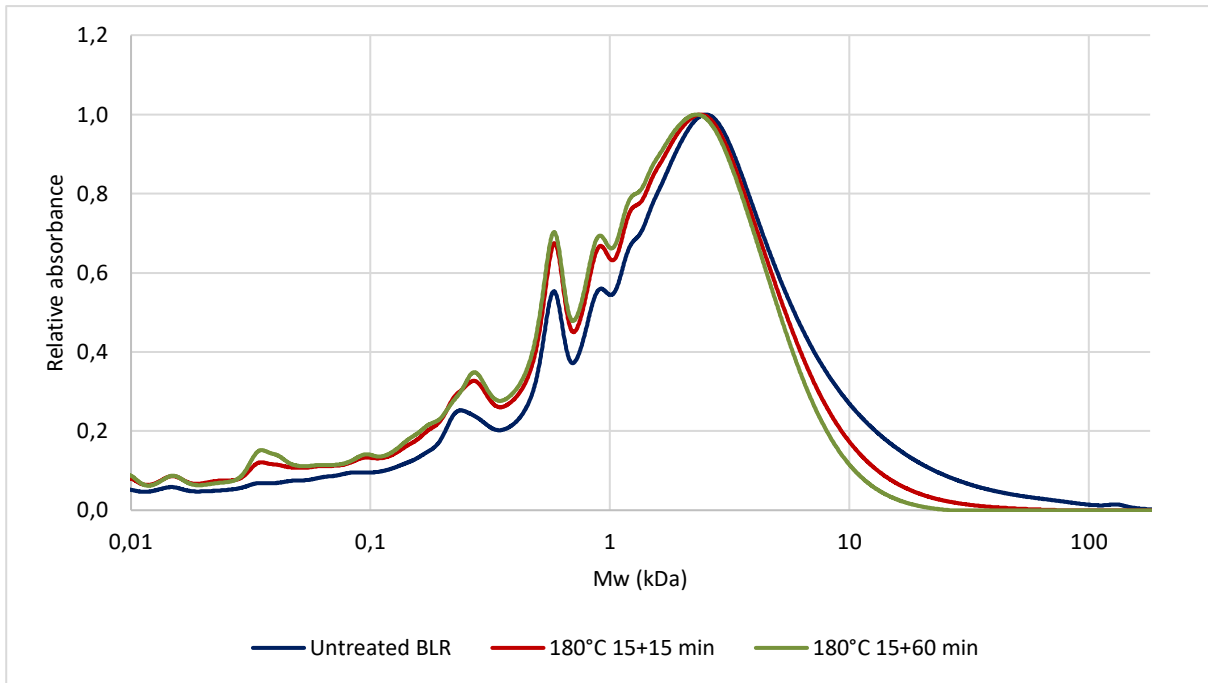


Figure 14. Molecular weight distribution of untreated BLR and material treated at 180°C, comparison between different treatment times.

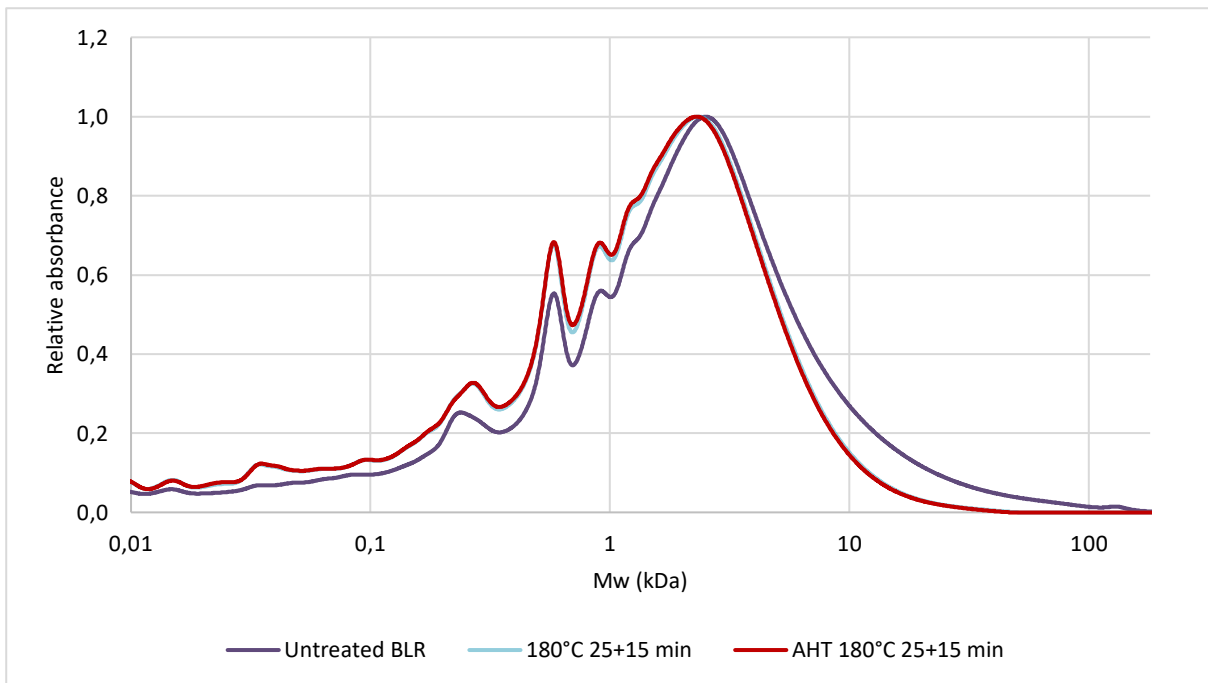


Figure 15. Molecular weight distribution of untreated BLR and material treated at 180°C, comparison between MWT and AHT.

The concentration of soluble lignin in the BLR was determined with UV absorption to be 22%_{weight}, which was used to determine the concentration of molybdenum catalyst as 3%_{weight}

of the lignin content. The use of molybdenum does not show any effect on degradation of lignin (see Figure 16). If the molybdenum would have had a catalytic effect, this could have led to poorer degradation when exchanging the molybdenum-containing steel reactor to another material. These results indicate that such an effect should not be noticeable.

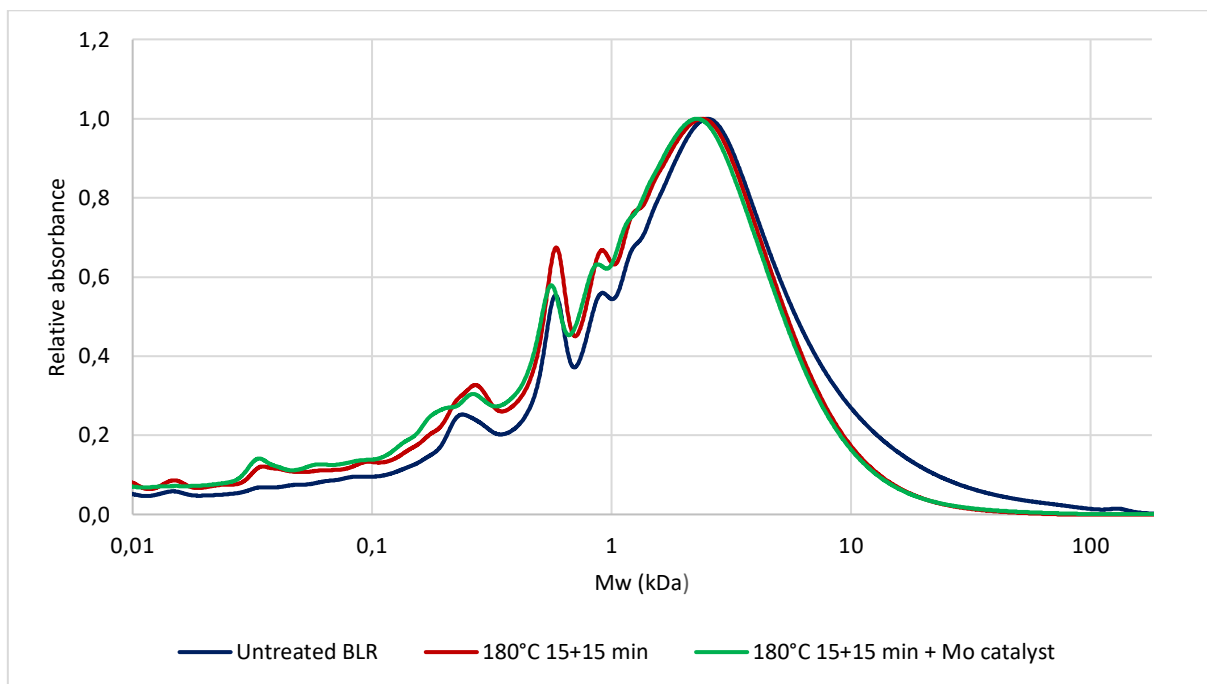


Figure 16. Molecular weight distribution of 180°C MWT with and without molybdenum catalyst. Untreated BLR is also included in the figure for comparison.

MWT at 200°C was performed for 15 minutes, with 15 minutes heating time (see Figure 17). It was not possible to run for longer time, due to leakage from the microwave vessels. Two samples from a longer run can be seen in Figure 18. These samples were solidified during MWT. To analyze with SEC, they were dissolved in water. The results indicate that degradation has stopped when the sample turned solid, as the decrease in molecular weight is smaller.

The results indicate that the effect on molecular weight of MWT is very similar to that of AHT in the PARR autoclave. The highest molecular weight is even slightly lower in the MWT sample, despite the shorter heating time. The decrease in molecular weight compared to untreated BLR is clear; the approximated numbers show a decrease from 170 kDa to 15 kDa for 15+15 minutes MWT (Figure 12).

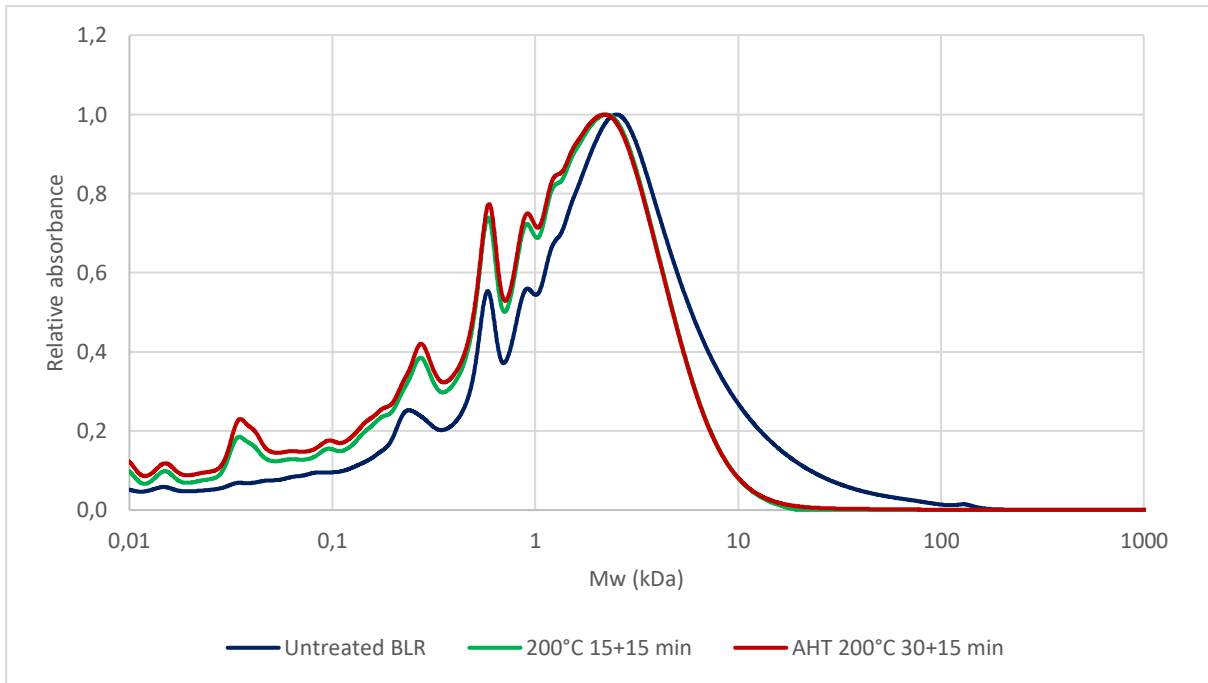


Figure 17. Molecular weight distribution of untreated BLR and material treated at 200°C, comparison of MWT and AHT.

Figure 18 shows the behavior of the solidified samples. A decrease in the highest molecular weight has occurred: from 170 kDa to 44 kDa (see Figure 12). The both samples from different vessels have almost identical molecular weight distribution curves, despite the observed difference in composition. However, the decrease in molecular weight is greater for samples that did not become solid, despite the shorter treatment time. This indicates that degradation is slowed down or stopped when the liquor turns solid.

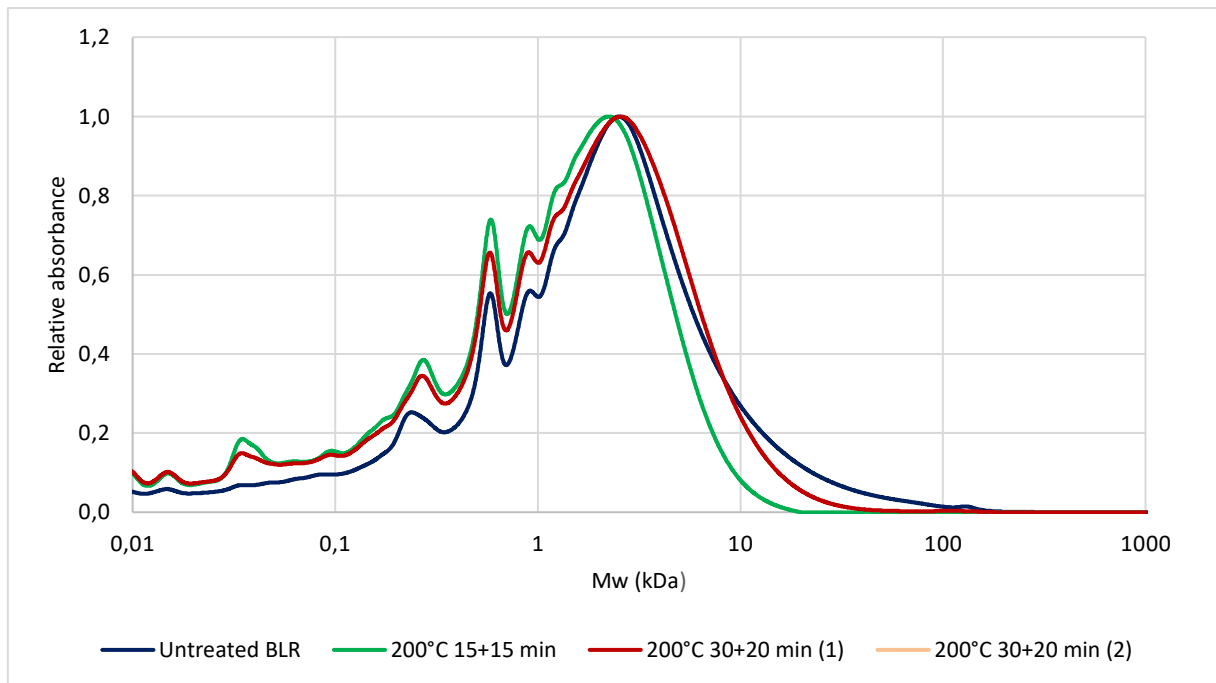


Figure 18. Molecular weight distribution of untreated BLR and material treated at 200°C, comparison of material treated for 15 minutes and those that were treated for longer time and turned solid (samples (1) and (2)). Samples (1) and (2) are overlapping in the graph.

Trials of MWT at 200°C were also performed with shorter treatment times to investigate how this affects degradation. The results presented in Figure 19 indicate that the effect of treatment time is very little. This has been seen in previous studies by Abdelaziz et al. (2017). The material that has only been treated for 5 minutes show the same molecular weight distribution as material treated for 15 minutes.

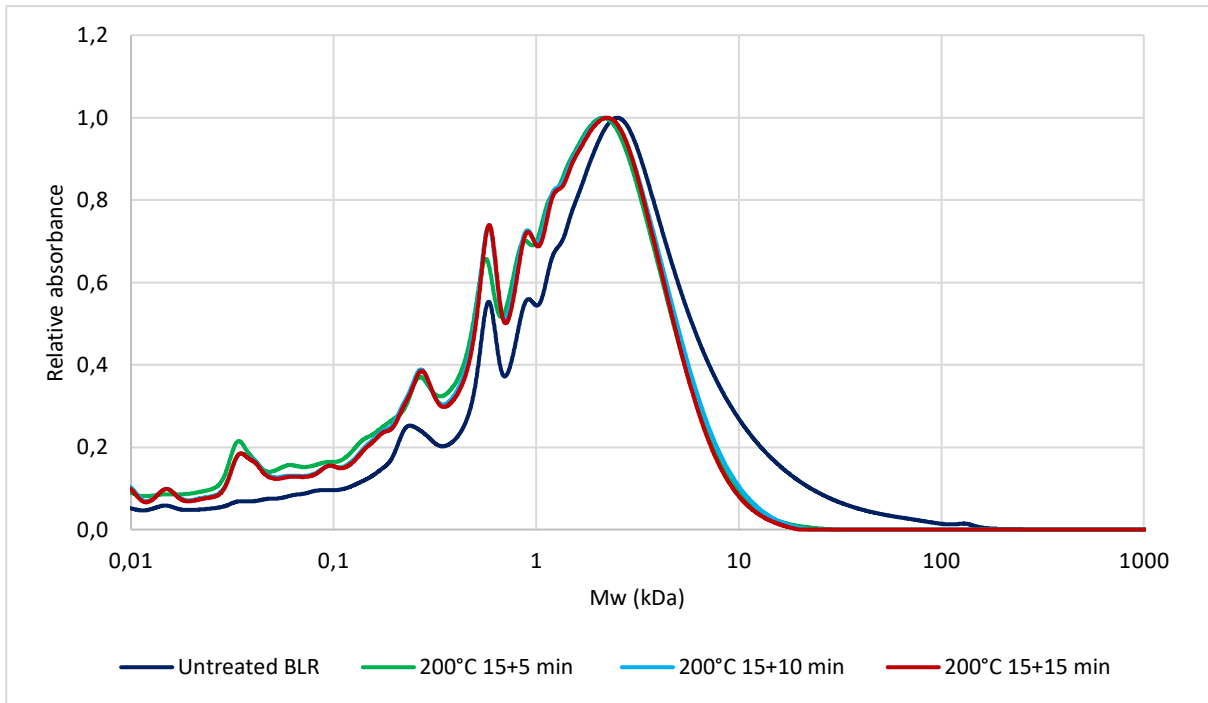


Figure 19. Molecular weight distribution of 200°C MWT with varying treatment times of 5, 10 and 15 minutes. Untreated BLR is also included as reference.

In Figure 20, it can be seen that an increase in temperature from 180°C to 200°C has a bigger effect on degradation than increasing the treatment time from 15 to 60 minutes when treating at 180°C. This has also been seen in previous studies by Abdelaziz et al. (2017).

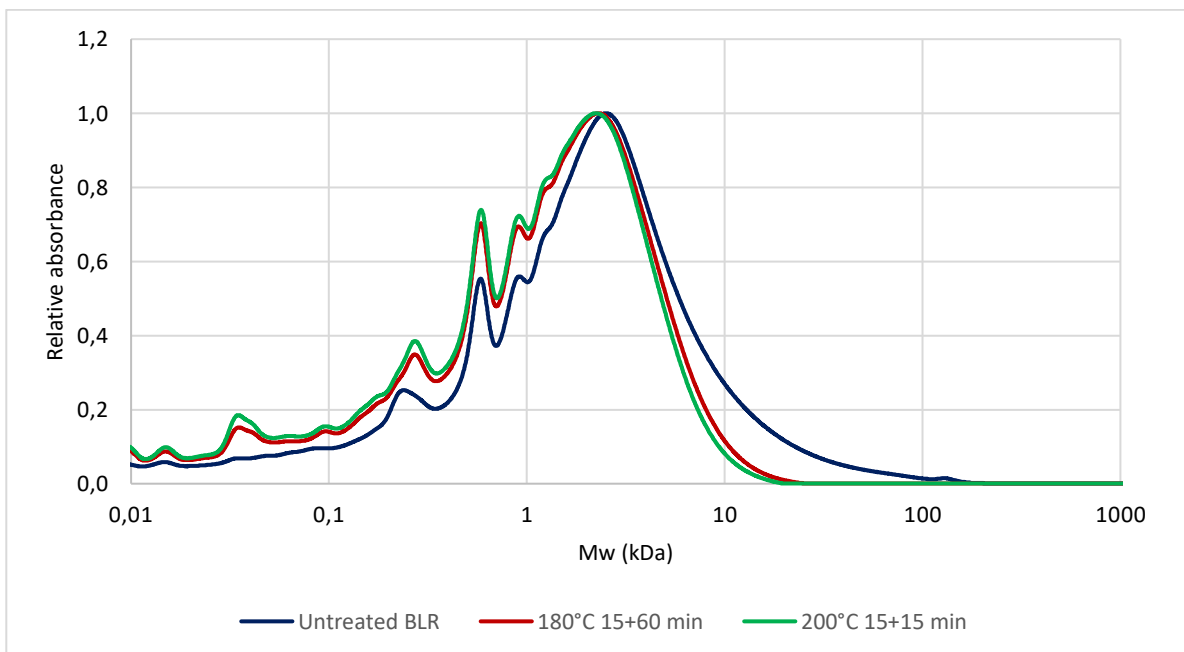


Figure 20. Molecular weight distribution of untreated BLR and material treated at 200°C for 15 minutes, and 180°C for 15 and 60 minutes.

4.5 Separation of Lignin by Acidulation with CO₂

Absorption with UV-Vis spectrometry was used to determine the concentration of soluble lignin in the starting material and in the light phase after the separation process. Since the absorbance at 280nm depends on the number of carbon double bonds, other compounds that are not lignin may also affect the results. However, the content of other disturbing components is expected to be low and does not differ much between the samples. Conclusively, the UV absorbance does not provide a precise measure of the lignin concentration, but it is a good estimate and enables the comparison between samples. Moreover, the absorbance extinction factor which is used in the calculations is a weighted value for a mix of hardwood and softwood, and not a precise value, which also is an uncertainty factor in the estimation of lignin content. The yield of lignin in the heavy phase, presented in Table 1, was calculated according to equations 3-6.

$$\text{Lignin in liquid} = C_{\text{lignin in liquid}} \cdot m_{\text{liquid}} \quad (3)$$

$$\text{Total lignin} = C_{\text{lignin in starting material}} \cdot m_{\text{starting material}} \quad (4)$$

$$\text{Lignin in solid} = \text{Total lignin} - \text{Lignin in liquid} \quad (5)$$

$$\text{Yield} = \frac{\text{Lignin in solid}}{\text{Total lignin}} \quad (6)$$

Table 1. Lignin yield in the solid phase after the acidulation process for the separation of lignin.

Lignin yield from 200°C AHT material	76.9%
Lignin yield from 200°C MWT material	76.4%

The pressure and temperature observations at critical times during the experiment can be found in appendix section 7.3, Table 4. Previous studies have shown that a higher pressure of CO₂ leads to higher yield, due to the decrease in pH, which causes more lignin to precipitate (Sundin, 2017). However, the lignin yield is similar for the both materials, indicating that the properties of material treated in the microwave is very similar to the material heat treated in the autoclave.

4.6 Acid hydrolysis and quantification of sugars with HPLC and UPLC

During acid hydrolysis of BLR, one solid phase is formed, consisting of lignin. Hydrolysis was performed on the heat-treated BLR as well as untreated BLR for comparison.

After hydrolysis at pH 3, HPLC analysis was performed with the Waters HPLC with the Bio-rad, Aminex HPX-87P column on replicates of different microwave runs with equal conditions,

as well as three different vessels from the same run (see appendix section 7.4, Figure 43). Large variances could be seen, indicating instability. Furthermore, the concentrations were lower than the calibration standards and the chromatographic peaks that represent the different sugar species were not well defined. The conclusion was made that an analysis method suited for lower concentrations was required, which is why it was decided to use UPLC.

4.6.1 Analysis with UPLC

Initially, samples were treated with hydrolysis at pH 3. Subsequently, sample preparation for the UPLC analysis included dissolving the samples in 50% acetonitrile. This is when crystals precipitated, which is further described in section 4.7. These samples were not analyzed in the UPLC, due to the risk of solid particles damaging the column. Subsequently, the samples were diluted prior to hydrolysis at pH 0.5.

The first analysis with UPLC also showed large variances between samples of the same MWT run (see appendix section 7.4, Figure 44). The sugar concentrations were lower than the standards used for calibration, which suggests that the result is not reliable. Thus, in the following analyses a more diluted standard sample was used in the calibration, and the test samples were diluted less prior to analysis. The results of UPLC analysis can be seen in appendix section 7.4, Figure 44. All tests yielded concentrations between 16 and 27 g/L, which does not correlate with the expected results. Previous studies by SunCarbon have yielded concentrations as low as 8.4 g/L, from a starting concentration of 16.6 g/L in untreated BLR, and 9.9 g/L from a starting concentration of 34.7 g/L. The sugar content could thus be expected to decrease by 50-70% after heat-treatment. Conclusively, the concentration in the heat-treated material was expected to be lower and differ more from the untreated material.

It appears as if the concentration difference between untreated BLR and heat-treated BLR is very low, and hemicellulose does not seem to have degraded as expected. Perhaps, some of the hemicellulose has only degraded to shorter chains, or to sugar monomers, instead of being fully decomposed to organic acids. This hypothesis is supported by that some of the samples had a higher viscosity after MWT, which can be caused by more sugar.

Another possible explanation is that the material has not been fully hydrolyzed in the acid hydrolysis. The question arises if the pH (approximately pH 1) is adequate and if longer treatment time in the autoclave is required. Conclusively, further investigations were required to find out if the analysis was reliable or not, and if so, why the sugar concentration does not decrease with heat treatment as expected.

4.6.2 Analysis of sugar and organic acids with HPLC

Analysis was performed with a different HPLC instrument, from Shimadzu with an Aminex HPX-87H column, analyzing both the sugar content and the content of organic acids. Samples were compared before and after going through acid hydrolysis, to see if a difference in the concentration of sugars and organic acids could be seen. The difference in sugar concentration can be seen in Figure 21. An increase in the sugar concentration with acid hydrolysis, of approximately 20%, can be observed. This indicates that the hydrolysis has worked in the sense that sugar polymers have been degraded to monomers, as intended. However, the possibility that some unhydrolyzed sugar polymers or oligomers remain cannot be excluded. Furthermore, the concentration difference between untreated and heat-treated material is very small.

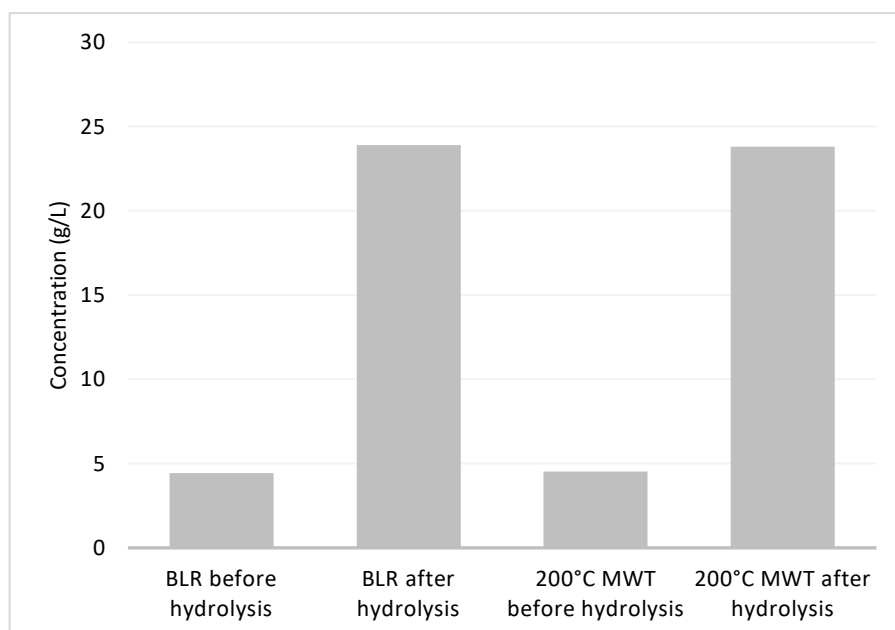


Figure 21. Comparison of sugar concentrations before and after acid hydrolysis, in untreated BLR and 200°C MWT BLR, measured with HPLC. The figures represent the sum of cellobiose, glucose, xylose, galactose, mannose and arabinose.

The results of HPLC analysis with a Concise CHO782 column, of hydrolyzed material, are presented in chromatograms in Figure 22 to Figure 24. It is difficult to define a baseline for the peaks, leading to high uncertainties in quantification. Conclusively, concentration values are very rough estimations and it is more reliable to observe the trends graphically.

The different peaks correspond to different compounds, usually sugars or organic acids. Figure 23 shows a zoom-in on a peak representing the content of the sugar species galactose, xylose and mannose. Figure 24 shows the peak of lactic acid. The concentrations are low compared to the standards, and thus approximations of values are unreliable. However, a trend can be identified from the figures, indicating higher concentrations of sugars (glucose, arabinose, xylose, galactose, mannose) in the untreated BLR compared to the heat-treated material. In addition, the concentrations of organic acids (lactic acid, formic acid, acetic acid, levulinic acid, HMF and furfural) are all higher in the heat-treated material. The trends indicate that the heat treatment causes degradation of sugars, and organic acids are released, for both MWT and AHT. However, the degradation is not of the expected scale, possibly because the temperature in the heat treatment is not high enough. According to literature, hemicellulose degrades mainly in the temperature range 180-340°C (Lv, et al., 2010). As 200°C is in the lower range of this interval, a higher temperature could probably increase degradation. However, the microwave oven used in this study is not suitable for treating BLR at higher temperatures.

Moreover, the chromatograms indicate that the AHT material has degraded more than the MWT material. The greater degradation in the AHT could be explained by the longer treatment time and higher stability, since some leakage (2%_{weight}) occurred in the microwave oven.

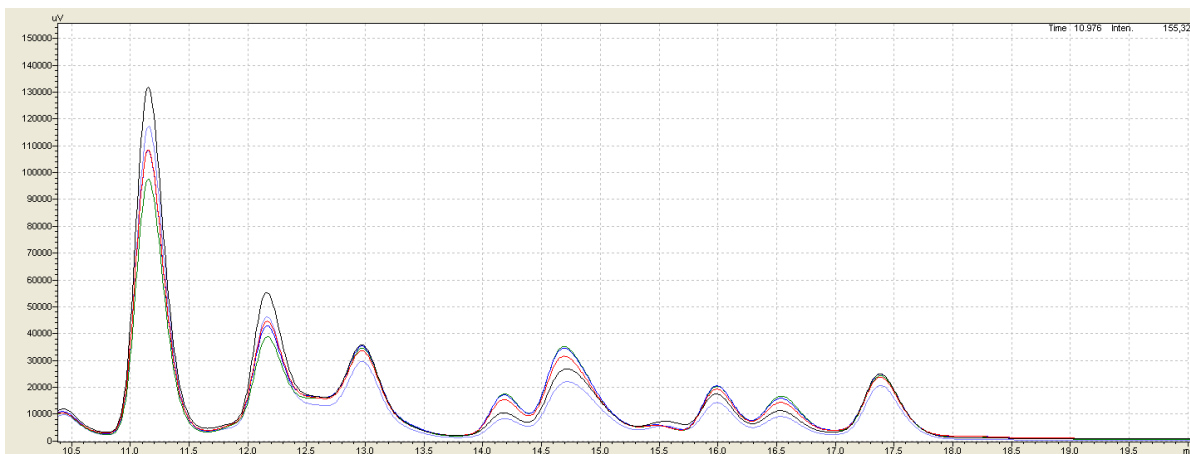


Figure 22. HPLC chromatogram of untreated material (black and light blue), 200°C MWT material (red and dark blue) and 200°C AHT (green), as response (μV) through time (min). All samples have been treated with acid hydrolysis.

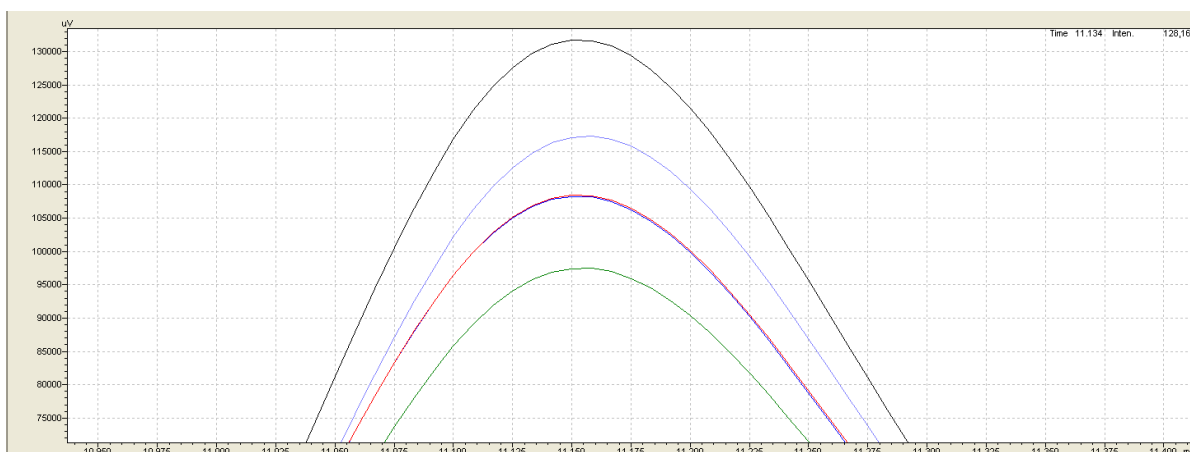


Figure 23. HPLC chromatogram of untreated material (black and light blue, the two curves with the highest peaks), 200°C MWT material (red and dark blue, the two curves are overlapping) and 200°C AHT (green), as response (μV) through time (min). Zoom in on the peak representing the sum of xylose, galactose, and mannose. All samples have been treated with acid hydrolysis.

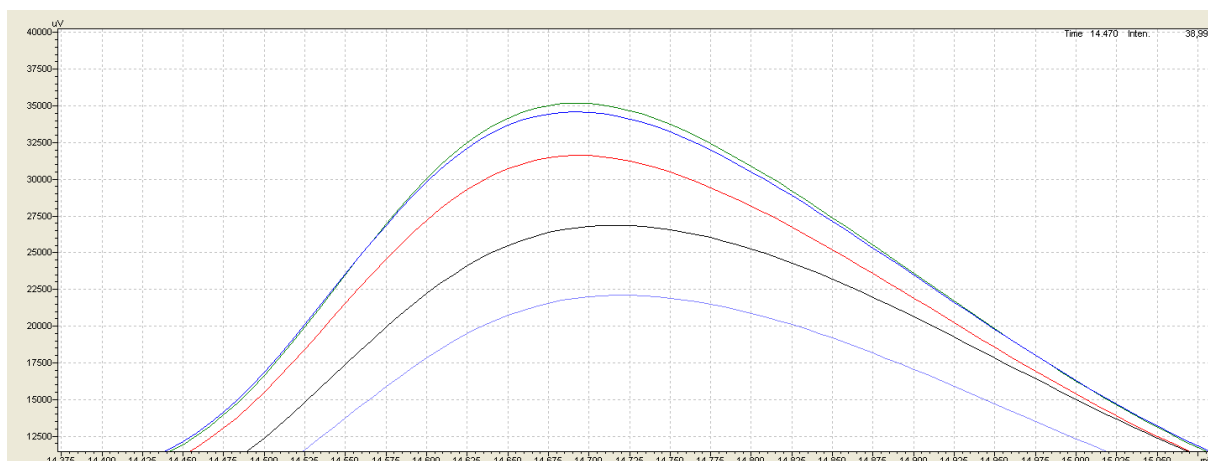


Figure 24. HPLC chromatogram of untreated material (light blue and black, the two curves with the lowest peaks), 200°C MWT material (red and dark blue) and 200°C AHT (green), as response (μV) through time (min). Zoom in on the peak representing lactic acid. All samples have been treated with acid hydrolysis.

A sum of the sugar concentrations provides an over-view of the degradation with heat treatment (Figure 25). The sugar concentration has decreased by $\sim 10\%$ after 200°C MWT, and by $\sim 20\%$ after 200°C AHT. As mentioned before, the better degradation in the AHT could be explained by the longer treatment time and higher stability, since some leakage (2% weight) has occurred in the microwave oven. To investigate if the length of treatment time and leakage influences hemicellulose degradation, samples treated with MWT and AHT at 150°C with equal heating and treatment times were compared (see Figure 26). In addition, the chromatograms of two samples from the same microwave run are presented in Figure 27, to demonstrate the variability between equally treated samples. From Figure 26 and Figure 27, it can be concluded that the difference is lower between AHT and MWT when the treatment time is the same and no leakage has occurred. The difference is even lower than the natural variability between replicates from the same microwave run.

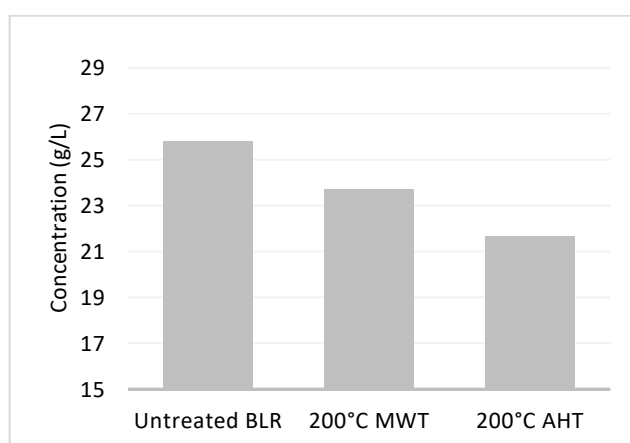


Figure 25. The sum of cellobiose, glucose, xylose, galactose, mannose and arabinose in untreated BLR, 200°C MWT and AHT, measured with HPLC, for hydrolyzed material.

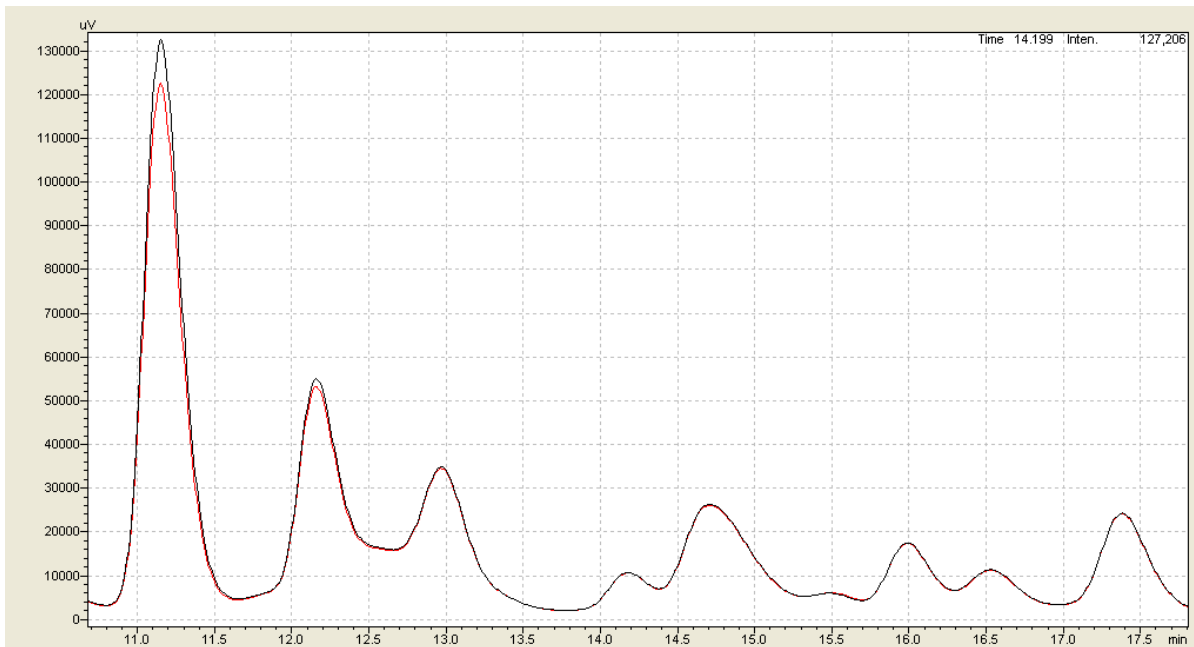


Figure 26. HPLC chromatogram of material treated with AHT (black) and MWT (red) at 150°C with equal heating and treatment times.

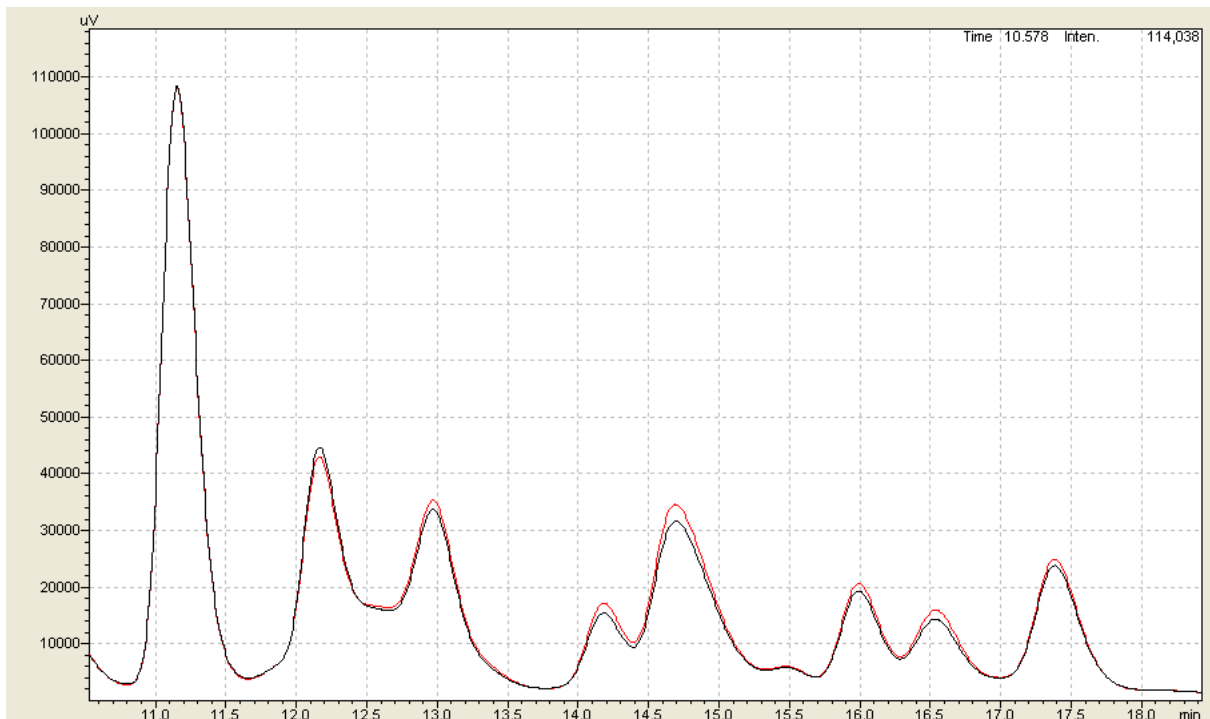


Figure 27. HPLC chromatogram of BLR treated with 200 MWT. The two samples represent different vessels of the same microwave run. A variability between equally treated samples can be observed.

4.6.3 Analysis of non-hydrolyzed material

Non-hydrolyzed material was also analyzed with Shimadzu HPLC with an Aminex HPX-87H column to compare the content of sugar and organic acids before and after heat-treatment. This analysis was made to investigate what reactions might take place during heat treatment, without the effect of the acid hydrolysis.

Heat-treated material treated with 200°C MWT is compared to untreated BLR in Table 2. The results show a 38% decrease in the total concentration of xylose, galactose and mannose. This means that sugar monomers of these species, present in the starting material BLR, are degraded during heat treatment. In addition, a degradation of formic acid can be observed. Compounds that are formed during heat treatment, and give rise to a concentration increase above 10%, are cellobiose, arabinose, lactic acid and glycerol.

Table 2. The percental concentration change of different sugars, as a result of 200°C MWT. Measured with HPLC. The samples have not been treated with acid hydrolysis.

Cellobiose	Glucose	Xylose, Galactose, Mannose	Arabinose	Lactic acid	Glycerol	Formic acid	Acetic acid
+12%	+1.2%	-38%	+16%	+15%	+23%	-24%	+6.7%

Non-hydrolyzed material was also analyzed with Shimadzu HPLC. In Figure 28, the resulting chromatogram can be seen. The untreated BLR (orange) yields a much higher peak around 6 minutes, representing a higher concentration of carbohydrates, i.e. hemicellulose. In the 200°C MWT material (blue), the concentration has decreased significantly. The peak to the right represents hydroxy-methylfurfural (HMF), which is the product of degradation of hexoses.

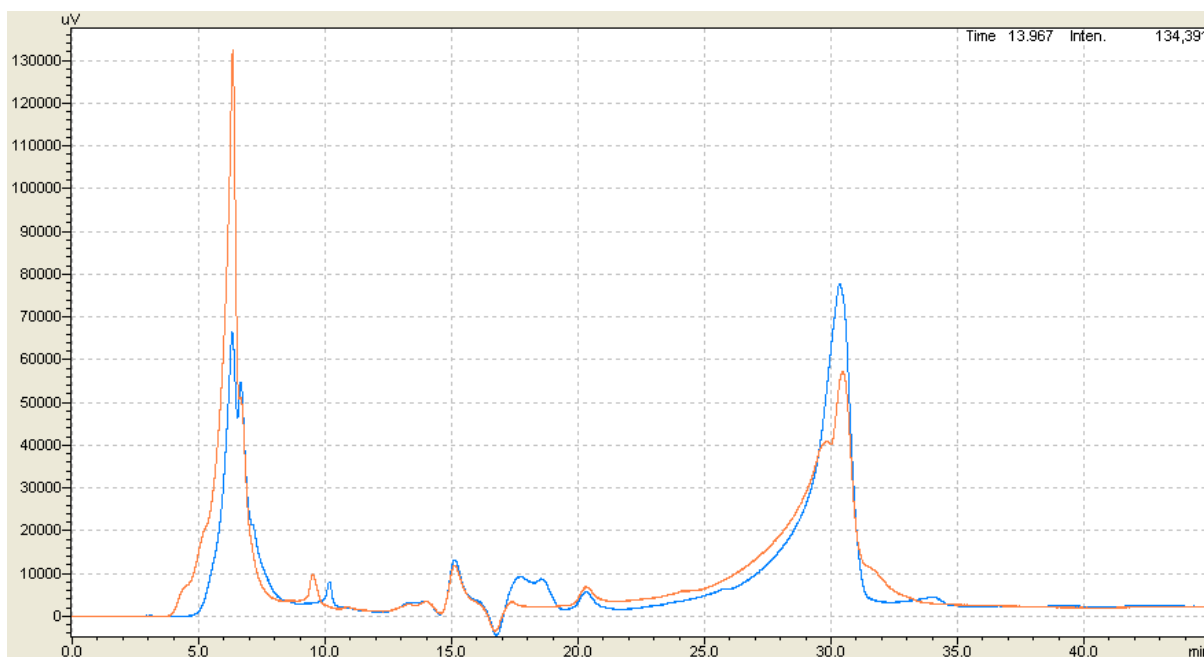


Figure 28. HPLC chromatogram of untreated BLR (orange) and 200°C MWT material (blue) as response (μV) through time (min). The first peak to the left represents carbohydrates, and

the peak to the right represents HMF. The samples have not been treated with acid hydrolysis.

4.7 Precipitation of Crystals

During the preparation of the first set of hydrolyzed samples for UPLC analysis, an unexpected discovery was made: something had crystallized at the bottom of the vials (Figure 29). An investigation was initiated to examine what the crystals consisted of and how they had formed. The crystals were cleaned from BLR by rinsing with 50% acetonitrile. Subsequently, the acetonitrile was removed through evaporation, leaving the clean crystals in the vials (see Figure 30).

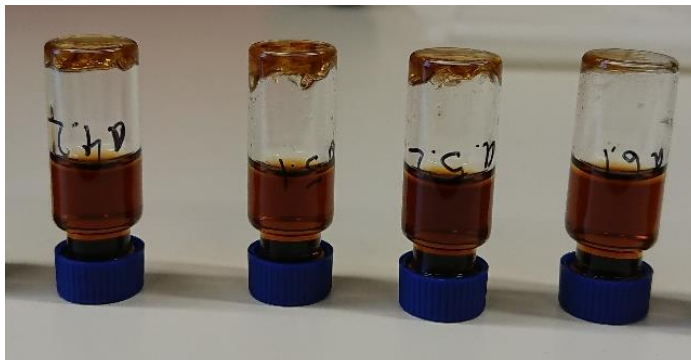


Figure 29. Crystals formed in hydrolyzed BLR dissolved in 50% acetonitrile.



Figure 30. The crystals left in the vials after purification and evaporation.

4.7.1 Analysis of the crystals with SEC, HPLC and DI-MS

To investigate what the crystals consist of, it is apt for a summary of the content of the sample vials. The samples consisted of BLR, containing mainly lignin, cellulose, hemicellulose and NaOH. H_2SO_4 was added before acid hydrolysis in an autoclave, and after hydrolysis, MgCO_3

was added for neutralization. Lastly, the samples have been diluted once with 50% acetonitrile/water (see Figure 31). During the acid hydrolysis, degradation products in the form of sugars and organic acids should have formed.



Figure 31. Acetonitrile.

Firstly, it was confirmed that the crystals were soluble in water. This indicates that it is not cellulose or MgCO_3 , but more likely a sugar. One sample of crystal was dissolved in 0.1M NaOH and analyzed with SEC. Calibration was made by comparing the RI absorption spectrum to standards of polyethylene glycol (PEG) and the absorption of $\text{UV}_{280\text{nm}}$ to polystyrene sulfonate (PSS). PEG is commonly used as a standard for sugars, while PSS is used for lignin. The RI absorption curve can be seen in Figure 32. The absorption of $\text{UV}_{280\text{nm}}$ was never higher than in the range of 10^{-6} , which supports that the sample is free from lignin.

It could be seen that the crystal differs from the BLR by comparing the concentration levels for different molecular sizes. It is thus likely that the compound of the crystal is not present in the BLR samples, meaning that it has been created at some point in the process of acid hydrolysis, neutralization and dilution with 50% acetonitrile.

The highest absorption occurs for a molecular weight of 617.5 g/mole (see Figure 32). This could be a sugar chain of 5-6 rings. The most common hemicellulose structure in softwood, galactoglucomannan (GGM), is known to be able to be separated from water extracts with lignin and other biomolecules found in wood. Separation by membrane filtration and precipitation in ethanol-water has been investigated by Song et.al (2013). Another method, investigated by Westerberg et al. (2012), is the separation by cross-flow filtration and adsorption chromatography. Precipitation of GGM by using the anti-solvents methanol, acetone and ethanol has also been investigated by Al-Rudainy et al. (2018). The studies by Westerberg et al. (2012) and Al-Rudainy et al. (2018) show that GGM precipitates in organic solvents, which supports that it most likely would precipitate also in acetonitrile.

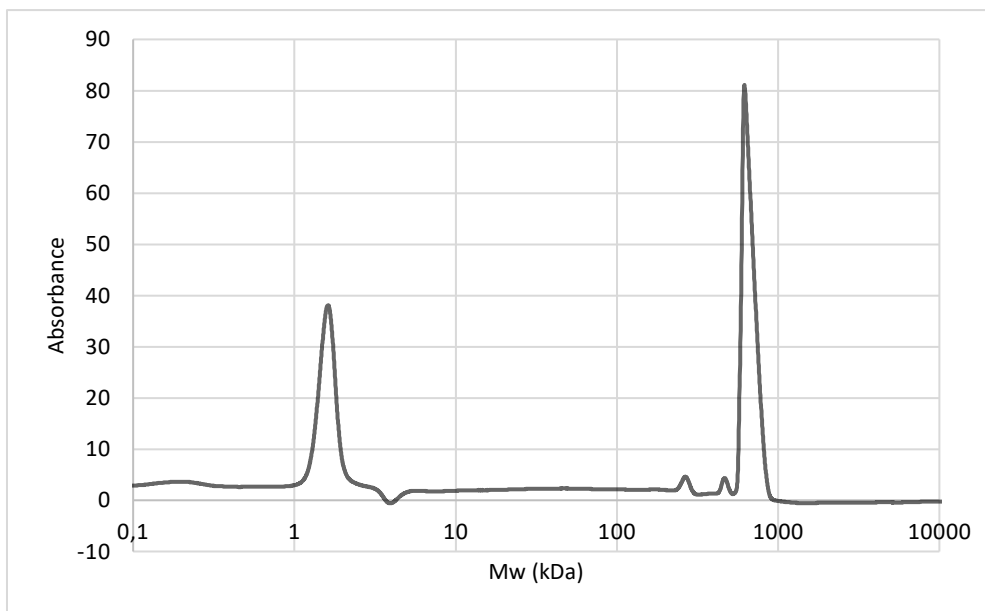


Figure 32. The RI absorption spectra of the crystal, analyzed with SEC. The first peak to the left is likely to be salt (NaOH), and the peak to the right is the crystal polymer.

To investigate further the content of the crystal, HPLC analysis was made (see Figure 33). A peak appeared after 5 minutes, indicating that the crystals consist of one single kind of sugar. However, the peak does not correspond to any known monomeric sugar, but is likely to consist of a chain, which supports the conclusion of the SEC-analysis.

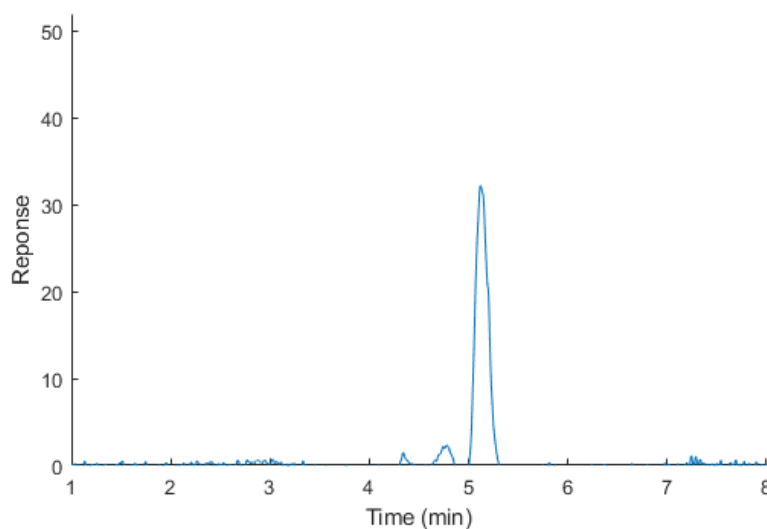


Figure 33. HPLC chromatogram of the crystal.

The crystal was dissolved in water prior to analysis of the mass spectra. The mass spectra from the DI-MS analysis can be seen in Figure 34. Fractionation gives five units of the molecular mass 141.9313 g/mol.

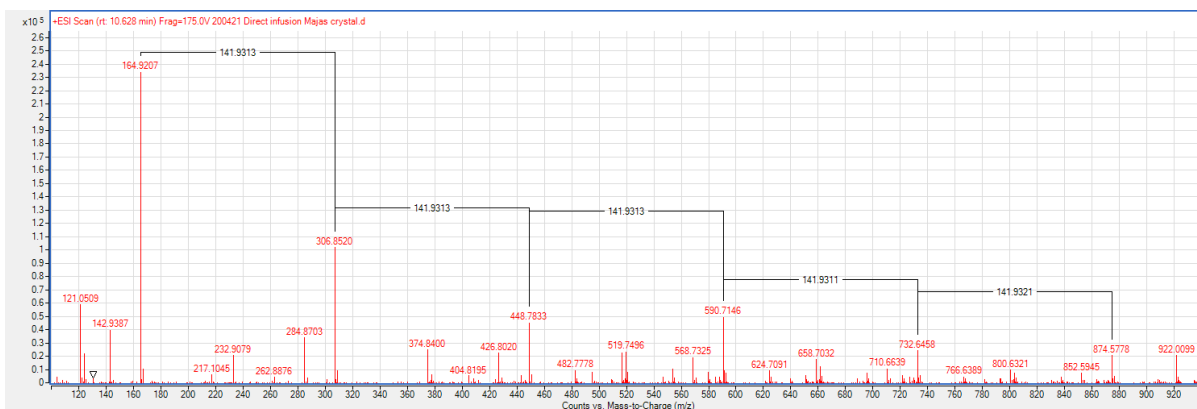


Figure 34. Mass spectra of the crystal from the DI-MS analysis. Fractionation gives five units of the molecular mass 141.9313 g/mol.

The weight of some other degradation products can be identified. The weight 21.98 could be trideuterium oxide (D_3O) or ND_4^+ . The weight 43.86 is most likely CO_2 , and 73.94 could be formic acid anhydride or acetic acid, oxo.

An attempt was made to identify compounds consisting of C, H, O, N, S, Mg and/or Na with a weight close to 141.9. Alternatives include thiophens with functional groups of carboxylic acid, acetic acid, as well as substituted versions of benzoic acid and acetonitrile, for example:

- Benzoic acid, 3-amino-, methyl ester
- 2-Thiopheneacetic acid
- 2-Thiophenecarboxylic acid, 5-methyl-
- Acetonitrile, 2-(3-cyanophenyl)-
- Benzenesulfinic-acid

These could possibly form from lignin residues. However, these structures are not likely to precipitate and form crystals. Another possibility is that magnesium salt may have formed complexes with acetic acid, namely:

- Acetic acid, magnesium salt, tetrahydrate
- Magnesium di(acetate)

Yet, this is contradicted by the HPLC analysis, which aims at an oligomeric sugar. Magnesium salt would most likely be completely dissolved and appear as salt in the HPLC chromatogram.

4.7.2 Investigation of the formation of crystals

To investigate how the crystals had been formed, the acid hydrolysis was repeated with different concentrations of acid. The tests are summarized in Table 3. The samples were treated in the autoclave at $120^\circ C$ for one hour, and then neutralized with $MgCO_3$ before addition of the 50% acetonitrile. Furthermore, a control was made by preparing the same mix, without treating it in the autoclave. This control did not lead to the formation of crystals. Crystals were formed in samples that had been acidified to pH 3 – pH 1. The sample that was acidified to $pH < 1$ was difficult to neutralize. More $MgCO_3$ was required than the amount that could be dissolved. Crystals did not form in these samples, that contained undissolved white solids.

Table 3. Investigation of acid concentration influence on crystal formation.

	pH	Formation of crystals when adding 50% acetonitrile
40 mL BLR, not treated with acid hydrolysis	13.5	No
40 mL BLR + 1.5 mL H ₂ SO ₄	6	No
40 mL BLR + 3 mL H ₂ SO ₄	3	Yes
40 mL BLR + 6 mL H ₂ SO ₄	1	Yes
40 mL BLR + 9 mL H ₂ SO ₄	<1	No

4.8 Discussion of analysis methods

Analysis of molecular weight distribution with SEC yields stable results in the form of overlapping chromatograms for sample replicates. Subsequently, some samples were measured only with SEC for quicker checks on the stability of the microwave treatment and the effect of heating time. The analysis of soluble lignin with UV-Vis yields larger standard of deviation, but the results confirm the trend observed with the SEC analysis and the pH measurements.

HPLC analysis confirms that the acid hydrolysis results in degradation of hemicellulose to monomeric sugar (see Figure 21, section 4.6.2, and Figure 28, section 4.6.3). However, it cannot be excluded that some of the hemicellulose is not fully degraded. The concentration differences between heat-treated and untreated BLR is smaller than expected, based on previous studies by SunCarbon. This might be due to insufficient temperature and treatment time, as temperatures up to 240°C are commonly applied. The higher temperature also implies longer time required to reach this temperature and to cool down, resulting in a longer time at high temperatures.

The low concentrations and low variance between different tests observed in the HPLC and UPLC analysis, along with the difficulty in defining the baseline of the chromatograms, result in high uncertainties in the estimations of concentrations. However, trends can be observed graphically in section 4.6.2, Figure 22 to Figure 28. In Figure 26, it can be observed that the difference is lower between AHT and MWT when the treatment time is equal and no leakage has occurred. The difference is even lower than the natural variability between replicates from the same microwave run, presented in Figure 27.

Non-hydrolyzed material was also analyzed with HPLC to compare the content of sugar and organic acids before and after heat-treatment. This analysis gives an indication of what reactions might take place during the heat treatment, avoiding possible sources of error caused by the acid hydrolysis.

5 Conclusions

Microwave heat treatment (MWT) degrades lignin and results in a molecular weight distribution very similar to that of material treated with standard autoclave heat treatment (AHT). This conclusion is supported by analysis of the molecular weight distribution with SEC, the drop in pH and the measurements of soluble lignin with UV-Vis spectrometry. Also, the lignin yield obtained with an acid separation process, which is the subsequent step in the SunCarbon process, is nearly equal for MWT and AHT material, implying that the two heat treatment methods are equally good at degrading lignin.

Sugar analysis with HPLC after acid hydrolysis shows that the sugar concentration has decreased by ~10% after 200°C MWT, and by ~20% after 200°C AHT. The better degradation in the AHT could be explained by the longer treatment time and higher stability, since some leakage (2% by weight) has occurred in the microwave oven. The sugar concentrations in MWT and AHT material were similar in material treated at lower temperatures, where no leakage has occurred, and the treatment time is equal. Neither of the two heat-treatment methods degraded hemicellulose as much as in previous studies by SunCarbon. This might be due to insufficiently high temperatures, as higher temperatures above 200°C could not be investigated with the current laboratory microwave equipment.

The time required to heat up the liquid is shorter in the microwave. Heating to 200°C takes 30 minutes in the standard autoclave, while it only takes about 15 minutes in the microwave, for heating with a stable effect. Investigations to optimize the heating time have not been included in this study. As mentioned before, previous studies by Lv et al. (2010) have indicated that a higher heating rate could slightly delay the decomposition process of hemicellulose to higher temperatures, which could explain why the sugar analysis indicates higher decomposition for the AHT material. However, the molecular weight distribution of samples treated for varying times of heating indicate very similar decomposition of lignin. Conclusively, only a short heating time is sufficient to degrade lignin, but to degrade hemicellulose longer treatment times are required.

The use of molybdenum (Mo) catalyst does not show any effect on degradation of lignin. If the Mo would have had a catalytic effect, this could have led to poorer degradation when exchanging the Mo-containing steel reactor to another material. These results indicate that such an effect should not be noticeable.

When treating BLR with acid hydrolysis in a pH range of pH 1-3, a substance is formed that precipitate and form crystals when dissolving the mixture with 50% acetonitrile/water. Analysis indicates that the crystals are composed of oligomers of five monomers, each with the molecular weight 142 Da. Further investigation is required to identify the composition of the crystals, for example using NMR analysis.

Conclusively, this study indicates that heat treatment using microwaves has the same effect on degradation of lignin and hemicellulose as regular heat treatment in an autoclave. However, further investigations at higher temperatures are recommended to confirm that the hemicellulose can be degraded as much as desired. To do this, microwave experiments need to be carried out at higher temperatures without leaking, which requires another microwave equipment.

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7 Appendix

7.1 Test of stability between microwave vessels with SEC

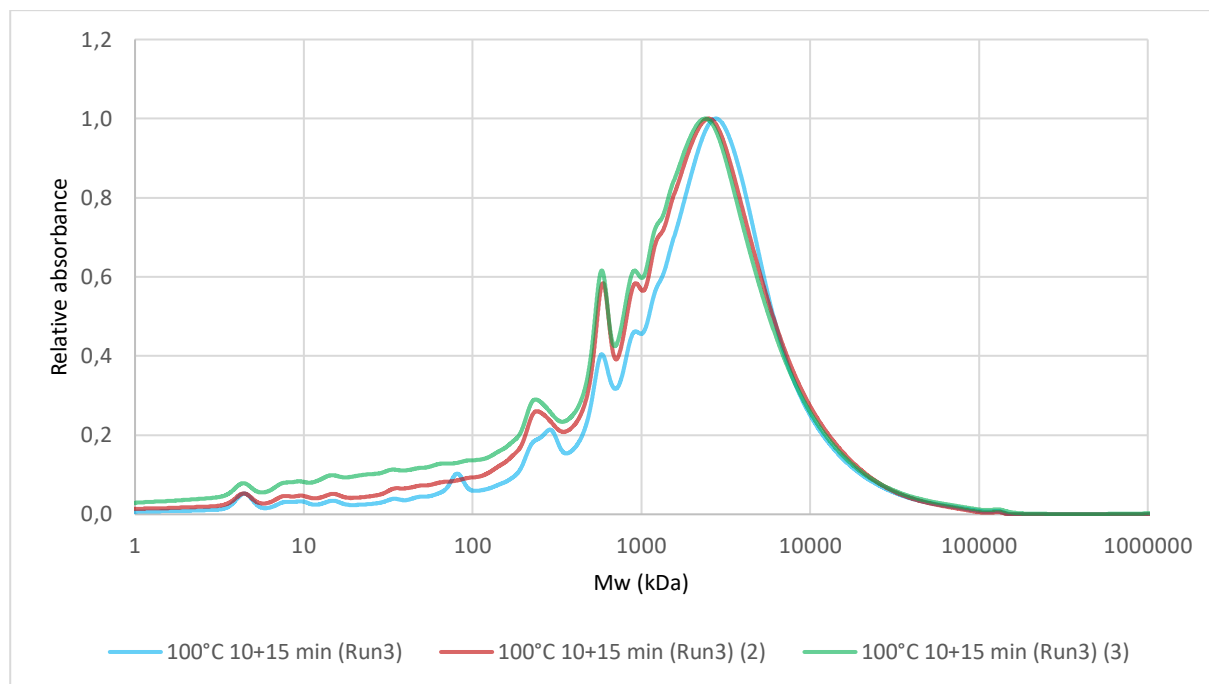


Figure 35. Molecular weight distribution of three samples of BLR treated with 100°C MWT. The samples are from the three vessels of one microwave run.

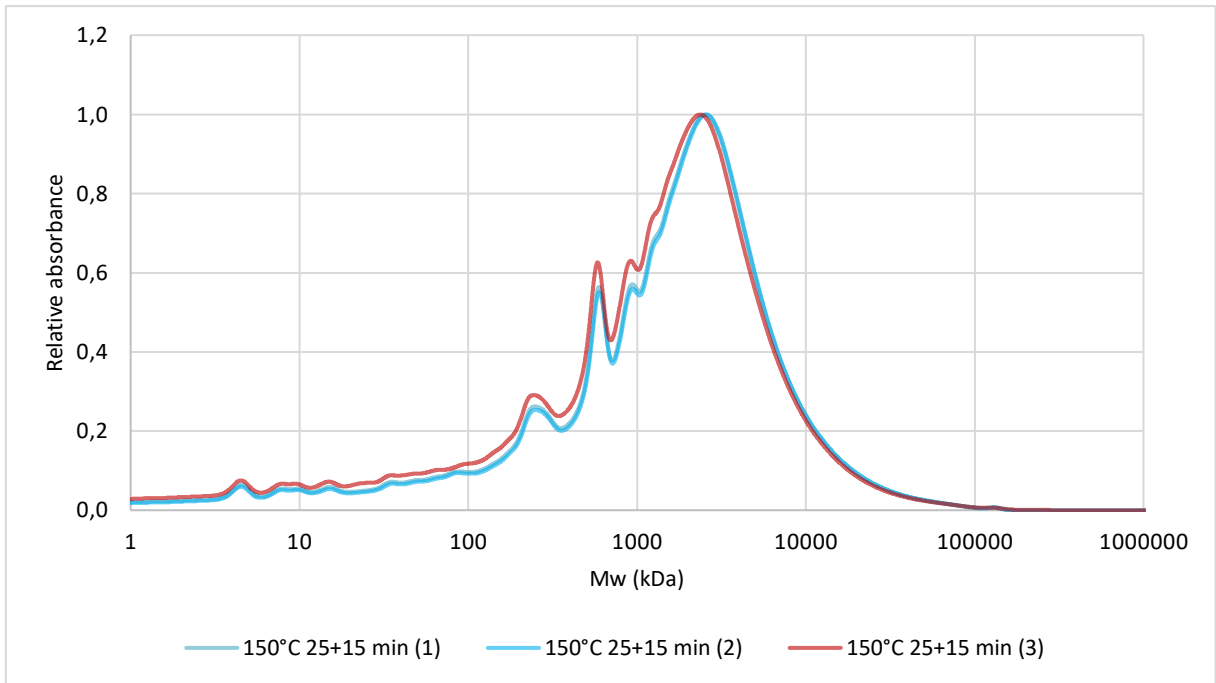


Figure 36. Molecular weight distribution of three samples of BLR treated with 150°C MWT. The samples are from the three vessels of one microwave run.

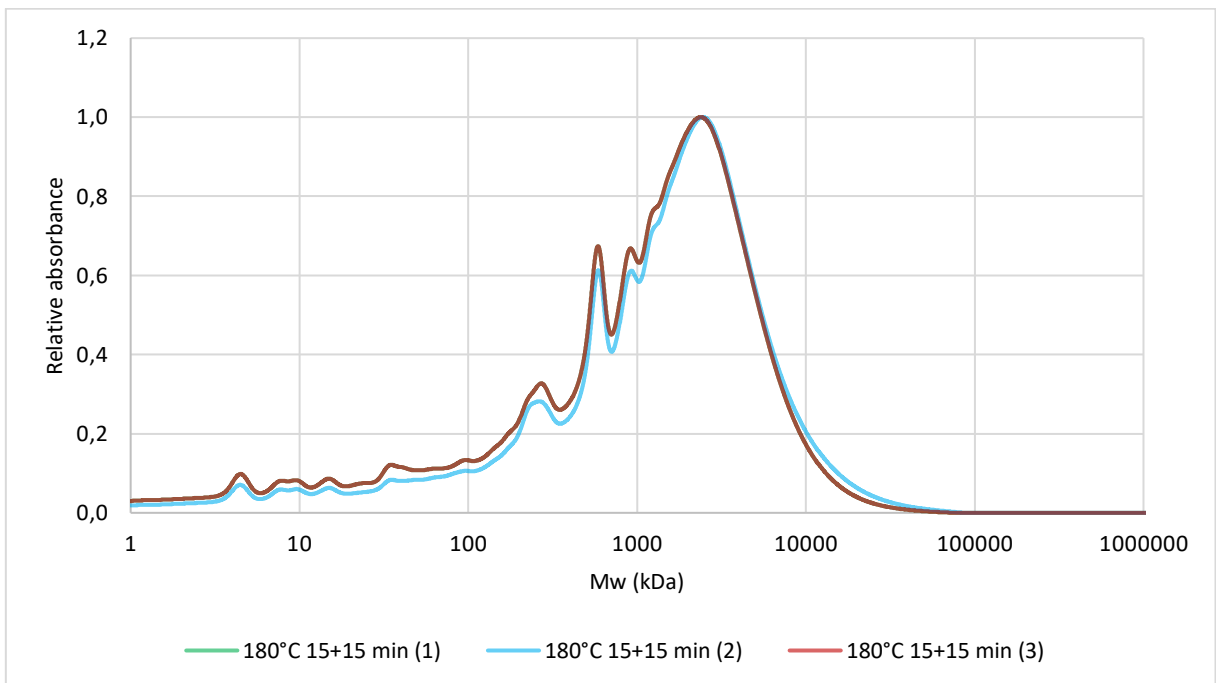


Figure 37. Molecular weight distribution of three samples of BLR treated with 180°C MWT. The samples are from the three vessels of one microwave run.

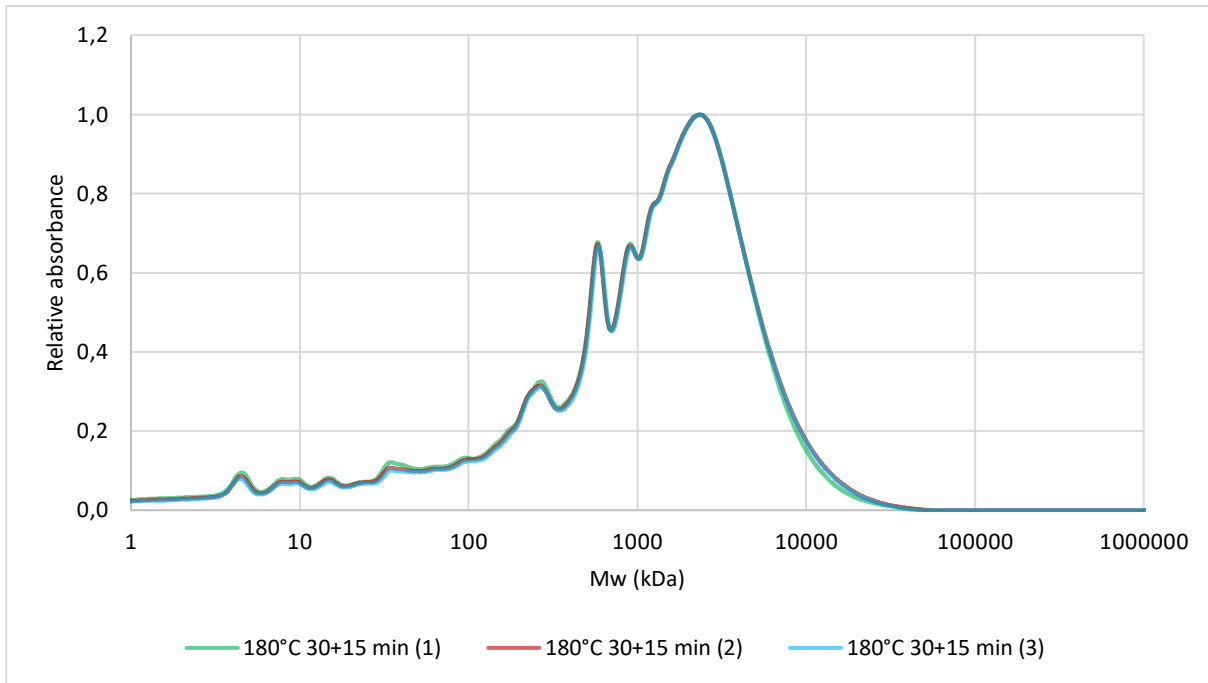


Figure 38. Molecular weight distribution of three samples of BLR treated with 180°C MWT. The samples are from the three vessels of one microwave run.

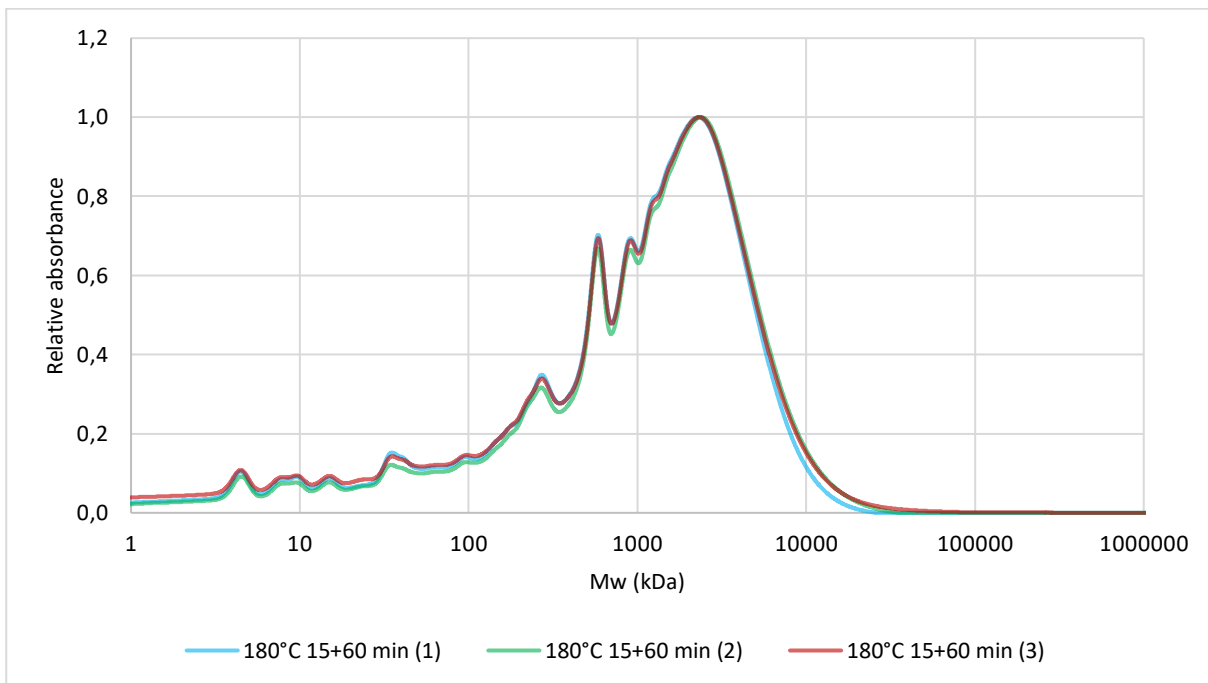


Figure 39. Molecular weight distribution of three samples of BLR treated with 180°C MWT. The samples are from the three vessels of one microwave run.

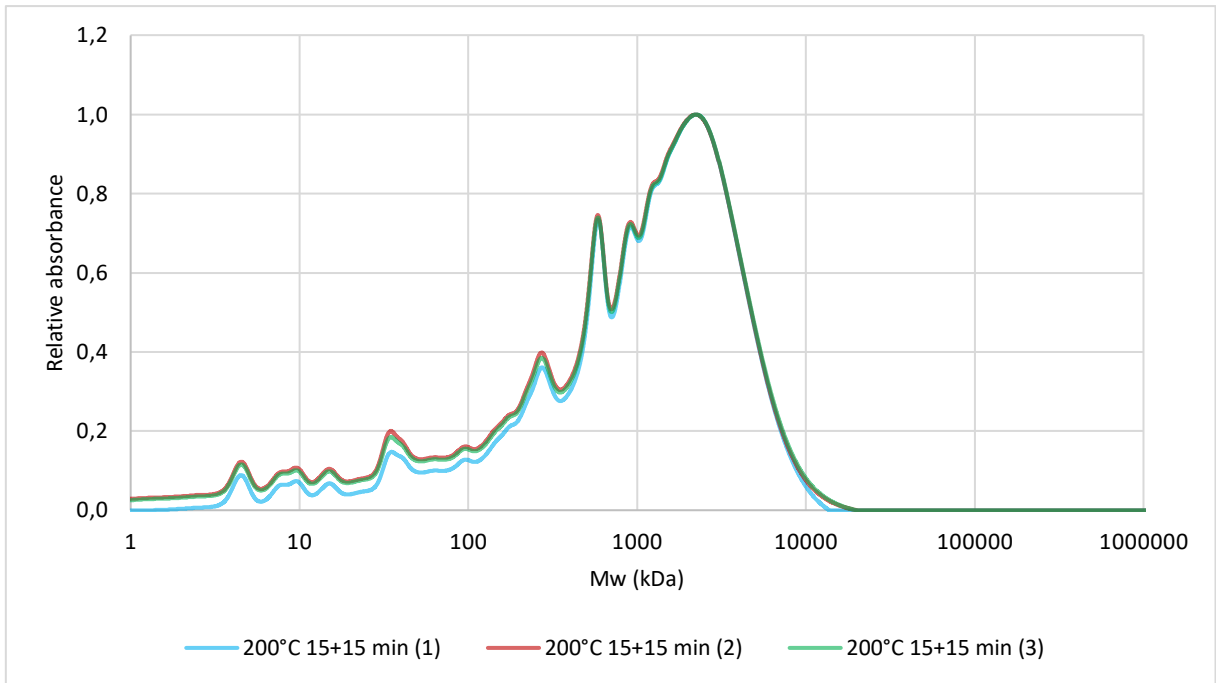


Figure 40. Molecular weight distribution of three samples of BLR treated with 200°C MWT. The samples are from the three vessels of one microwave run.

7.2 Test of stability between MWT runs of equal conditions

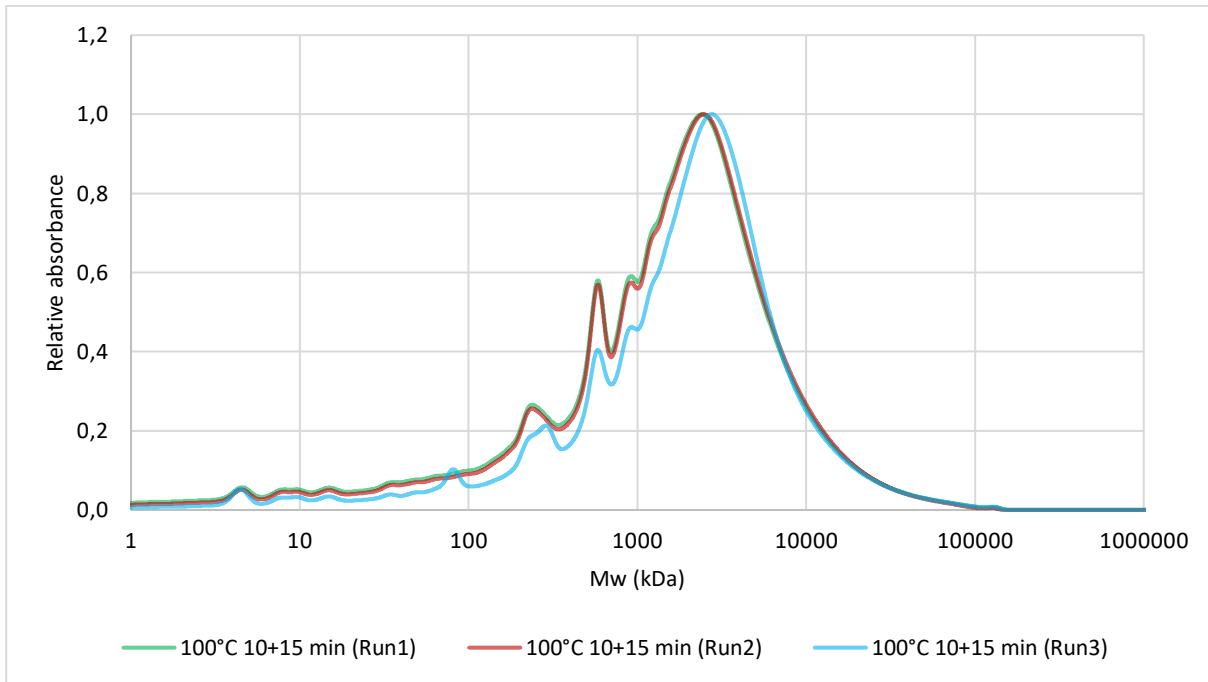


Figure 41. Molecular weight distribution of three samples of BLR treated with 100°C MWT. The samples are from three different microwave runs.

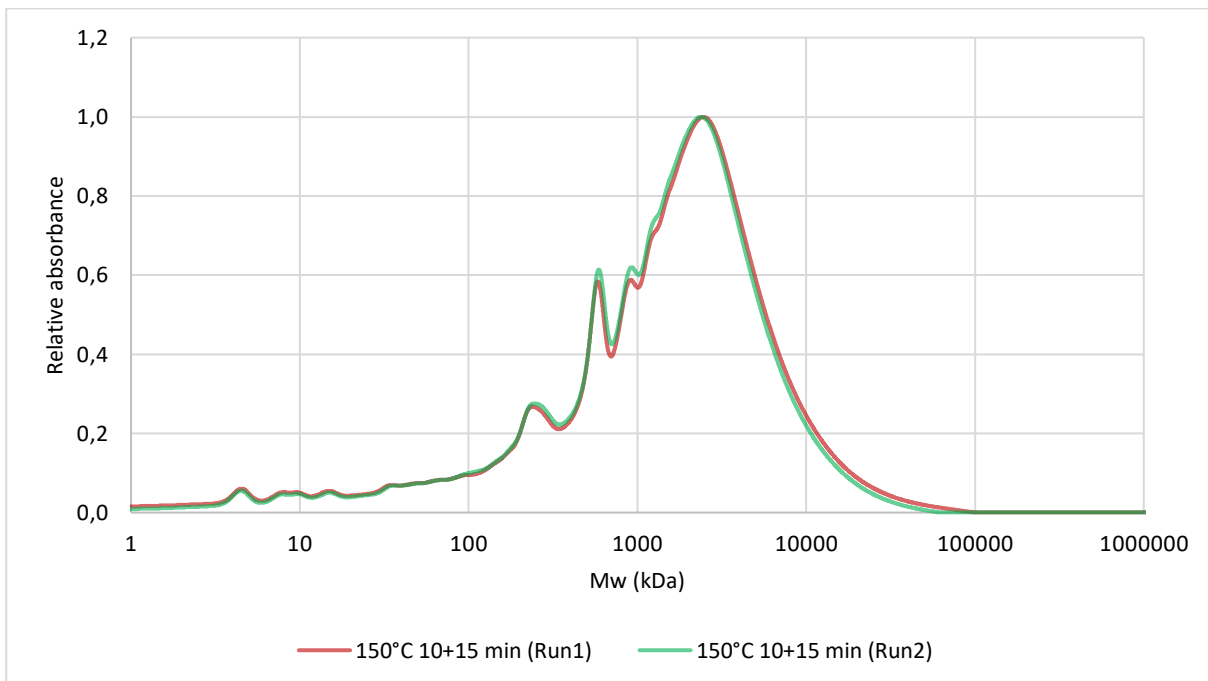


Figure 42. Molecular weight distribution of two samples of BLR treated with 150°C MWT. The samples are from two different microwave runs.

7.3 Pressure and temperature during the acidulation with CO₂ for the separation of lignin

The material that was heat treated in the PARR autoclave was treated with CO₂ gas to acidulate directly after the heat treatment, which is why the temperature and pressure are higher at this test. The intention was to achieve equal pressure differentials when increasing the pressure by adding CO₂. As can be seen in Table 4, the pressure differentials are 24 and 21.8 bar, thus there is a difference of approximately 2 bar. This could explain the slightly lower yield of lignin in the MWT material.

Table 4. Pressure and temperature at critical times of the separation process.

	P before CO ₂ addition (bar)	P after CO ₂ addition (bar)	ΔP (bar)	P constant (bar)	P end (bar)	T before CO ₂ addition (°C)	T at constant P (°C)
200°C AHT	8.5	32.5	24	15.1	14.9	101	100
200°C MWT	7.3	29.1	21.8	12.9	12.7	110	100

7.4 Analysis of sugar content after acid hydrolysis with HPLC

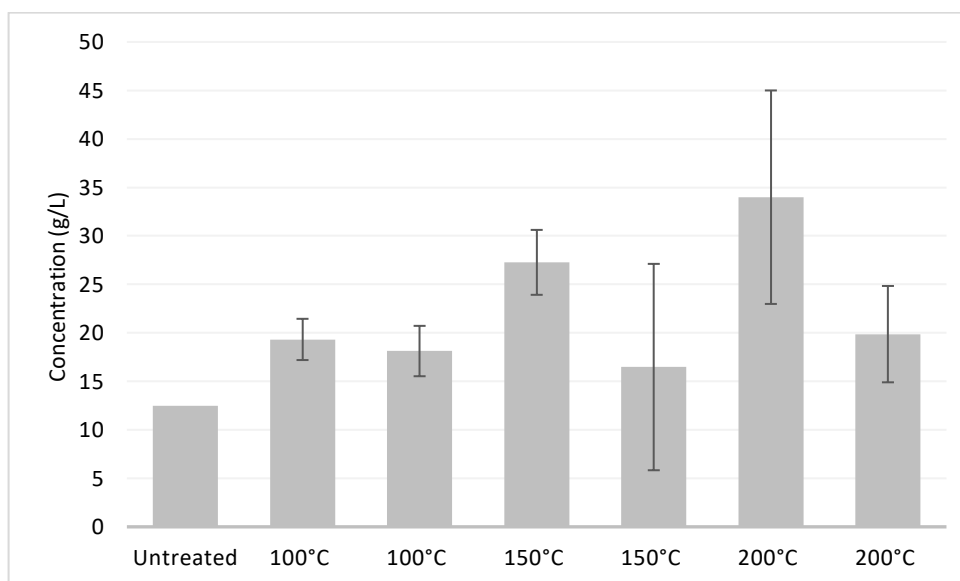


Figure 43. Total sugar concentration measured with HPLC. The sugars measured were glucose, xylose, mannose, galactose and arabinose.

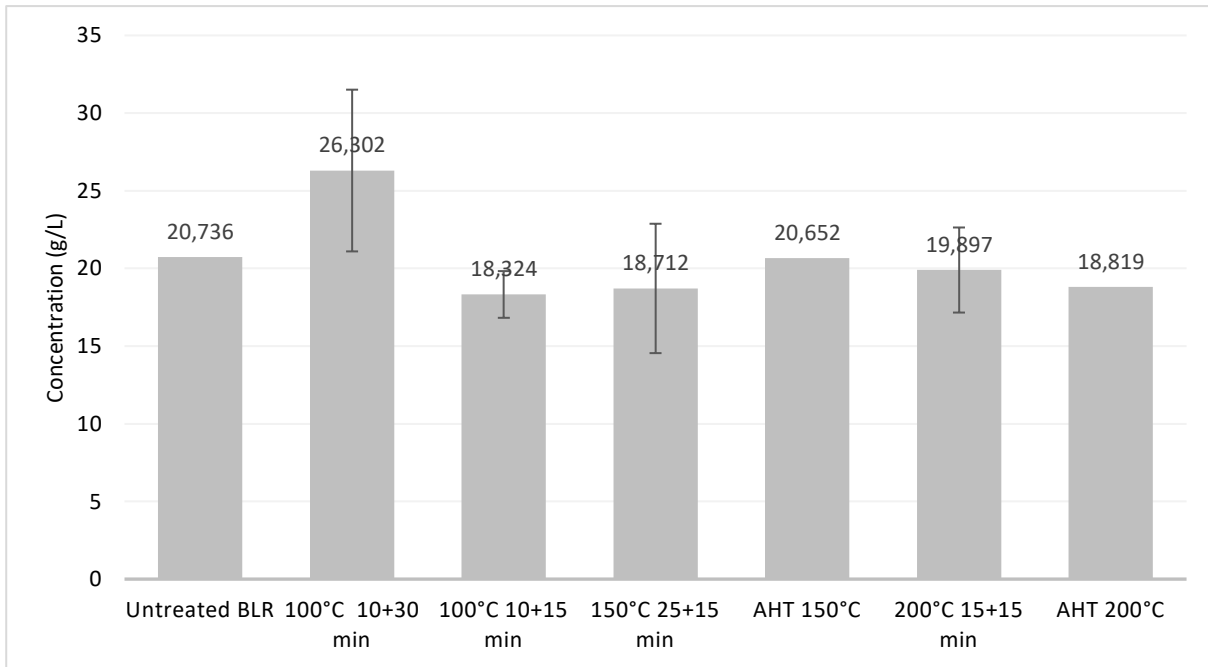


Figure 44. Summation of concentrations of the sugar species glucose, xylose, galactose, mannose and arabinose. The concentrations were measured with UPLC after acid hydrolysis.