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**CORRELATIONS BETWEEN LIGNIN-PHENOL-FORMALDEHYDE
RESIN PROPERTIES AND MOLECULAR WEIGHT DISTRIBUTIONS**

TIIVISTELMÄ

LAPPEENRANNAN-LAHDEN TEKNILLINEN YLIOPISTO
LUT School of Engineering Science
Kemiantekniikka

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KORRELAATIOT LIGNIINI-FENOLI-FORMALDEHYDI HARTSIN OMINAISUUKSIEN JA MOOLIMASSAJAKAUMIEN VÄLILLÄ

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32 sivua, 10 kuvaa, 5 taulukkoa

Ligniini-fenoli-formaldehydihartsien ominaisuuksien tutkimisessa ja laadun optimoinnissa käytetään useita analyysimenetelmiä. Hartseista tyypillisesti mitattavia ominaisuuksia ovat viskositeetti, pH, alkalisuus, kuiva-aine pitoisuus, kovettumisnopeus sekä vapaan fenolin ja formaldehydin osuus hartsissa. Tämän työn tavoitteena oli selvittää, mitä tietoa LPF hartsien kokoekluusiokromatografilla (SEC) analysoiduista moolimassajakaumista voidaan saada selville sekä etsiä korrelaatioita molekyylipainojakaumien, valmistusparametrien ja mitattujen ominaisuuksien välillä. Lisäksi tässä työssä selvitettiin, miten molekyylipainolla voidaan vaikuttaa LPF hartsin ominaisuuksiin sekä tarkennetaan LPF hartsien moolimassajakaumien integrointia.

Työssä tutkittiin kahta eri hartsityyppiä, jotka sopivat ominaisuuksiltaan eri käyttökohteisiin. Tutkittavia hartseja, joiden moolimassajakaumat analysoitiin SEC:n avulla oli yhteensä 32 kappaletta. Osan tutkituista hartseista vapaa formaldehydi pitoisuus oli liian korkea standardiarvoihin verrattuna. Lisäksi käytössä oli näiden hartsien ominaisuuksista (esimerkiksi pH, alkalisuus, kuiva-ainepitoisuus, viskositeetti) mitattuja tuloksia, joita käytettiin hartsin ominaisuuksien ja moolimassajakaumien välisten korrelaatioiden tutkimiseen.

Tulokset osoittavat, että etenkin hartsin A moolimassajakaumien ja hartsista mitattujen parametrien välillä voidaan löytää korrelaatioita. Työssä havaittiin myös selkeä korrelaatio hartsien komponenttien osuuden, joiden molekyylipaino on >2000 g/mol ja hartsin ligniinin määrän välillä. Korkeamman moolimassan alue korreloi lisäksi hartsista mitattujen B-aikatulosten kanssa, jotka kertovat hartsin kovettumisominaisuuksista. Edellä mainittujen tulosten pohjalta voidaan päätellä, että LPF-hartsi ja ligniinipitoisuus voidaan erottaa tällä korkeamman moolimassan alueella. Yksi mielenkiintoinen korrelaatio oli vapaan fenolipitoisuuden ja

molekyylipaino alueen 0–60 g/mol välillä. Vastaava korrelaatio voidaan havaita myös hartseilla B. Vapaa formaldehydi ei puolestaan korreloi tällä molekyylipaino alueella kummankaan hartsin tapauksessa. Tutkimuksissa myös havaittiin, että LPF hartseissa oli PF hartseja enemmän pieniä molekyylejä (0–200 g/mol). Tulosten pohjalta muodostettiin malli LPF hartsiin moolimassajakaumien integroimiseksi sekä tehtiin havaintoja hartsiin moolimassajakaumista, joita voidaan hyödyntää hartsilaatujen ja mittausmenetelmien edelleen kehittämisessä.

ABSTRACT

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Several analytical methods are used to determination of the properties and optimization of the quality of lignin-phenol-formaldehyde resins. Typically, measured properties of the resins are viscosity, pH, alkalinity, dry content, cure rate, and the proportion of free phenol and formaldehyde in the resin. The aim of this thesis was to study what kind information the molecular weight distributions of LPF resins, analyzed by size exclusion chromatography (SEC), can give and calculate the correlations between the molecular weight distributions and the manufacturing parameters and the measured properties of the resins. In addition, this thesis is studied how the molecular weight affects to the properties of LPF resin and how to improve the integration of the molecular weight distributions.

In this thesis, two different types of resin that are suitable for different application were studied. The total number of the resins which were analyzed by the SEC was 32. Some of the investigated resins had too high formaldehyde concentrations compared to standard values. In addition, the data of the measured properties (e.g. pH, alkalinity, dry matter content, viscosity) was used to calculate the correlations between the properties and the MWDs.

The results show that correlations can be found especially between the molecular weight distributions of LPF resin type A and its measured parameters. A clear correlation was observed between the proportion of resin components with a molecular weight > 2000 g/mol and the phenol substitution rate. In addition, the higher molecular weight area correlates with the B-time results. B-time is an analytical method for studying curing properties of the resin. Based on the above results, it can be concluded that LPF resin and lignin content can be found in this area. Furthermore, one interesting correlation was found between the free phenol content and the molecular weight area of 0–60 g/mol. A similar correlation can also be observed with LPF resin type B. In turn, free formaldehyde content does not correlate in this molecular weight area for either of the studied resins. It was also found that LPF resins had higher content of small molecules (0–200 g/mol) than PF resin. Based on the results, the integration model was formed for the MWD of LPF resins, and in general, the findings about the correlations between the MWDs of resins and their properties can be utilized in the further development of resin types and analytical methods.

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Symbols

LPF	Lignin-Phenol-Formaldehyde resin
PF	Phenol-formaldehyde resin
SEC	Size-Exclusion Chromatography
MWD	Molecular weight distribution
MW	Molecular weight
M_n	Number average molecular weight
M_w	Weight average molecular weight
M_p	Maximum value of MWD
PD	Polydispersity, Width of MWD

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1. Introduction

The forest industry has been for decades one of the corner stones for Finland's economy. One of the first export products was burnt tar, which was used specially to protect the surfaces of wooden ships. In addition to exports, wood has been used in construction, heat and energy production, and manufacturing of various necessities. The forest industry developed and thus, the production diversified in the middle of 19th century when paper and board production began with wood fibers (Lamberg, 2012). With digitalization and change in consumer behavior, demand for traditional forest industry products such as paper and board has been declining, leading to a transition in the industry towards replacing fossil materials with wood-based end products. Nevertheless, the forest industry is still important to the Finnish economy and its share of all Finnish good exports was about 20 percent in 2018 (Ministry of Agriculture and Forestry, 2019).

With environmental pollution and the reduction of fossil fuels, more sustainable solutions have replaced oil-based raw materials. (Sarika, Nancarrow, Khansaheb, & Ibrahim, 2020) In recent years, wood has been used in new applications such as the production of biofuels and chemicals. Wood is a heterogeneous material, which is why its use in new applications requires more accurate understanding of the structure of wood and its components. Lignin is the most potential component to replace aromatics in many different applications, for example, as a substitute for phenol in the production of phenolic resins. The availability of lignin is good, with up to 50 million tonnes of lignin produced each year as a by-product of pulp and paper processes. However, its main use is currently energy production (Klett, Chappell, & Thies, 2015) because applicability of lignin in value-added products has been limited by the lignin's intrinsic heterogeneity and complex structure. Therefore, more research is needed about its different properties such as reactivity and solubility to optimize the properties of the lignin-based resin and its end-products.

In this bachelor's thesis, the correlations between the molecular weight distributions (MWD) of lignin-phenol-formaldehyde resin (LPF) and its properties measured from the resin were investigated. The development and properties of the LPF resin can be studied by measuring, for example, its viscosity, pH, alkalinity and free formaldehyde content. The aim of this work is to identify the effects of different manufacturing parameters on the MWD and on the other hand the effect of MWD on the LPF resin properties. The research method used are a literature

review and computational processing of MWD data. The literature part focused to find information about the MWD of the LPF- and PF-resins, resin polymerization and how MWD are affected the resin properties. The work was done in collaboration with UPM, where the data for this bachelor thesis was obtained.

The theoretical part of the work deals with the production of LPF resins, characteristic production parameters, as well as the properties of lignin and the formation of the polymer structure of the resin. The results of the work are presented and interpreted at the end. Based on the results, the summary provides suggestions for heading future research.

LITERATURE REVIEW

2. Wood and phenolic resins

The woods and annual crops are the two main sources of renewable biomaterials and that's why they have the highest potential to replace oil-based raw materials. The wood like other plants consist mainly of three components: cellulose, hemicellulose and lignin. They are large molecules with complex structures that are difficult to analyze. All these components have their own function in the wood structure. Cellulose gives strength on the wood and it is highly crystalline. The backbone consists of chained glucose units ($C_6H_{12}O_5$) with an average of 10.000 repeat units (Figure 1). Cellulose molecules are bind to each other to form long fibrous structures called microfibrils. (Ilvessalo-Pfäffli, 1977)

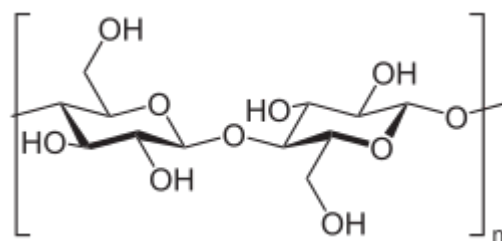


Figure 1. The structure of cellulose.

Hemicellulose and lignin surround the cellulose microfibrils and fibers and they are acting as a glue. Hemicelluloses are branched polysaccharides made up of several different sugar monomers and structures depend on the wood source. The main component of softwood hemicelluloses is xylan, whereas the hardwood contains both xylan and galactoglucomannan.

Lignin, in turn, is a phenolic macromolecule that makes the cell wall of wood fiber more flexible and mechanically strong. (Pasangulapati et al., 2021) Lignin also protects the wood from biological degradation. The structure of lignin is complex and not yet fully understood. It is generally accepted that lignin and hemicellulose form covalently bonded complexes. The strength of these bonds depends on both the type of bond and chemical structure of the compounds. (Alén, 2000)

Table 1 shows the average proportions of the tree main components as a percentage of the dry weight of the wood. It can be noted that the proportion of lignin in the softwood is on average higher than in the hardwood. On the other hand, the proportion of hemicellulose is higher in hardwood. Both have the same amount of the cellulose. It can also be seen from the Table that wood also contains small amounts of other compounds. These are mainly extractives, accounting for less than 5% of both wood types.

Table 1. Average chemical composition of softwood and hardwood. (Modified (Alén, 2000))

Biomass	Component (Dry weight %)			
	Cellulose	Hemicellulose	Lignin	Extractives
<i>Softwood</i>	40	25-30	25-30	<5
<i>Hardwood</i>	40	30-35	20-25	<5

2.1. Lignin

Lignin is the one of the most common natural polymers in the world and all plants contained it. (Väisänen, Vuorinen, 2018) Lignin is a phenolic macromolecule, and it is composed of branched phenylpropane units. It has three precursors: sinapyl alcohol, coniferyl alcohol and *p*-coumaryl alcohol that are presented in the Figure 2. (McDonald, Pant, 2001) It can be noticed that main difference between the precursors is the number of substituents in the benzene ring. Sinapyl alcohol has attached two methoxy groups. Coniferyl alcohol has one and *p*-coumaryl alcohol and two free places for the reactions in the aromatic ring.

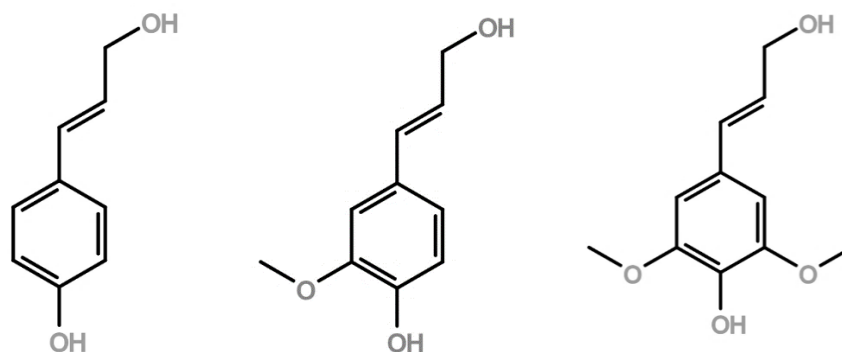


Figure 2. The three precursors of lignin from the left to the right: *p*-coumaryl alcohol (150 g/mol), coniferyl alcohol (180 g/mol) and sinapyl alcohol (210 g/mol).

The structure of lignin depends on the species of wood from which it originates. Softwood lignins consist mainly, up to 95% of coniferyl alcohol units, while hardwood lignin coniferyl and sinapyl alcohol units. So, it can be said that softwood lignin has more free reactive aromatics in its structure. Softwoods such as spruce and pine contains relatively more lignin than hardwood. Studies have shown that softwood lignin is more suitable for the production of LPF resins. This can be explained by the fact that conifer lignin contains reactive sites for formaldehyde. In addition, growth conditions such as climate and nutrients have been found to have an effect on lignin structure formation, but also on the processing and separation methods. Structure of lignin affects strongly on which applications it is suitable.

Lignin's precursors polymerize to each other forming complex network structure. The formed bonds are either carbon-carbon or ether bonds. The most typical inter-carbon bonds are biphenyl (5-5) and phenylcoumarin bonds (β -5). The most common ether bonds of lignin are β -0-4 and α -0-4 bonds. These bonds are shown in the Figure 3.

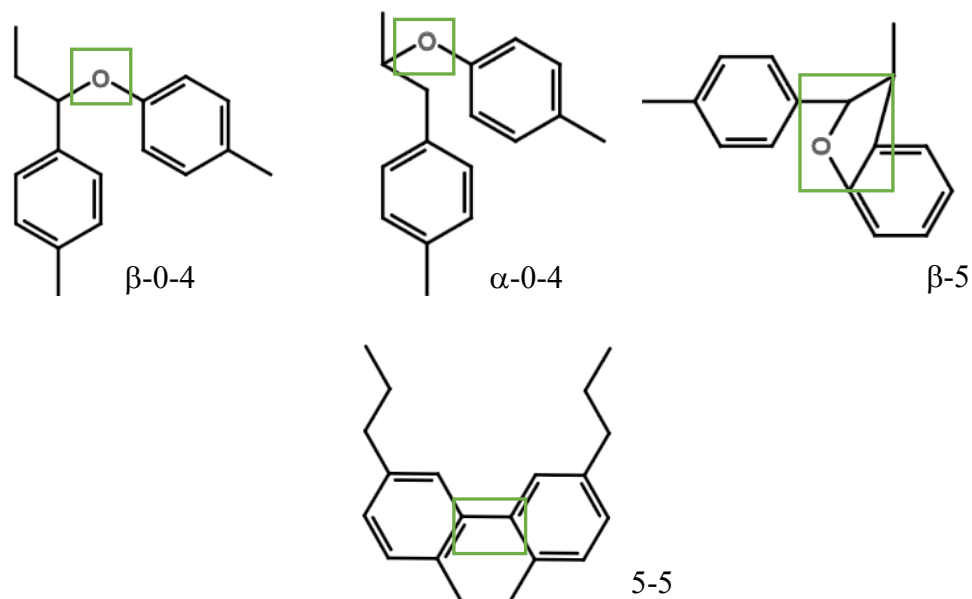


Figure 3. The most common ether (β -0-4, α -0-4) and carbon (β -5, 5-5) bonds between lignin monomers.

Although the extract structure of lignin has been extensively studied, knowledge about it is still incomplete. Particularly challenging in the structure examination is successful isolation of lignin from plant tissue without breaking the structure. The Figure 4 shows one of the generally accepted forms of coniferous lignin. In the Figure the free reactive aromatic positions are marked with green circles and it can be said that there are not so many of those in the unprocessed lignin compared to the size of polymer.

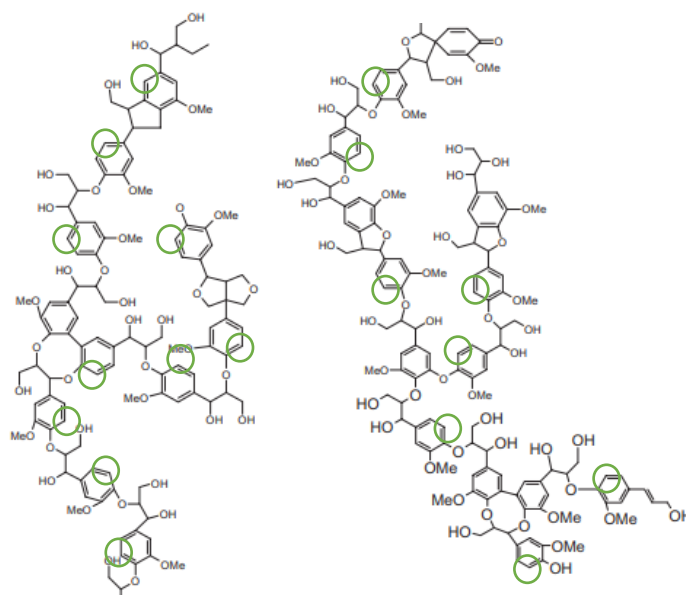


Figure 4. The complex structure of conifer lignin modified from (Huang et al., 2019). Free aromatic positions are high-lighted with the circles.

The utilization of lignin in various applications is challenging due to its permanent structure and low reactivity. The functional groups contained in lignin, such as hydroxyl, carbonyl, carboxyl, methoxyl, and sulfonic acid, has a central importance to its reactivity with other compounds. Hydroxyl groups and free aromatic positions have an important role in the preparation of lignin modified materials.

In the manufacturing process of cellulose pulp both lignin and hemicellulose must be separated from cellulose. The most general method is Kraft process where the lignocellulosic biomass is threated at high temperature with cooking chemicals, aqueous sodium hydroxide and sodium sulfide. As a result of chemical treatment, lignin can be separated from the pulp as a black liquor. These alkaline conditions ionize lignin, and the structure is degraded. Black liquor passes through several evaporators and the product is solid substance that contains lignin. Lignin is normally used in energy production of factories where its contained energy is released by burning. (Alén, 2000) In addition to energy production, lignin has many potential applications, depending on its structure like cement additives, bitumin, carbon cracker, biofuel, activated carbon, phenolic resins, carbon fibers and fine chemicals. (Gosselink, 2011)

2.2. Preparation and properties of resins

Phenolic resins are the one of the first industrially produced synthetic polymers. They are still widely used due to their mechanical strength, performance stability and heat and flame resistance. Phenolic resins have low production costs, and the raw materials are widely available. (Brydson, 1999) Resins are used as a binder in the manufacture of various wood products such as plywood, laminates and particle boards.

Phenolic resins can be produced in the condensation reaction of phenolic compounds and formaldehyde where the water molecule is released. Phenolic resins can be divided into two types according to the molar ratio of raw materials and used catalyst. When there is equimolar more formaldehyde than phenol and used catalyst is base, the resole resin is formed. In turn, molar ratio of phenol higher than formaldehyde, Novolac resin is obtained. In the Figure 5 is shown simplified description of the formation of the resins in different conditions. (Pilato, 2010)

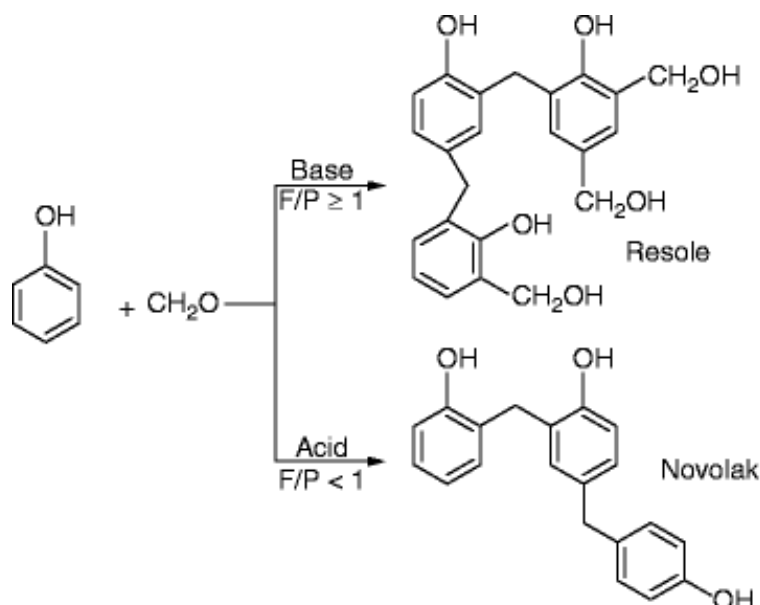


Figure 5. Simplified description of the formation of the Resole and Novolac resins. (Pilato, 2010)

2.2.1. Resole and Novolac resins

As it can be noticed in the Figure 5 resole resins are produced in the condensation reaction of phenols and formaldehydes by using base catalyst which is typically NaOH. Molar ratio of formaldehyde to phenol is ≥ 1 and it can vary between 1:1 and 4:1. At first phenol reacts with formaldehyde to form *ortho*- or *para*-hydroxymethylphenol. In the condensation reaction of two hydroxymethylphenols, methyl and ether bonds are formed between the molecules. The condensation product is reactive phenolic resin that polymerizes with itself.

In the second case when molar ratio of phenol is < 1 under acidic conditions, formed compound is linear a Novolac resin. It consists of the phenyl rings which are attached together by methyl bonds. The first step is similar to the Resole resin reaction when phenol and formaldehyde form hydroxymethylphenols. Hydroxymethylphenol still reacts with phenol in which forms *o,p'*-, *p,p'*- or *o,o'*- dihydroxyphenylmethanates and released water. Main products are *o,p'*-, *p,p'*- dihydroxyphenylmethanates, but when higher temperature is used, a third form is also possible. In the structure of a linear Novolac has not hydroxymethyl groups so its polymerization with itself is not possible. Novolac resins require an additional cross-linking agent like hexamethylenetetramine, which releases formaldehyde during cross-linking.

In the Figure 6 is presented the reaction mechanism of phenol and formaldehyde under basic conditions. Under the action of the base, phenol forms negatively charged anion. The methoxyl group of formaldehyde reacts to the phenol ring and it can be seen that the groups are attached to the *para*- and *ortho*- positions of the benzene ring. (Pilato, 2010) The linear structure is formed when phenol and formaldehyde react in same ratio. Phenol continues to react with formaldehyde if there are left free formaldehyde molecules. As a result of excess formaldehyde, the structure begins to branch and form a network and molecular weight and polydispersity increases. (Park, 2001)

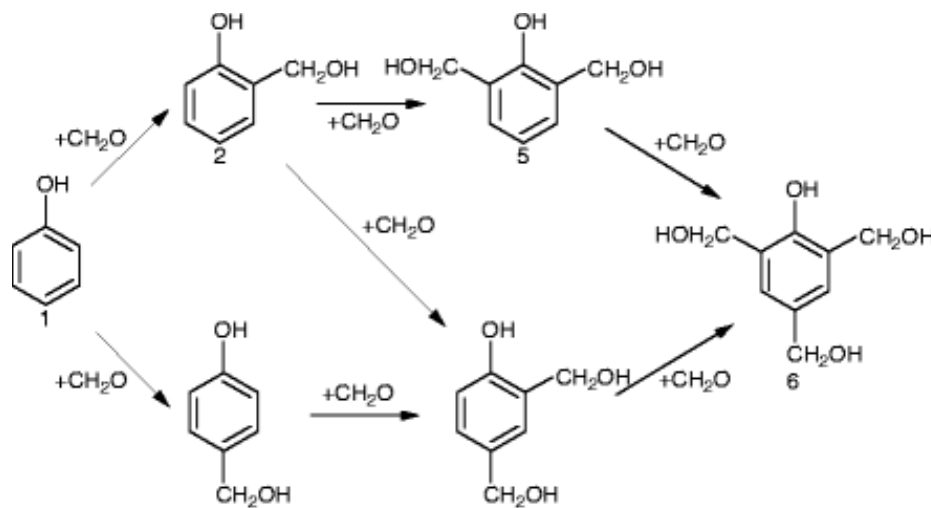


Figure 6. Reaction between phenol and formaldehyde when a base catalyst is used. (Pilato, 2010)

Most of resoles are waterborne, but in certain applications, water can be replaced with alcohol or ketone solvents. Properties of resoles are often modified with different additives. Various fillers can be added to provide the final resin to achieve the desired properties such as flame retardancy, plasticization and pigmentation. In addition, various surfactants as in release and wetting agents can improve the processability of the resin.

Phenol is other mainly used raw material in manufacture of phenolic resins. Phenols are organic compounds that consist of one or more hydroxide groups which are attached to the benzene ring and the combination of these groups makes the phenols extremely reactive. The most commonly used phenolic compounds are monohydroxyphenols but also alkylphenols, dihydroxybenzenes and bisphenol-A can be used as a raw material in the phenolic resin production. Pure phenol is clear liquid that forms white crystals. Phenol is a very harmful and that is why it should be replaced with more environmental alternatives. It can be synthesized or isolated from the nature. Phenol is mainly produced by hydrolysis of chlorobenzene or oxidation of isopropylbenzene. Phenol is chemically similar than alcohols and it forms strong hydrogen bonds due to which it has a higher melting point than same molecular weight hydrocarbons. These bonds also make it very soluble in water. (Carlroth, 2015)

The second raw material of phenolic resin is formaldehyde that can be produced by oxidizing methanol. It is transparent, easily flammable and it has a typical pungent odor. Formaldehyde is the simplest aldehyde, and it is formed by a one carbon and an aldehyde group that is attached

to it. Formaldehyde is highly soluble in water because its carbonyl group forms hydrogen bonds with water molecules. It is used industrially as formalin which is 37 % aqueous formaldehyde solution. (LabChem, 2013)

2.2.2 Replacement of phenol with lignin

The phenolic resin can be manufactured by substituting part of phenol with lignin. In the use of lignin are several advantages. In addition to replacing harmful phenol, it has also been found to accelerate the initial curing rate. Interest in the utilization of lignin in the manufacture of phenolic resins has increased over the last decades as result of depletion of fossil raw materials and increased knowledge of the environmental impacts of phenolic resin manufacturing. Lignin is a structurally similar compound to phenol and has been used successfully to replace phenol up to 75% (Valkonen, 2017). However, high lignin substitution rates cause technical challenges because lignin has lower reactivity with formaldehyde than phenol due to macromolecular and branched structure, sterical hindrance and lower content of free reactive positions of phenol ring. Examples of these challenges are reduced strength properties, increased curing time and temperature.

The reactivity of lignin can be improved by several different methods such as phenol and formaldehyde treatment (phenolation and methylation) and cleavage (de-polymerization) of molecule structures by heat. The pretreatments aim to increase the number of structural sites that can react with formaldehyde. The most important sites are *ortho*- and *para*- positions of phenol and these positions often have methoxy or alkyl groups (Figure 4). Advantages of substituting phenol with lignin are its low cost and its good availability as a by-product of the forest industry. (Siddiqui, 2013)

2.2.3 Manufacturing parameters, resin properties and end-uses

Polymerizable structure of the resole resin, the density of the resin network, its curing, and residual monomer content can be influenced by modifying the molar ratio of formaldehyde and phenol. Another manufacturing parameter are the alkali content and the reaction temperature/time profile, which describes the change in the temperature at different stages of the reaction. Temperature optimizations affect the structure of the formed resin by controlling the condensation reaction, the degree of condensation and competing methylation. The reaction speeds of the competing the condensation reaction and methylation depend on temperature. In

general, higher temperatures accelerate more condensation reactions and lower temperatures favor addition reactions. When the production temperature profile is invariable, a uniform product is obtained.

During the resin production many properties are measured to provide information about progress of the reaction and whether the resin is ready to the next step. (Pilato, 2010) The most important parameters are alkalinity, and they are measured by using in-line measurement. The viscosity is important resin property because a low viscosity resin is better absorbed into wood. pH measurement uses electrodes that are quite similar with standard laboratory pH meters. The sensors require careful cleaning in order to the results to be considered correct. In-line viscosity measurement can be executed in several methods. One method is based on the determining the oscillation emitted by the sensor which response to a fixed oscillating force is measured. The viscosity can be also defined by measuring the required power to maintain oscillation frequency/amplitude.

Important resin properties for curing and end-uses are pH, viscosity, dry content, water tolerance, gel-time and amount of free formaldehyde. The Resole resins can be applied to various uses by modifying these parameters.

PF and LPF resins can be used as adhesives as in various wood components. Examples of different applications are different building materials such as particle board, plywood, laminated veneer and medium- and high-density fiberboard. LPF resins that are produced for these applications are made by slightly different parameters to meet the desired properties. (Akude, 2017)

2.3. Correlations between LPF resin properties

Kalami et al. used several lignins and investigated to the correlations between resin and lignin properties. Table 2 summarizes their correlation results. As a result, they noticed that when the pH increase, the viscosity of the resin increases simultaneously. This leads to shorter gel time, which improves the thickening of the resin. (Kalami et al., 2018) The viscosity of the resin has an important role in the adhesion properties of the resin because low viscosity improves the absorption of the resin into the wood.

Previous study (Kalami et al, 2018) has also presented effects of increasing lignin content of the resin. Use a higher lignin content increased the needed curing temperature. It was also shown that higher water resistance can be related to the higher reactivity of the lignin with formaldehyde groups. Moreover, a positive correlation has been found earlier between molecular weight of lignin and manufactured resin viscosity (Christiansen and Gollob, 1985; Pang et al, 2017).

Kalami et al. found also one significant correlation between free formaldehyde concentration and curing temperature. When free formaldehyde content increased, the curing temperature decreased. Several positive correlations were also observed between adhesive strength and other properties. It was found that the curing temperature, both the *p*-hydroxyphenyl content of lignin and the phenolic acid content increased the shear strength. The adhesive shear strength also correlated with the formaldehyde content of the resin and lower free formaldehyde content made the resin stronger. The results showed that the lignins with the highest content of free reactive aromatic positions were the most suitable for LPF resins. It was observed that when phenol was replaced with lignin, the amount of aldehyde could be decreased at the same time. (Kalami et al., 2018)

Table 2. Correlation coefficients between properties of lignin-phenol-formaldehyde resins and lignin (Kalami et al., 2018).

Variable	Shear strength	Resin pH	Gelation Time	Free formaldehyde	Curing Temperature	Syringyl	Guaiaacyl	Hydroxyl Phenyl	Total Phenolic	Ash	Ferulic acid	<i>p</i> -Coumaric acid
Shear strength												
Resin pH	-0.76											
Gelation Time	0.37	-0.78										
Free formaldehyde	-0.86	0.42	0.08									
Curing Temperature	0.75	-0.41	0.28	-0.84								
Syringyl	-0.38	0.19	-0.09	0.86	0.94							
Guaiaacyl	0.4	0.29	-0.4	-0.31	0.45	-0.42						
Hydroxy Phenyl	0.78	-0.9	0.48	-0.4	0.35	-0.09	-0.07					
Total Phenolic	0.23	0.08	-0.26	0.39	-0.4	0.59	0.41	0.25				
Ash	0.28	0.02	0.22	-0.43	0.37	-0.46	0.25	-0.26	-0.32			
Ferulic acid	0.74	0.83	0.5	-0.39	0.31	-0.07	-0.18	0.98	0.16	-0.29		
<i>p</i> -Coumaric acid	0.75	0.85	0.51	-0.4	0.33	-0.1	-0.15	0.99	0.16	-0.3	0.98	

3. Analysis methods for the molecular weights of lignin and LPF resins

Properties of wood polymers such as molecular weight, shape and density have been studied mainly from isolated samples and therefore may not fully reflect the true properties of the polymers. As noted earlier, the isolation process of lignin, like in case of other large biopolymers, change the whole structure. Lignin consists of phenylpropane units with abundant bonds between them. Based on this, lignin is estimated to be a three-dimensional macromolecule. As a result of the isolation of lignin, the bonds between the phenylpropanes are broken and it is possible that the size of the molecule decreases. It is also worth to notice that as a result of treatments, lignin can be simultaneously cleaved and polymerized again. It has been found that the molecules of soluble lignin preparations have a similar structure, but they can vary greatly in size. Several different methods have been used to measure the molecular weight distributions of the lignin, the best known of which is size exclusion chromatography (SEC).

3.1. Size-Exclusion Chromatography (SEC)

Size-Exclusion Chromatography is a physical method to separate molecules of different size based on their hydrodynamic radiuses. The method can be used for liquids but also for solid samples that are soluble in the eluent solution. Molecules are distinguished according to their ability to penetrate the pores of the columns gel material. Molecules are identified by retention times which increases as the molecular size decreases. Larger molecular size components pass through the column faster and smaller components penetrate to the porous material. The molecules of sample and the columns packing material must not affect the enthalpy interactions. The elution volume correlates with molar mass when ΔH is 0. Using known molecular weight standards and measuring their retention times, the molecular weights of the sample compounds can be calculated. (Philipsen, 2016)

The molecular weight distribution of the sample is described by using different statistical averages. Number average molecular weight (M_n) is calculated by using equation 1, dividing the compound weight by the total number of molecules. Weight average molecular weight (M_w) is determined using equation 2 (Philipsen, 2016) where the number of polymers is replaced by the molecular weight of the polymer fraction.

The SEC also has some limitations and challenges because the method is not based on absolute measuring. The method is measuring how fast standard substances and analytes pass through

the column. If the analyte interacts differently with the column material than the standard, it can pass through the column at different time even though those compounds would otherwise be the same size and have similar structures. In this way the results could be incorrect ja analyte can be identified smaller or bigger based on the retention time.

Number average molecular weight,

$$\overline{M}_n = \frac{\sum N_i M_i}{\sum N_i} = \frac{\sum W_i}{\sum W_i / M_i} \quad (1)$$

and weight average molecular weight,

$$\overline{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{\sum W_i M_i}{\sum W_i} \quad (2)$$

where	N_i	number of molecules
	M_i	molecular weight
	W_i	weight of molecules

Polydispersity index describes the broadness of a molecular weight distribution of a polymer and it can be calculated with the following equation:

$$PD = \frac{M_w}{M_n} \quad (3)$$

M_n , M_w and PD are most common parameters to describe MWD of sample, but especially M_n is very sensitive, if the sample has small content of small molecules. M_z and M_{z+1} highlight the effect of longer molecules and they are calculated by using equations 4 and 5.

$$\overline{M}_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2} \quad (4)$$

$$\overline{M}_{z+1} = \frac{\sum N_i M_i^4}{\sum N_i M_i^3} \quad (5)$$

3.2. Vapor pressure osmometry

Vapor pressure osmometry can be used to determine the number average molecular weights. This method is based on measuring the decrease in the vapor pressure of the solvent when diluted polymer solution at a certain temperature. The instrument is calibrated with a compound of known molecular weight. The sensitivity of vapor pressure osmometry is the best for compounds with a molecular weight of 10–10,000 g/mol. Despite this limitation, it has been found to be suitable for measuring the average molecular weights of lignin and lignin-derived end products. (Tolbert et al., 2014)

3.3. Light scattering

Low angle scattering photometers have also been used to determine the number average molecular weight, but it has been found that the results are not very repeatable. It is possible that lignin form aggregates, or molecular clusters which can cause interference. Another possible source of error is the absorbance or fluorescence of lignin. (Tolbert et al., 2014)

3.4. Membrane filtration

The molecular weight distributions of lignin can also be studied by membrane filtration. Membranes are available for compounds with molecular sizes ranging from 1,000 to 300,000 g/mol. In the filtration several filters are used, and they are arranged in series. The shares of the separated fractions are determined either by weighing or by ultraviolet absorption. (Tolbert et al., 2014)

EXPERIMENTAL SECTION

4. Materials

This section is a compilation of the samples examined, their properties and the analytical methods that are used for measuring the properties. In addition, the peak integration and calculation to examine the correlations is presented in this section.

4.1. Analyzed resins and the properties

The studied resins in this bachelor thesis are manufactured according to the practices of the collaborating company. The number of resins was 32. Moreover, the molecular weight distributions of PF resin and lignin, were used as reference and for the identifying the peaks. Resins were of two different types and they are used in slightly different applications. The resins have different phenol substitution rates (30, 50 and 65%) and target viscosities. The phenol substitution rate means that how many weight percent of phenol is substituted with lignin. Phenol substitution is based on weight, by meaning 1 kg of phenol is replaced with 1 kg of lignin. Other manufacturing parameters are the amount of NaOH catalyst and the molar ratio of formaldehyde to phenol and lignin. In addition, some resins have urea, which binds free formaldehyde.

4.2. Analysis methods to measure resin properties

The analysis methods and standards that are relevant to interpretation of the data investigated in this thesis, are shown in the Table 3. The investigated MWD curves had always 25 measurement points. The material having lower polydispersity (PD) had also lower percentage values than the similar resin with higher PD. This made interpretation of MWD curves difficult and that is why percentage values in different MW areas for each resin were calculated (e.g. MW 0-60 g/mol or MW >2000 g/mol) and used in the correlation analysis.

Table 3. Analysis methods for the resins and standards used in this thesis.

Analysis	Standard	Explanation
Molar weight distribution	internal method	Based on the SEC and NaOH eluent.
Dry content	internal method	Dry content is determined by drying the resins samples in 120 °C for 2 hours and measuring the weight of samples before and after.
B-time	EN ISO 8987:2005	An important method to determine curing of the resins. The temperature is 120 °C. The resin is stirred with a glass rod and it is lifted several times. B-time is the measured time at which filament of the resin produced in the end of glass rod is broken in a rubber-like manner.
Viscosity	EN ISO 2555:2018 and EN ISO 12092:2001	Viscosity is determined by rotational viscometer. Used sample volume is 500-1000 ml. Temperature of the sample is 25 °C and it is heated in water bath. Sample must be homogenous and air bubbles formation is avoided. The rotation speed is set to 50 rpm and viscometer rotates for 30 seconds.

Free formaldehyde	internal method	The free formaldehyde content is determined by potentiometric titration. This method can be used to resins with free-formaldehyde content up to 15 % by mass.
Free phenol	internal method	The free phenol content is determined by gas chromatography with flame ionization detector (GC-FID). Response coefficient for phenol is calculated based on internal standard and phenol solution.
pH	internal method	The pH of sample is determined by potentiometric measurement which is appropriate for water containing samples.
Alkacity	internal method	Alkacity of LPF resins and alkated lignin is determined by titration. Alkalinity of material is defined as the ability to neutralize acid when to material is bonded NaOH.

4.3. The integration of the Molecular weight distributions

Figure 7 shows the integration of the molecular weight distribution peaks. The integration was made by fitting the lines to the cumulative percentage graft. The equation of fitted line was used to calculate the value of cumulative graft at the desired molecular weight and percentages of selected weight fractions.

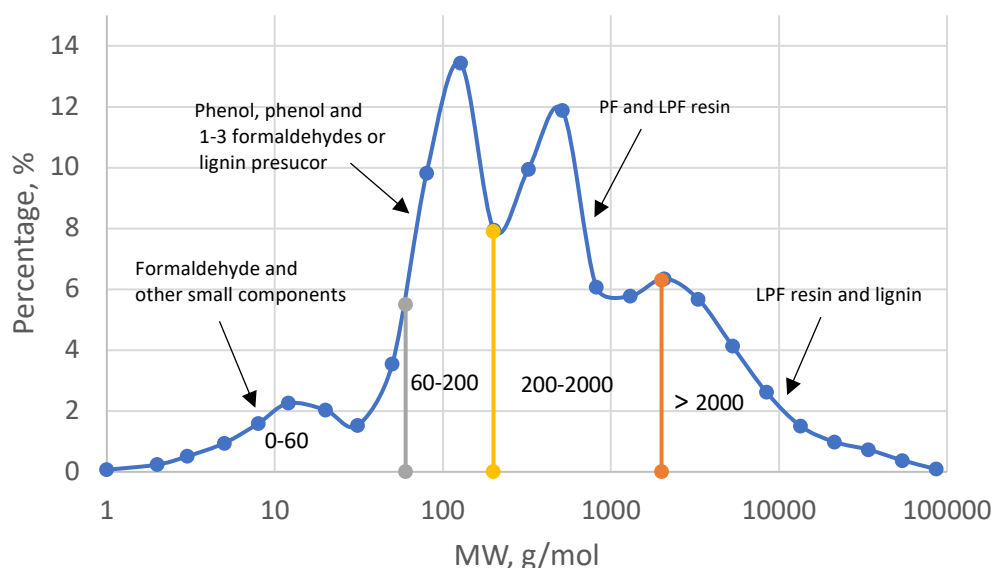


Figure 7. Integrated areas of the molecular weight distribution.

Peaks of molecular weight distributions were integrated into four regions. The first range was integrated onto molecular weight area 0–60 g/mol as it was assumed that this range would

consist of formaldehyde and other small compounds. The second area was limited to a molecular weight in the range of 60–200 g/mol, because in this range phenol, the structure of one phenol and 1–3 formaldehydes and lignin precursors are located. The third range was limited to a molecular weight between 200–2000 g/mol because our reference PF resin measured with the same device and columns had only very small content of components with higher molecular weight than 2000 g/mol (Figure 8). According to Hashimoto & Hisaho (2020) the PF resin has limited amount of components above this molecular weight range. It can also be seen from Figure 8 that the majority of the lignin is above the molecular weight of 2000 g/mol.

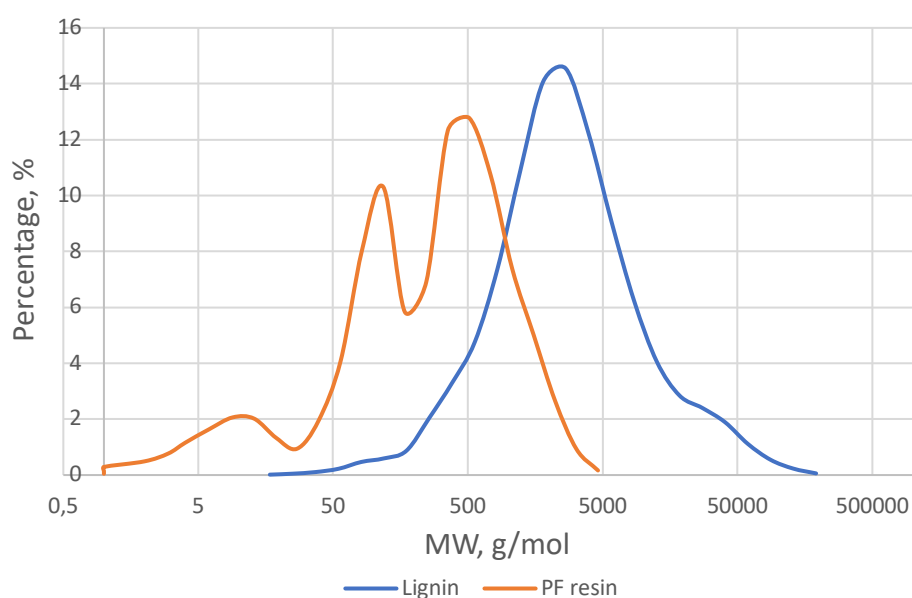


Figure 8. Phenol-formaldehyde resin and lignin molecular weight distributions.

5. Results

This section complies the results of thesis and discusses the differences between MWD of the lignin and LPF resins. The calculated correlations between MWD of the LPF resins, resins' production parameters and measured properties of the resins are also presented. The results are critically reviewed and based on the results suggestions are presented for the future research.

Suitable literature sources were searched using Google Scholar and Scopus. The used keywords were molecular weight of lignin and lignin-phenol-formaldehyde resin. In this thesis was also searched information about the molecular weight distributions of lignin, phenol, formaldehyde,

PF resin, and LPF resin. In addition, were searched previous studies about correlations between LPF resin and its properties.

Kalami et. al (2018) investigated correlations between resin and lignin properties. The starting point of this study was slightly different from this thesis. Resins were produced by using lignins from different plants and processes and the study focused on understanding the effect of different lignin structures and their properties on resins. The LPF resins in this thesis were produced by using lignin from Kraft process that is separated by using LignoBoost process.

5.1. The typical molecular weight distributions of LPF resins with a different substitution rates

The molecular weight distribution of the LPF resin type A that is studied in this bachelor thesis is spread over a relatively wide molecular weight range. Four peaks can be distinguished from the distribution. The average molecular weight of sharpest and highest peak is in the range of 100 g/mol. The first points of the MWD curves are observed in the molecular weight range 1–4 g/mol, which are from the chemical point of view really low values taking into account that the molecular weight of carbon is 12 g/mol. The largest components have the molecular weight from 80,000 to 250,000 g/mol, depending on the sample. This may be due to the heterogeneity of lignin and that the length of the lignin containing polymer chains may vary in different LPF resins.

It can be seen from Figure 9 that the proportion of the components with a higher molecular weight increases (>1000 g/mol) as the lignin substitution rate increases. The location of the peaks does not change much compared to PF resin and lignin as it can be seen by comparing Figures 8 and 9. This can be sign of that polymerizable lignin is visible in this area. One notable difference between LPF and PF resin curves is that the content of small molecules (MW 0–200 g/mol) is higher in LPF resins. Difference is very clear but the reason for this behavior was not found from the literature.

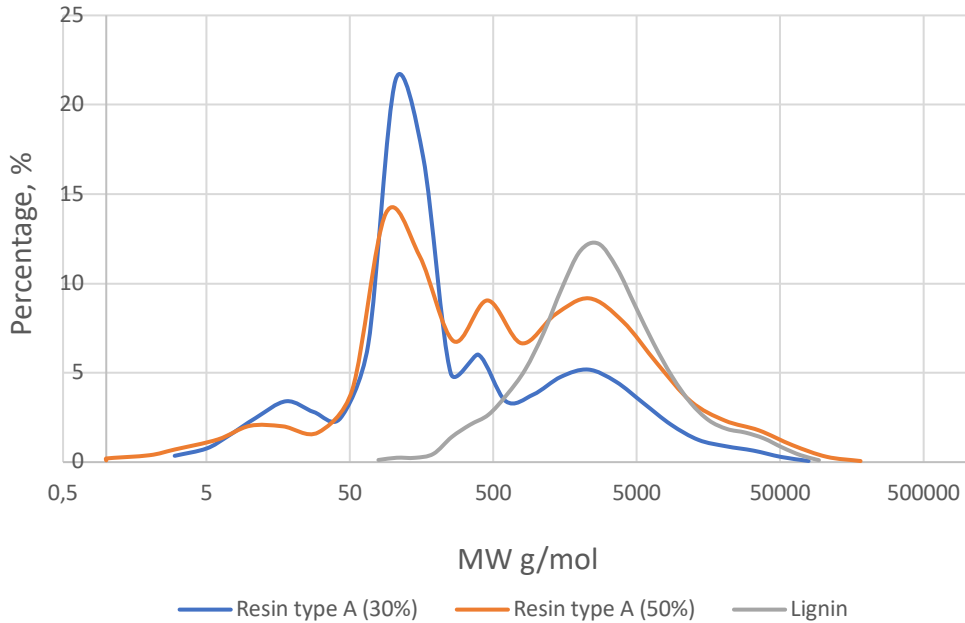


Figure 9. The typical molecular weight distribution of the LPF resin types A when the phenol substitution rates are 30 % and 50 % and lignin.

Figure 9 shows the molecular weight distributions of the two previous resins and the lignin used in their preparation. The fourth peaks of the resin distributions and the peak of the lignin distribution are overlap. When comparing the heights of these peaks, it can be seen that the highest point of the lignin distribution is at 2050 g/mol, which is slightly lower value than that of the resins. (2329 g/mol and 2396 g/mol) From this it can be concluded that the polymerization of formaldehyde and phenol with lignin takes place in this range of the MWD. On the other hand, the width of the LPF resin with 50 % phenol substitute rate distribution increases over a larger molecular weight range. The content of very large polymers of both resins are higher than that any of the raw materials. This also suggests that lignin reacts with formaldehyde and phenol at this point. It is worth noting, however, that this graph compares the molecular weight distributions of non-activated lignin and LPF resins. The fact that the molecular weight distribution of lignin and the fourth peak of the resin are located at the same area may also possibly indicate that part of the sample is free lignin, which is not chemically bound to formaldehyde or that the lignin had limited reactivity with formaldehyde and phenol. On the other hand, the lignin in this distribution, has not treated with NaOH, so it cannot be seen from this Figure how the molecular weight distribution would change as a result of this treatment.

Three peaks of LPF resins at 30 g/mol, 100 g/mol and 400–500 g/mol are located in the same areas than the peaks of PF resin. The molecular weight 30 g/mol and 100 g/mol are small, compared lignin and its precursors. Content of LPF resin having molecular weight below 200 g/mol can be up to 46 %. Based on this information it is possible that some of reacted formaldehyde and phenol are not connected to lignin.

5.2. The differences with Molecular weight distributions of lignin

Figure 10 shows the differences in the molecular weight distributions of two lignins that are separated in a similar process. It can be notice that the distribution values can differ relatively much. It can be seen that the peak values of MWD curves are close to each other, but Lignin 1 has much higher PD that Lignin 2.

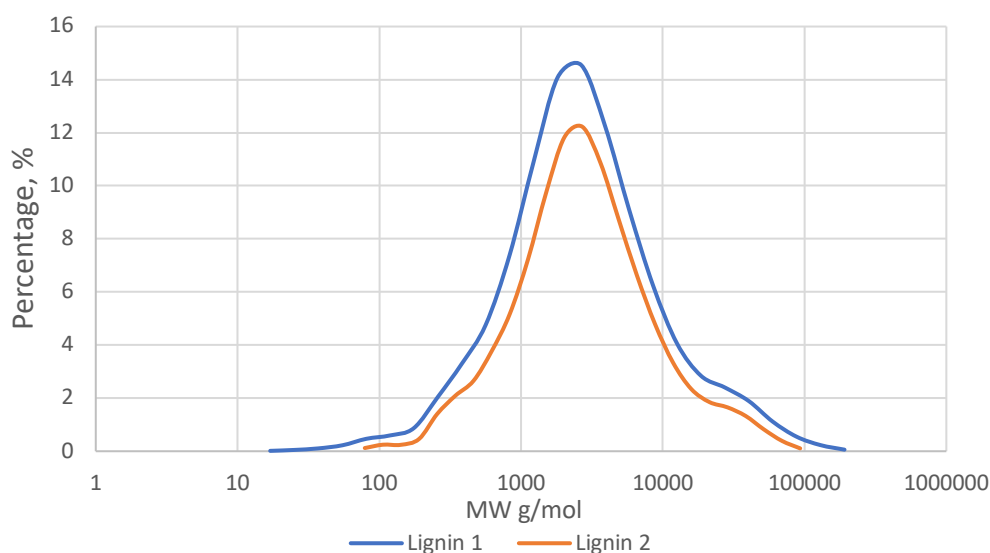


Figure 10. MWD of two lignin which have been separated in a similar process.

5.3. Correlations between molecular weight distributions and production parameters and measured properties

The Table 4 shows the correlation coefficients (R^2) of LPF resin type A between different production parameters, resin properties and molecular weight distributions. Variables between which a significant linear correlation can be noticed are highlighted with color. One noteworthy correlation is formed between the degree of phenol substitution and the proportion of

components with a molecular weight above 2000 g/mol. Content of components with MW higher than 2000 g/mol increased with lignin content. This supports the previously presented result that the fourth peak of the distribution would describe the LPF resin and possible free lignin. A similar comparison could not be done for the second resin (Table 5) because the lignin substitution rate of those resins was the same (50 %). Temperature, reaction time and viscosity did not show correlation with MWD. (Christiansen 1985; Pang et al., 2017) have previously noticed a correlation between molecular weight and viscosity. Nonetheless, this is understandable in the case of this studied resins, because often viscosity is the target value for the resin and all resins had very similar values. On the other hand, if the temperature is lower, a longer reaction time is needed. Also at the same time many other process parameters can be changed, which may have higher effect on MWD than time or temperature. Dry content of the resins can differ and that can also explain why there is no correlation.

Table 4. Correlation coefficients between molecular weight distributions of LPF resin type A, the production parameters and measured properties.

		Molecular weight distribution										
		Mn	Mw	Mz	Mz+1	PD	0-60	60-200	200-2000	>2000	0-200	60-2000
Process parameters	Lignin content	0,55	0,79	0,63	0,59	0,01	0,79	0,77	0,12	0,93	0,57	0,88
	Temperature	0,45	0,30	0,29	0,27	0,03	0,20	0,02	0,05	0,10	0,07	0,06
	Time	0,45	0,30	0,29	0,27	0,03	0,20	0,02	0,05	0,10	0,07	0,06
	Visco	0,02	0,00	0,00	0,01	0,04	0,05	0,11	0,03	0,05	0,09	0,07
Resin properties	Formaldehyde	0,35	0,20	0,11	0,09	0,20	0,20	0,04	0,03	0,12	0,02	0,08
	Phenol	0,80	0,70	0,46	0,44	0,22	0,92	0,77	0,01	0,76	0,85	0,60
	B-time	0,59	0,77	0,57	0,52	0,03	0,81	0,75	0,08	0,87	0,44	0,79
	pH	0,54	0,27	0,13	0,11	0,09	0,21	0,08	0,00	0,19	0,12	0,01
	Alkanity	0,03	0,01	0,04	0,05	0,20	0,12	0,07	0,20	0,25	0,09	0,27
	Dry content	0,85	0,66	0,46	0,42	0,04	0,67	0,43	0,06	0,59	0,53	0,48
	B-time	0,59	0,77	0,57	0,52	0,03	0,81	0,75	0,08	0,87	0,44	0,79

Another interesting correlation can be observed between the portion of the free phenol and the material with a molecular weight of less than 60 g/mol. Initially, it was assumed that a better correlation would have been formed between the MW 60–200 g/mol portion, taking into account the molecular weight of phenol (94.11 g/mol) and because there was a clear peak in this area. However, a positive but smaller correlation can also be observed between the higher molecular weight range (60–200 g/mol) and the phenol content. With successful calibration of the analyzer, the compounds should be separated at the same time as those compounds having the same size hydrodynamic radius, i.e. practice the same molecular weight have the same retention time. On the other hand, it is noteworthy that the device is calibrated with polymer compounds with a high molecular weight, so its calibration accuracy may not be so good for small compounds. This could explain the better correlation of phenol with the fraction having

MW below 60 g/mol and that the content of very small molecules is not zero. This correlation is also good with LPF resin type B (Table 5).

Table 5. Correlation coefficients between the molecular weight distribution of LPF resin type B, the production parameters and the measured properties.

		Molecular weight distribution										
		Mn	Mw	Mz	Mz+1	PD	0-60	60-200	200-2000	>2000	0-200	60-2000
Process parameters	MR	0,22	0,00	0,01	0,00	0,59	0,68	0,43	0,49	0,02	0,50	0,01
	NaOH	0,03	0,05	0,10	0,06	0,35	0,36	0,14	0,49	0,02	0,19	0,12
	Temperatu	0,02	0,00	0,00	0,01	0,01	0,11	0,05	0,06	0,00	0,06	0,00
	Time	0,29	0,05	0,00	0,00	0,85	0,67	0,62	0,38	0,10	0,66	0,01
	Viscosity	0,06	0,00	0,00	0,00	0,06	0,08	0,06	0,07	0,00	0,07	0,00
Resin properties	Formaldeh	0,15	0,00	0,02	0,00	0,60	0,62	0,46	0,54	0,02	0,52	0,01
	Phenol	0,30	0,02	0,00	0,00	0,77	0,90	0,68	0,57	0,07	0,76	0,00
	B-time	0,00	0,62	0,54	0,75	0,14	0,08	0,18	0,29	0,67	0,14	0,51
	pH	0,00	0,17	0,28	0,25	0,56	0,51	0,12	0,69	0,13	0,22	0,28
	Alkanity	0,49	0,00	0,05	0,04	0,55	0,54	0,26	0,38	0,04	0,34	0,32
	Dry conten	0,20	0,02	0,00	0,00	0,61	0,69	0,57	0,43	0,07	0,62	0,00

It was assumed that there would be correlation between free formaldehyde and compounds with a molecular weight 0–60 g/mol because the molecular weight of formaldehyde is 30.03 g/mol. However, in the case of LPF resin type A, no correlation is formed (0.2) but it is surprising that the correlation is better with LPF resin type B (0.62). On the other hand, it should be noted that some of the measured resin samples have too high formaldehyde content, compared to the permitted standard values, which can explain why there is no correlation between resin type A. Also the content of free formaldehyde was modified by adding urea which will affect the results.

It was expected that both M_w and the proportion of compounds which molecular weight is > 2000 g/mol is correlate with B-time. The B-time describes the curing rate of the resin and it is known that the curing time decreases with increasing average length of polymer chains. Correspondingly, higher molecular weight compounds (LPF resin structures and lignin) are these compounds with longer chain structures which result in faster curing. One interesting correlation can be found between the molecular weight range of 0–60 g/mol and M_n . This is possibly due to the fact that the low molecular weight range contains numerically more small compounds, such as a free phenol or formaldehyde.

6. Conclusions

This bachelor's thesis studies correlations between molecular weight distributions of two LPF resin types and production parameters and measured properties. The literature section reviews

the chemical composition of wood and especially the structure and properties of lignin which is used in resins. A comparison of the chemical similarities of the lignin and phenol has been made to support the experimental section. In this section has been combined information about resin types, its manufacture and polymerization. In addition, information about methods to measure molecular weight of lignin and LPF resins has been collected and the SEC which is used in this thesis is presented in more detail.

In the experimental section peaks of MWD were integrated into four areas. The correlations between MWD and production parameters and measured properties were determined by plotting parameters as a xy -graph and defining the correlation coefficients. One good correlation can be noticed between the portion of lignin and the proportion $MW > 2000$ g/mol from which it could be concluded that the fourth peak describes LPF resin and lignin. The proportion of components with a higher MW correlates with the increasing content of lignin. B-time, which describes the curing time of resin also correlated with a higher MW. This makes sense because the faster curing occurs in samples containing longer molecular structures. This finding was also supported by literature.

One noticed correlation is between free phenol content and MW 0–60 g/mol. In turn, the measured free formaldehyde content did not correlate with this MW area. This may possibly be explained by the fact that there is a variation between the free formaldehyde concentrations. There was also resins which free formaldehyde content that was too high compared to the standard. Other interesting correlation was between M_n and MW area 0–60 g/mol. Even the content of small molecules is low, the number of them is very high. This easily decreases M_n . One interesting finding was that the content of small molecules (MW 0–200 g/mol) was higher in LPF resins than PF resins. Reason for this was not found and it could be studied further.

When we are looking critically at the above results, it should be remembered that testing has been done on a limited number of samples that can cause errors in the results. It is worth of mentioning that resins and the measurements are done with relatively long time period. This may have had an effect on the raw materials, resins and results. It is also always possible that a human error has happened in the processing of the results.

During this thesis, further research ideas was found and could be studied if there is time and other resources. First, it would be interesting to study in more detail how activation and heating

of lignin affects its MWD. The lignin could be treated by heat and soluble NaOH and then measure MWD of this lignin samples. In addition, the content of phenol and formaldehyde could be studied by measuring the molecular weight distributions of pure compounds. However, these are quite harmful chemicals, so compounds of similar molecular weight could be better for this purpose. Examples of compounds which have quite similar molecular weights and chemical structure are benzyl alcohol and methanol. This could provide more information on the low MW area and be used to improve the accuracy of the calibration.

Another considered issue during this thesis was, whether the molecular weight distribution describes the whole resin or whether it is possible that the sample is not completely soluble in the NaOH eluent and be separated during resin filtration. The accuracy of the calculation could be increased by increasing the number of measurement points (now 25).

The chemometric PLS method could also be used to study correlations. Gosselink et al., 2010 have used this method to study correlations between molecular weight distributions of lignin and binder properties. The method has also been used to study the effects of different pretreatments on the amount of wood extract lignin and molecular weight distributions. (Strand et al., 2014) The method is suitable for handling large amounts of data when detecting correlations is challenging. For this method it would be good to have higher number of samples with production parameters.

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