Characterization of Natural and Technical Lignins using FTIR Spectroscopy

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MASTER THESIS
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ABSTRACT

Characterization of lignins is an extremely difficult task because of their diversity in respect both to source and extraction method. In the present work, the possibility to use infrared spectroscopy instead of chemical analysis to characterize the changes in the functional groups of lignin during cooking was evaluated and a library of infrared spectra from different lignin samples was created.

Lignin samples from different sources were obtained under different cooking conditions and the structure of the functional groups of the samples were determined by both chemical methods and infrared spectroscopy. Two different types of cooking procedures were carried out resulting in 24 lignin samples. The changes in the functional groups during cooking were determined and analysed and the results obtained with chemical- and spectroscopic methods were compared.

The results of the work shows that, with the methods employed in the present work, it is not possible to use infrared-spectroscopy instead of chemical analysis to characterize the changes in the functional groups of lignin during cooking.

KEYWORDS: lignin, FTIR spectroscopy, functional structure.
1 INTRODUCTION

1.1 Wood composition and chemical treatment

Wood is a widely used renewable natural resource and is for example the main raw material for the pulp and paper industry. Wood can be described as a matrix material consisting of cellulose (45 – 55 %), hemicelluloses (25 – 30 %), lignin (20 – 30 %) and extractive substances (1 – 3 %) [1].

Paper is basically produced from cellulose and hemicelluloses. It is therefore necessary to liberate the cellulose and hemicellulose fibres from the lignin matrix. This is termed cooking and is done by treating the wood in a alkaline or acidic solution at high temperatures examples of processes may be kraft (chemicals are Na\textsubscript{2}S, NaOH and water), sulphite (chemicals are H\textsubscript{2}SO\textsubscript{3} and water), soda (chemicals are NaOH and water). The aim of every cooking is to remove the lignin from cellulose and hemicelluloses fibres, since the lignin acts as a glue between the fibres.

Wood can be divided into two groups i.e. soft wood (ex. pine, spruce) and hard wood (ex. birch, aspen). On average softwood contains about 28-30 % of lignin whereas hardwood contains 18-24 %.

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Wood can be divided into two groups i.e. soft wood (ex. pine, spruce) and hard wood (ex. birch, aspen). On average softwood contains about 28-30 % of lignin whereas hardwood contains 18-24 %. The extracted lignin may either be withdrawn and further processed into valuable chemicals or burnt for energy production. Lignin coming from sulphite pulping is commonly used as e.g. additive in building and structural mixtures (additives for cast iron production), in addition vanillin may be produced from lignin. Lignin from kraft pulping is burned in order to get energy. Lignin may also be used as antioxidant [1, 2, 3].

Nowadays there is a great interest in studying the lignin properties and structure of lignin. This can be explained by the number of lignin applications. The knowledge of the lignin properties and structure are important to:
- develop new pulping and bleaching methods;
- obtain new chemicals based on lignin compounds;
- use lignin in industry without additional chemical modification.

1.2 Lignin

1.2.1 General

Lignin has a complex structure that can be vaguely described as a mixture of branched polymers, having similar structure. The lignin macromolecule is built of polyphenyl propane units, see
Different plants contain lignins with small differences in their chemical structure. Lignin, obtained from the same source but under different conditions may also show different structures and properties. At the same time all kinds of lignin contain similar functional groups. Softwood lignin is built of guaicyl propane units which include a methoxyl group which is bonded to the third carbon atom of the aromatic ring, for labelling, see figure 1. Hardwood lignin is built of guaicyl propane units and syringyl propane units. Syringyl propane units have methoxyl groups which are bonded to the third and the fifth carbon atom of the aromatic ring [2, 3].

According to Freudenberg’s formula, natural lignin contains the following functional groups: methoxyl, phenolic hydroxyl, primary and secondary aliphatic hydroxyl, ketone and aldehyde groups [2, 3].

Depending on method of isolation and chemical treatment, new functional groups not present in natural lignin may appear.
1.2.2 *Functional groups*

**METHOXYL GROUPS**

Methoxyl groups (-OCH₃) are found in lignin from all plants [3]. The amount of the groups depends on plant species and on method of isolation. In general, the content of methoxyl groups found in softwood and hardwood are 0.92 and 0.94 per 1 phenyl propane unit respectively [1, 2, 3].

The amount of the metoxyl groups is often used as a criterion of the purity of lignin preparation, since isolated lignins sometimes are contaminated with hydrocarbons [3].

**HYDROXYL GROUPS**

There are primary aliphatic hydroxyl groups (bonded to the γ-C-atom), secondary aliphatic hydroxyl groups (bonded to the α-C-atom) and phenolic hydroxyl groups (bonded to the 4-C-atom of the aromatic ring) in lignin. On average, lignin contains 0.2 primary aliphatic hydroxyl groups per 1 phenyl propane unit, 0.84 secondary aliphatic hydroxyl groups per 1 phenyl propane unit and 0.30-0.35 phenolic hydroxyl groups per 1 phenyl propane unit [2, 3]. However, the accurate determination is difficult since they have very similar chemical properties and reactivities.

**CARBOXYL GROUPS**

Natural lignin also contains a low amount of COOH-groups, about 0.05 per 1 phenyl propane unit [2, 3]. Further carboxyl groups are produced during delignification as a result of oxidisation of hydroxyl and carbonyl groups. After alkaline delignification the amount of carboxyl groups may reach 0.15-0.16 per 1 phenyl propane unit. The increase of the COOH-groups results in an increase of the hydrophilicity of lignin. Carboxyl groups are able to connect to other functional groups via H-bonds which may result in increased lignin macromolecule netting [4].

**CARBONYL GROUPS**

According to Freudenberg’s lignin formula, the number of carbonyl groups are lower than other oxygen-containing groups. The total amount of carbonyl groups in lignin is about 0.21 per 1 phenyl propane unit. However, these can be of four different kinds, there are a few aldehyde
groups at the γ-C-atom (0.04 per 1 phenyl propane unit) [2, 3]. The rest of the carbonyl groups (about 0.17 per 1 phenyl propane unit) are ketonic groups. 0.07 groups per 1 phenyl propane unit are located at α-C-atom and 0.1 groups per 1 phenyl propane unit are located at β-C-atom. In addition, lignin contains also a few quinonic groups [2, 3].

Strongly modified, especially oxidized lignin, can also contain other types of carbonyl groups.

1.3 Fourier Transform Infrared Spectroscopy

1.3.1 Principles of molecular spectroscopy

All spectroscopy methods are based on the interplay of electromagnetic radiation with a medium or the measurement of radiation emitted from the medium [5].

Electromagnetic radiation can be characterized by its energy $E$ (J), wavelength $\lambda$ (µm), frequency $\nu$ (Hz) or wavenumber $\tilde{\nu}$ (cm$^{-1}$) – the number of waves per unit of distance.

There are related to each other through:

$$E = h \cdot \nu = \frac{h \cdot c}{\lambda} = h \cdot c \cdot \tilde{\nu},$$

where $h$ is Plank’s constant ($6.63 \cdot 10^{-34}$ J·s), and $c$ is the velocity of the radiation in vacuum ($2.9979 \cdot 10^8$ m/s).

Infrared radiation is electromagnetic radiation which covers the wavenumbers between 13300 cm$^{-1}$ and 3.3 cm$^{-1}$. The infrared region is usually divided into 3 regions: near-infrared ($13300 – 4000$ cm$^{-1}$), middle-infrared ($4000 – 200$ cm$^{-1}$) and far-infrared ($200 – 3.3$ cm$^{-1}$) regions. Organic compounds have fundamental vibration bands in the mid-infrared region, which is why the region is widely used in infrared spectroscopy. An infrared spectrum is unique to each substance and can hence, in principle, be used as an unbiased characteristic to identify the sample.

When radiation passes through a sample, part of the radiation may be absorbed by the sample provided that there is a change in the dipole moment during the vibration. By definition, the transmittance is the ratio of the intensity of the transmitted beam to that of incident beam, as shown in figure 1 and Eq. 1 [6].
Concentration of sample: \( C \)

\[ \text{Incident beam: } I_0 \quad \text{Transmitted beam: } I_t \]

Length of optical path

Figure 1. Definition of transmittance

\[ T = \frac{I_t}{I_0} \times 100 \%, \quad (1) \]

1.3.2 Fourier Transform Infrared Spectroscopy

The infrared spectrometers can be divided into 2 groups: dispersive infrared spectrometer (IR) and Fourier transform infrared spectrometers (FTIR).

In a dispersive IR spectrometer, a grating type monochromator is used to disperse the radiation of a polychromatic source into different spectral elements, which are then measured by detector, one element at the time. This makes sampling tedious and since only a small portion of the radiation is measured at each time, the signal intensity is rather weak. In an FTIR spectrometer an interferometer is used to generate an interferogram. In an FTIR instrument, all wavelengths are measured simultaneously which results in faster sampling and in better signal to noise ratio as compared to dispersive instruments. The most commonly used interferometer is the Michelson interferometer, as shown in Figure 2. The interferogram is subsequently Fourier transformed yielding the spectrum, see Figure 3 [5, 6, 7].

Figure 2. Construction of Michelson Interferometer
1.4 Interpretation the lignin infrared spectra

Infrared spectroscopy has been widely used for identification in lignin preparation since the 1970s [8]. Infrared spectra of lignin were recorded and partially interpreted for the first time by Johnson in 1948 [8].

There are about 20 main asymmetric absorption bands, which are typical for high-molecular compounds with irregular structure. Spectra differ from each other in band’s intensity, but the number of bands and their frequencies are similar [3].

Every lignin IR spectrum has a strong wide band between 3500 – 3100 cm\(^{-1}\) assigned to OH stretching vibrations. This band is caused by presence of alcoholic and phenolic hydroxyl groups involved in hydrogen bonds [3, 8]. The intensity of the band increases during demethylation and decreases during methylation since during demethylation the O-CH\(_3\) bonds in methoxyl groups bonded to 3-rd or 5-th carbon atom of the aromatic ring are split and CH\(_3\) is replaced by a hydrogen atom producing a new OH group. During methylation the O-H bonds are split and H is replaced by CH\(_3\) group and amount of OH groups is decreasing hence intensity of the band is decreasing [9, 10]. Acetylation of the lignin causes a partial or full band loss since almost all OH groups is replaced by CH\(_3\)COO [11].

Hergert assigned bands at 2920 and 2850 cm\(^{-1}\) to C─H stretching vibrations of the methoxyl group [12]. Spectra of lignin show no absorption bands in the 2800-1800 cm\(^{-1}\) wavenumber range [3, 8 - 12].

Absorption bands caused by stretching vibrations of carbonyl groups are located in the 1765-1615 cm\(^{-1}\) wavenumber range [12, 13]. By analysing the spectra of lignin model compounds, Hergert concluded that the absorption band located at 1660 cm\(^{-1}\), originated from a ketone group located at α-position, see figure 1, and that the absorption band located at 1712 cm\(^{-1}\) emanates from a ketone group located at β-position [13].

The absorption band at 1660 cm\(^{-1}\) is referred to conjugated carbonyl groups since it disappears after reduction with sodium borane, whereas the absorption band at 1720 cm\(^{-1}\) does
not. The absorption band at 1720 cm\(^{-1}\) is assigned to carboxyl groups since it disappears after reduction with lithium aluminium hydrate [13, 14].

Stretching vibrations of C═C bonds are found in the 1608-1626 cm\(^{-1}\) region. Deformation vibrations of C—H bonds related to double bonds are normally located in the region 988-960 cm\(^{-1}\). The absence of absorption bands at 1626-1608 cm\(^{-1}\) and low intensity of the band at 970 cm\(^{-1}\) indicates that lignin has a small amount of C=C double bonds [12].

Absorption bands located around 1600 cm\(^{-1}\) and 1500 cm\(^{-1}\) are related to vibrations of aromatic rings present in lignin [9, 12, 15, 16]. IR spectra of some lignin samples contain a week absorption band at 1585-1580 cm\(^{-1}\), assigned to aromatic rings, conjugated with \(\alpha\)-carbonyl group.

As regarding absorption bands at 1465 cm\(^{-1}\) and 1420 cm\(^{-1}\), there is not consensus concerning their assignment. Kudzin and Nord relate the absorption band at 1420 cm\(^{-1}\) to deformation vibrations of the CH-group in the aromatic ring [15]. On the other hand, Duri reported that the absorption band at 1420 cm\(^{-1}\) relates to symmetric bending vibrations of C-H bonds in metoxyl groups, whilst the band at 1465 cm\(^{-1}\) was assigned to both CH\(_2\)-, and OCH\(_3\)-groups [9].

It was shown, that the intensity of the absorption band at 1460 cm\(^{-1}\) showed no changes during methylation, demethylation and acetylation of lignin, hence the band has been assigned to deformation vibrations of CH\(_2\)-groups[12, 16]. On contrary, the band at 1420 cm\(^{-1}\) disappeared during demethylation of lignin, and the spectra of the acetylated lignin samples with methoxyl groups, contain 2 absorption bands at 1420 cm\(^{-1}\) and 1455 cm\(^{-1}\), that is why absorption band at 1420 cm\(^{-1}\) is related to methoxyl groups, and absorption band at 1455 cm\(^{-1}\) is related to CH\(_3\) in acetyl groups [10, 17].

Sarkanen related the band at 1450-1420 cm\(^{-1}\) to aromatic ring vibrations [18]. Skurihin has related the absorption band at 1430 cm\(^{-1}\) both to asymmetric deformation vibrations of C—H bonds in methoxyl groups and to vibrations of the aromatic ring [19].

Interpretation of the spectra in the 1400-1000 cm\(^{-1}\) wavenumber region show no less contradictions in their assignments. By studying the spectra of deuterated guaiacol and its derivatives, Lindberg made the conclusion that the absorption bands at 1360 and 1210 cm\(^{-1}\) are caused by vibrations of phenolic hydroxyls [20]. Studies of lignin model compounds made it possible to assign the absorption bands at 1380 and 1340 cm\(^{-1}\) to phenolic hydroxyls and absorption bands at 1365 cm\(^{-1}\) to symmetric deformation vibrations of C—H in metoxyl groups [21]. Pilipchuk observed an intensity increase of the absorption bands at 1370 cm\(^{-1}\) in the spectra of methylated and acetylated lignin samples while the bands are absent in the demethylated
lignin spectra. Hence the absorption bands were assigned to symmetric deformation vibrations of C─H in metoxyl groups [17].

The intensity increase of the absorption band between 1240-1210 cm\(^{-1}\) in the spectra of methylated and acetylated lignin allows to relate the band to asymmetric stretching vibrations of the C─O─C linkages in ethers and esters or to phenolic hydroxyls [10, 22].

By using the deuteration method, Kavamura and Higushi assigned the absorption bands observed at 1210 cm\(^{-1}\) as related to phenolic hydroxyls [23]. Hergert related the absorption band at 1265 cm\(^{-1}\) to asymmetric vibrations of the C─O─C linkages in methoxyl groups [12], while Duri assigned the band to phenolic ether linkages, because methylation and oxidation of lignin has no effect on the intensity of the band [9].

On the other hand, Pilipchuk reports that there is no absorption band in the 1280-1260 cm\(^{-1}\) region in the spectra of the acetylated lignin samples. The absence of the band conflicts with the band relation to ether linkages vibrations and to methoxyl groups vibrations [22].

Hergert reports, after having studied model compounds, that the bands at 1190, 1125 and 1031 cm\(^{-1}\) originates from methoxyl groups and the bands at 1090-1075 and 1040 cm\(^{-1}\) emanates from primary and secondary alcoholic groups [12].

By studying spectra of treated lignin (acetylated, methylated, oxidated), Duri assigned the bands at 1130, 1115 and 1030 to stretching vibrations of the C─O bonds in aliphatic alcohols and aliphatic ethers [9]. Further, it was found that the band at 1030 is caused by primary alcoholic and aliphatic ethers groups and that the band at 1115 is caused by ether linkages adsorption.

Sarkanen assigned the absorption bands at 1160 and 1040 to deformation vibrations of the C─H bonds on benzene rings [18].

The bands at 1100, 1072 and 1033 might be caused by vibrations of C─O bonds in primary and secondary alcoholic groups and the bands at 1130 and 1030 might be caused by dialkyl ether bonds [11, 23].

In the region 900-700 cm\(^{-1}\) absorption bands caused by deformation vibrations of C-H-bonds on the benzene ring are located [12, 20, 23].

1.5 Objective of this work

Characterization of lignin is an extremely difficult task because of their diversity in respect both to source and extraction method. The heterogeneity of lignin is due to the changes in polymer composition, shape and size of the morphological units, crosslinking, nature of the functional
groups, linkage types between various moieties such as phenylpropanoic, p-hydroxyphenyl, guaicyl, syringyl, etc.

The main objective of this work is to evaluate the possibility to use the IR-spectroscopy instead of chemical analysis to characterize the lignin’s functional structure changes and to create a library of infrared spectra from different lignin samples.
2 EXPERIMENTAL

2.1 Instrumentation

Infrared spectra were recorded using an IRPrestige-21 spectrometer, equipped with a deuterated L-alanine + triglycinesulphate (DLATGS) detector. Lignin-in-liquid paraffin emulsion was prepared. A drop of the emulsion was enclosed (sandwiched) between two KBr windows. The sample was subsequently put into the sample compartment of the spectrometer and spectra were recorded in transmission mode. All spectra were recorded in the 4000-400 cm\(^{-1}\) wavenumber range at a resolution of 2 cm\(^{-1}\), by averaging 20 scans.

2.2 Wood cooking

In order to get the lignin samples spruce chips were cooked the chips used were 2-4 cm long, 2-3 cm wide, 0.4-0.6 cm thick. Two methods of wood cooking were carried out: soda cooking and organosolv cooking. For each method, three cookings were carried out. In Soda cooking, water and NaOH (initial concentration 60 g/l) were used as cooking chemicals. In organosolv cooking, water, NaOH (initial concentration 60 g/l) and ethanol alcohol (25 %) were used as cooking chemicals. In all experiments, the wood to chemicals ratio by mass was 1:5. The cooking were carried out in the following way: the chips (dry weight 30 g) where loaded into an autoclave, subsequently the cooking chemicals where added. Thereafter the temperature was raised to 120 °C within 1 hour and then held at this temperature for 30 minutes to impregnate the chips with the cooking chemicals. After impregnation, the temperature was further raised to 165 °C in 30 minutes and kept at this temperature for 5 hours to cook the chips. The first samples were withdrawn 2 hours after the cooking temperature had been reached, after that, samples were withdrawn every hour until the cooking was complete. The lignins were subsequently isolated from the black liquor and from the pulp. To isolate the lignin from the black liquor (dissolved lignin), sulphuric acid was added to the black liquor until the pH reached a value of 3. The then precipitated lignin was washed with water until the pH of the percolate reached 7. Thereafter the lignin was dried at 40 °C under vacuum. The lignin from the pulp (residual lignin) was extracted according to the Pepper method [24] and finally dried at 40 °C under vacuum.

Thus, in total 6 samples of residual soda lignin, 6 samples of dissolved soda lignin, 6 samples of residual organosolv lignin and 6 samples of dissolved organosolv lignin were obtained. The samples were stored in a desiccator at room temperature.
Then infrared spectra of the samples were recorded and characteristics of the samples were determined. Before recording spectra the lignin samples were dried at 40 °C for 30 minutes.

2.3 Samples characterization

Percentages of functional groups (COOH; COOH + OH; CO; OCH$_3$; OH$_{ph}$) were determined with standardized procedures [24].

Relative absorbances (RA) for main absorption bands were calculated according to equation 1, in order to compare changes of functional groups’ percentages with changes of spectra. Relative absorbencies were calculated with respect to absorbance of the absorption band at 1512 cm$^{-1}$. This band was chosen as reference since it is accepted that the number of aromatic rings is constant during the cooking, and therefore the intensity of the 1512 cm$^{-1}$ absorption band caused by the vibrations of the aromatic ring, must be constant. Base line correction was made to calculate the absorbance of the certain absorption band, and absorbance was determined as the peak height [25].

$$RA = \frac{A_{ab}}{A_{1512}} \cdot 100, \%$$  \hspace{1cm} (1)

where $RA$ is the relative absorbance of the absorption band, $A_{ab}$ is the absorbance of the absorption band $ab$, $A_{1512}$ is the absorbance of the reference band at 1512 cm$^{-1}$.

2 parallel experiments were made in order to determine the percentages for each functional group (There was 1 week between them). Results differences were about 2-7 %. The numbers in the tables are arithmetic mean values of the experimental data.

2.4 Materials

Lignins used for the spectra library were isolated and characterized at the research centre of the Institute of chemistry (Komi Republic) (7 – 10 lignins) and at the Institute of chemistry and chemical technology of wood (Archangelsk) (1 – 6, 11 – 15 lignins). Lignins are listed in table 1.
Table 1 – Lignins used for the spectra library

<table>
<thead>
<tr>
<th>Lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Spruce dioxane lignin</td>
</tr>
<tr>
<td>2 Larch dioxane lignin</td>
</tr>
<tr>
<td>3 Hardwood sulphate lignin</td>
</tr>
<tr>
<td>4 Spruce Bjorkman lignin</td>
</tr>
<tr>
<td>5 Pine dioxane lignin</td>
</tr>
<tr>
<td>6 Birch dioxane lignin (1)</td>
</tr>
<tr>
<td>7 Oat stem dioxane lignin</td>
</tr>
<tr>
<td>8 Rye stem dioxane lignin</td>
</tr>
<tr>
<td>9 Birch dioxane lignin (2)</td>
</tr>
<tr>
<td>10 Aspen dioxane lignin</td>
</tr>
<tr>
<td>11 Softwood dioxane ligninine</td>
</tr>
<tr>
<td>12 Residual soda lignin</td>
</tr>
<tr>
<td>13 Dissolved soda lignin</td>
</tr>
<tr>
<td>14 Residual organosolv lignin</td>
</tr>
<tr>
<td>15 Dissolved organosolv lignin</td>
</tr>
</tbody>
</table>

Dioxane lignins were isolated using the standardized Pepper method.
Spruce Bjorkman lignin was isolated with semi mechanical Bjorkman method [24].
3 RESULTS AND DISCUSSION

3.1 Determination the lignins’ characteristics

The lignin’s characteristics are listed in table 2.

<table>
<thead>
<tr>
<th>Lignin</th>
<th>COOH, %</th>
<th>OH\textsubscript{ph}, %</th>
<th>OCH\textsubscript{3}, %</th>
<th>CO, %</th>
<th>(COOH + OH), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spruce dioxanelignin</td>
<td>0.8</td>
<td>3.1</td>
<td>15.8</td>
<td>3.6</td>
<td>3.4</td>
</tr>
<tr>
<td>Larch dioxanelignin</td>
<td>1.6</td>
<td>3.1</td>
<td>12.7</td>
<td>5.4</td>
<td>5.5</td>
</tr>
<tr>
<td>Hardwood sulphate lignin</td>
<td>2.7</td>
<td>-</td>
<td>16.6</td>
<td>2.8</td>
<td>-</td>
</tr>
<tr>
<td>Spruce Bjorkman lignin</td>
<td>0.6</td>
<td>2.7</td>
<td>14.9</td>
<td>2.2</td>
<td>3.0</td>
</tr>
<tr>
<td>Pine dioxanelignin</td>
<td>1.1</td>
<td>-</td>
<td>14.8</td>
<td>5.9</td>
<td>3.1</td>
</tr>
<tr>
<td>Birch dioxanelignin (1)</td>
<td>2.1</td>
<td>-</td>
<td>16.3</td>
<td>7.0</td>
<td>3.4</td>
</tr>
<tr>
<td>Oat stem dioxanelignin</td>
<td>3.8</td>
<td>2.6</td>
<td>15.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Rye stem dioxanelignin</td>
<td>2.2</td>
<td>4.7</td>
<td>15.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Birch dioxanelignin (2)</td>
<td>3.4</td>
<td>1.3</td>
<td>19.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Aspen dioxanelignin</td>
<td>1.5</td>
<td>2.3</td>
<td>19.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Softwood dioxanelignine</td>
<td>0.9</td>
<td>2.2</td>
<td>15.5</td>
<td>4.1</td>
<td>2.6</td>
</tr>
<tr>
<td>Residual soda lignin</td>
<td>0.9</td>
<td>1.9</td>
<td>13.7</td>
<td>3.9</td>
<td>4.6</td>
</tr>
<tr>
<td>Dissolved soda lignin</td>
<td>2.2</td>
<td>1.8</td>
<td>15.3</td>
<td>1.7</td>
<td>3.5</td>
</tr>
<tr>
<td>Residual organosolv lignin</td>
<td>6.0</td>
<td>1.3</td>
<td>12.3</td>
<td>9.1</td>
<td>8.0</td>
</tr>
<tr>
<td>Dissolved organosolv lignin</td>
<td>1.5</td>
<td>1.9</td>
<td>16.3</td>
<td>2.1</td>
<td>3.3</td>
</tr>
</tbody>
</table>

3.2 Lignin IR-spectra library

Recorded spectra are represented in the Appendix 1.

3.3 Interpretation and characterization of lignin spectra

All spectra show typical lignin patterns [2, 3] although some differences in the intensities and widths of the absorption bands are observed. All spectra have a strong wide band in the 3500-3100 cm\textsuperscript{-1} wavenumber range. The band is caused by presence of alcoholic and phenolic hydroxyl groups involved in hydrogen bonds.

The absorption bands located in the 3100 – 2800 cm\textsuperscript{-1} wavenumber range, are caused by vibrations of CH\textsubscript{2}- and CH\textsubscript{3}-groups. However they are covered by the absorption bands from the liquid paraffin used as dilutent.

Differences in the spectra are observed in the area of carbonyl group stretching vibrations (e.g. bands at 1708 cm\textsuperscript{-1} and 1656 cm\textsuperscript{-1}). The intensity of the absorption band at 1708 cm\textsuperscript{-1} is stronger than the intensity of the absorption band at 1656 cm\textsuperscript{-1} in the spectra of residual and
dissolved soda lignin (figure A 12, A 13). On the contrary, the intensity of the absorption band at 1656 cm\(^{-1}\) is larger than the intensity of the absorption band at 1708 cm\(^{-1}\) in the spectra of spruce dioxanelignin, spruce Bjorkman lignin, pine dioxanelignin, birch dioxanelignin, rye stem dioxanelignin, birch dioxanelignin (2), softwood dioxanelignine and dissolved organosolv lignin (figures A 1, A 4, A 5, A 6, A 8, A 9, A 11 and A 15 in Appendix A). The intensities of the absorption bands at 1708 and 1656 cm\(^{-1}\) are equal in the rest of spectra.

Differences in the spectra of softwood, hardwood and plant lignins are also observed in the area of aromatic ring vibrations (bands at 1600 cm\(^{-1}\) and 1512 cm\(^{-1}\)). In the spectra of hardwood and plant lignins the intensities of the absorption bands at 1600 cm\(^{-1}\) and 1512 cm\(^{-1}\) are nearly equal, whereas in the spectra of softwood, the intensity of the absorption bands at 1512 cm\(^{-1}\) is greater than the intensity of the absorption bands at 1600 cm\(^{-1}\) (figure 1).

There are two intense absorption bands in the 1470 – 1370 cm\(^{-1}\) wavenumber range at 1462 cm\(^{-1}\) and 1377 cm\(^{-1}\) which are caused by the absorption of the liquid paraffin. Besides, there are two shoulders on the 1425 cm\(^{-1}\) and 1370 cm\(^{-1}\) band, which are assigned to stretching vibrations of aromatic ring and deformation vibrations of C – H bonds, respectively.

Figure 1 – Differences in the spectra of hardwood, softwood and plant lignins in the 1620 – 1500 cm\(^{-1}\) wavenumber range
1 – softwood lignin; 2 – hardwood lignin; 3 – plant lignin
Significant differences are observed in the spectra of softwood, hardwood and plant lignins in the 1340-1320 cm\(^{-1}\) and 1140-1100 cm\(^{-1}\) wavenumber ranges (figure 2). The absorption bands in this range are caused by the stretching vibrations of syringyl rings (figure 2).

In the spectra of plant lignin the intensities of absorption bands at 1270 cm\(^{-1}\) and 1230 cm\(^{-1}\), caused by the stretching vibrations of guaiacyl rings, are nearly equal. In the spectra of hardwood lignins the intensity of the absorption band at 1270 cm\(^{-1}\) is less than the intensity of the absorption band at 1230 cm\(^{-1}\), in the spectra of softwood lignins the opposite is true.

Deformation vibrations of C – H bonds in the guaiacyl ring (1140 cm\(^{-1}\)) and deformation vibrations of C – O bonds (1080 cm\(^{-1}\)) cause the appearance of peaks in the spectra of hardwood lignin. The peaks are covered by the absorption band caused by the vibrations of syringyl ring. The peaks in the spectra of hardwood lignins are represented as a shoulder on the 1150 cm\(^{-1}\) and 1095 cm\(^{-1}\) bands.

![Figure 2 – Differences in the spectra of hardwood, softwood and plant lignins in the 1350 – 1000 cm\(^{-1}\) wavenumber range](image)

1 – softwood lignin; 2 – hardwood lignin; 3 – plant lignin

An intensive absorption band at 1030 cm\(^{-1}\) (assigned to deformation vibrations of the C – H bonds in the quaiacyl ring and to deformation vibrations of C–O bonds) is very typical for softwood lignin spectra, whereas the absorption band has low intensity in the hardwood lignin spectra (figure 2).
All spectra have absorption bands at 945, 870 – 850 and 781 cm\(^{-1}\), which are caused by the deformation vibrations of C–H bonds in the aromatic ring.

The band located at 721 cm\(^{-1}\) is caused by absorption of the liquid paraffin.

The results of the interpretation of the spectra are summarized in table 3.

<table>
<thead>
<tr>
<th>Absorption band location cm(^{-1})</th>
<th>Type of vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>3500 – 3100</td>
<td>Stretching vibrations of alcoholic and phenolic OH groups involved in hydrogen bonds</td>
</tr>
<tr>
<td>1715 – 1710</td>
<td>Stretching vibrations of C=O bonds at β location and in COOH group</td>
</tr>
<tr>
<td>1665 – 1655</td>
<td>Stretching vibrations of the C=O bonds at α and γ location</td>
</tr>
<tr>
<td>1605 – 1595</td>
<td>Aromatic ring vibrations</td>
</tr>
<tr>
<td>1515 – 1500</td>
<td></td>
</tr>
<tr>
<td>1430 – 1425</td>
<td></td>
</tr>
<tr>
<td>1340 – 1330</td>
<td>Vibrations of syringyl rings and stretching vibrations of C-O bonds</td>
</tr>
<tr>
<td>1272 – 1265</td>
<td>Vibrations of guaiacyl rings and stretching vibrations of C-O bonds</td>
</tr>
<tr>
<td>1225 – 1220</td>
<td></td>
</tr>
<tr>
<td>1140</td>
<td>Deformation vibrations of C-H bonds in guaiacyl rings</td>
</tr>
<tr>
<td>1150 (shoulder)</td>
<td></td>
</tr>
<tr>
<td>1125</td>
<td>Deformation vibrations of C-H bonds in syringyl rings</td>
</tr>
<tr>
<td>1085</td>
<td>Deformation vibrations of C-O bonds in secondary alcohols and aliphatic ethers</td>
</tr>
<tr>
<td>1085 (shoulder)</td>
<td></td>
</tr>
<tr>
<td>1035 – 1130</td>
<td>Deformation vibrations of C-H bonds in the aromatic rings and deformation vibrations of C-O bonds in primary alcohols</td>
</tr>
<tr>
<td>945</td>
<td>Deformation vibrations of C-H bonds in associated to aromatic rings</td>
</tr>
<tr>
<td>870 – 850</td>
<td></td>
</tr>
<tr>
<td>780</td>
<td></td>
</tr>
</tbody>
</table>

### 3.4 Analysis of the functional groups changes during cooking

Percentages of the lignins’ functional groups are represented in tables 4 and 5.

Sample 1 is a sample which was taken after 2 hours of cooking. Sample 6 is a sample which was taken after 7 hours of cooking, the other samples were taken each hour inbetween. The percentages of the functional groups (COOH; COOH + OH; CO; OCH\(_3\); OH\(_{ph}\)) were determined according to the standardized procedures described in section 2.3.
Table 4 – Organosolv cooking

<table>
<thead>
<tr>
<th>group</th>
<th>Percentage</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>residual lignin</td>
<td>dissolved lignin</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>OH*</td>
<td>3.5</td>
<td>4.1</td>
<td>5.4</td>
<td>3.8</td>
<td>5.2</td>
<td>8.0</td>
</tr>
<tr>
<td>COOH</td>
<td>1.9</td>
<td>1.1</td>
<td>2.4</td>
<td>0.9</td>
<td>2.2</td>
<td>6.0</td>
</tr>
<tr>
<td>C=O</td>
<td>2.9</td>
<td>4.2</td>
<td>3.0</td>
<td>7.4</td>
<td>8.6</td>
<td>9.1</td>
</tr>
<tr>
<td>OCH₃</td>
<td>8.2</td>
<td>13.0</td>
<td>11.6</td>
<td>11.8</td>
<td>12.2</td>
<td>12.3</td>
</tr>
<tr>
<td>OHₖh</td>
<td>0.8</td>
<td>1.5</td>
<td>1.5</td>
<td>1.7</td>
<td>1.9</td>
<td>1.3</td>
</tr>
</tbody>
</table>

* OH is COOH + OH

According to the data of table 4, the following changes were observed during the organosolv cooking: The amount of carboxyl groups in the dissolved lignin increases during the first 4 hours of cooking, then it is constant, and finally it decreases by the end of the cooking. The amount of carboxyl groups in the residual lignin seems to fluctuate between 0.9 and 6% during the cooking.

Further, the number of total acid groups (COOH + OH) increases from 3.5 to 5 % during 4 hours of cooking, and then it decreases to 3.2 %.

The amount of carbonyl groups is increasing in both the residual- and dissolved lignins during cooking. The increase is higher in the residual lignin than in the dissolved lignin.

The changes in concentration of methoxyl groups are negligible in the dissolved lignin, whereas in the residual lignin, the amount of methoxyl groups increases during the first 3 – 4 hours of cooking and then it remains constant till the end of cooking. The content of methoxyl groups in the dissolved lignin was 2.5 – 3 % higher than in the residual lignin.

Moreover, the amount of phenolic hydroxyl groups is increasing during the cooking, in both the residual and dissolved lignin. It was further found that the residual lignin contained smaller amounts of phenolic hydroxyl groups at the beginning of cooking than the dissolved lignin, however by the end of the cooking, the amount of phenolic hydroxyl groups was approximately the same in both the residual and dissolved lignin.

During the organosolve cooking, the residual lignin shows a higher amount of carboxyl-, carbonyl- and total acid groups (due to carboxyl groups) than the dissolved lignin. From the data

Table 5 – Soda cooking

<table>
<thead>
<tr>
<th>group</th>
<th>Percentage</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>residual lignin</td>
<td>dissolved lignin</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>OH*</td>
<td>2.7</td>
<td>3.2</td>
<td>4.1</td>
<td>3.6</td>
<td>3.9</td>
<td>4.6</td>
</tr>
<tr>
<td>COOH</td>
<td>1.7</td>
<td>1.5</td>
<td>1.2</td>
<td>0.7</td>
<td>1.4</td>
<td>0.9</td>
</tr>
<tr>
<td>C=O</td>
<td>2.3</td>
<td>2.5</td>
<td>4.6</td>
<td>3.0</td>
<td>3.5</td>
<td>3.9</td>
</tr>
<tr>
<td>OCH₃</td>
<td>8.9</td>
<td>10.2</td>
<td>12.1</td>
<td>13.8</td>
<td>13.5</td>
<td>13.7</td>
</tr>
<tr>
<td>OHₖh</td>
<td>0.9</td>
<td>1.4</td>
<td>1.8</td>
<td>1.6</td>
<td>1.8</td>
<td>1.9</td>
</tr>
</tbody>
</table>

* OH is COOH + OH
for the methoxyl groups’ it can be concluded that the dissolved lignin is more methoxylated than the residual lignin. Due to the lower content of carboxyl- and carbonyl groups in the dissolved lignin it can also be concluded that the dissolved lignin is less oxidized than the residual lignin.

According to the data of table 5, the following changes were observed during the soda cooking: The amount of carboxyl groups in the lignins decreases by the end of the cooking. During cooking, the dissolved lignin contains more carboxyl groups than the residual lignin. Further, the amount of total acid groups increases in the residual lignin, whereas there is no change in the amount of total acid groups’ in the dissolved lignin.

During cooking, the amount of carbonyl groups increases in the residual lignin, whilst the amount of carbonyl groups remains constant in the dissolved lignin.

It can also be seen that the changes of methoxyl groups amount are negligible in the dissolved lignin, whereas the amount of methoxyl groups in the residual lignin increases after 3 – 4 hours of cooking, and then it remains fairly constant till the cooking was completed.

Moreover, it was found that during cooking, the amount of phenolic hydroxyl groups increases in the lignins. It was further found that at the beginning of the cooking, the dissolved lignin contained higher amounts of phenolic hydroxyl groups than the residual lignin, although at the end of the cooking, the amount of phenolic hydroxyl groups were equal in both samples.

The dissolved lignin contains about twice as many carboxyl groups than the residual lignin. The high amounts of carboxyl and total acid groups may be caused by the higher oxidation of carbonyl and hydroxyl groups in the dissolved lignin than in the residual lignin, hence it can be concluded that dissolved lignin is more oxidized than the residual lignin. The figures indicate that the aliphatic hydroxyl groups were oxidized to a greater extent then the phenolic hydroxyl groups since the amount of phenolic hydroxyl groups are approximate equal in the dissolved and residual lignins.

By comparing the data for residual lignin for both organosolv and soda cooking it can be observed that the organosolv residual lignin contains more carboxyl, carbonyl and total acid groups, than soda residual lignin, hence it can be concluded that organosolve residual lignin is more oxidized than soda residual lignin.

By comparing the data for dissolved lignin for both organosolv and soda cooking it can be observed that the organosolv dissolved lignin contains less carboxyl groups, than soda dissolved lignin, and numbers of other functional groups in the lignins are about equal, hence it can be concluded that soda dissolved lignin is more oxidized than organosolv residual lignin.
3.5 Analysis of the relative absorption changes during the cooks

It is very difficult to determine the changes of the lignins’ functional groups percentages from the changes in the IR-spectra. This is due to the absence of absorption bands corresponding only to one functional group. Usually, functional groups take part in different absorption bands and absorption band caused by a certain functional group may be partly covered by the absorption band caused by another functional group.

Relative absorbencies of the main absorption bands are represented in the tables 6 and 7.

Table 6 – Organosolv cooking

<table>
<thead>
<tr>
<th>$\nu$, cm$^{-1}$</th>
<th>Relative absorbance, %</th>
<th>residual lignin</th>
<th>dissolved lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>3420</td>
<td>84 80 77 82 73 192</td>
<td>75 76 77 81 89 74</td>
<td></td>
</tr>
<tr>
<td>1708</td>
<td>71 33 41 35 37 58</td>
<td>41 25 32 37 33 27</td>
<td></td>
</tr>
<tr>
<td>1656</td>
<td>33 31 34 36 30 55</td>
<td>28 26 27 31 29 26</td>
<td></td>
</tr>
<tr>
<td>1597</td>
<td>46 48 58 86 53 65</td>
<td>44 46 49 53 48 54</td>
<td></td>
</tr>
<tr>
<td>1269</td>
<td>130 133 115 119 117 156</td>
<td>146 131 114 113 138 113</td>
<td></td>
</tr>
<tr>
<td>1215</td>
<td>98 105 99 95 94 167</td>
<td>93 101 88 92 109 89</td>
<td></td>
</tr>
<tr>
<td>1139</td>
<td>113 132 118 100 89 162</td>
<td>572 134 107 136 150 90</td>
<td></td>
</tr>
<tr>
<td>1099</td>
<td>130 181 100 102 90 160</td>
<td>98 160 94 128 206 83</td>
<td></td>
</tr>
<tr>
<td>1032</td>
<td>107 109 85 88 81 135</td>
<td>145 112 90 94 117 80</td>
<td></td>
</tr>
</tbody>
</table>

From the table 6 it can be seen that the intensity of the absorption band caused by vibrations of O-H bonds, is decreasing in the spectra of the residual lignin (from 84 to 73 (13,1 %)) and increasing in the dissolved lignin (from 75 to 89 (18,7 %)) during the cooking. The last sample of the residual lignin showed an unexpectedly high value, that could not be explained.

The intensity of the absorption band caused by vibrations of C=O bonds show a complex behaviour. Changes of the bands intensities in the spectra of dissolved lignins on the 1708 cm$^{-1}$ and 1656 cm$^{-1}$ bands are analogous in behavior. Intensities of the bands decrease in the beginning of the cooking, and then the intensities pass through a maximum after 5 hours of...
cooking and decrease at the end of the cooking. Intensity of the absorption band at 1708 cm\(^{-1}\) changes to a greater extent (from 25 to 37 (48 \%)) than the intensity of the absorption band at 1656 cm\(^{-1}\) (from 26 to 31 (19,2 \%)). For the residual lignin, the 1708 cm\(^{-1}\) band passes through a minimum with higher values in the beginning and at the end of the cooking. The intensity of the absorption band at 1656 cm\(^{-1}\) decrease by 3 hours of cooking, and then increases by 5 hours of cooking (from 31 to 36 (16,1 \%)), decreases by the 6 hours of cooking and rises sharply at the end of cooking (from 30 to 55 (83 \%)). The intensity of the absorption band caused by vibrations of aromatic rings increases during cooking in both the residual (from 46 to 65 (41,3 \%)) and the dissolved lignin (from 44 to 54 (22,7 \%)).

From the table 7 it can be seen that there is decreasing of the intensity of the absorption band, caused by vibrations of O-H bonds in the lignin spectra (from 74 to 65 (12,2 \%) for residual lignin, and from 84 to 77 (8,3 \%) for dissolved lignin).

The intensities of the absorption bands caused by vibrations of C=O bonds, are decreasing a lot during the cooking in the residual lignins (from 71 to 29 (59,16 \%) for the 1708 cm\(^{-1}\) band and from 37 to 22 (40,54\%) for the 1656 cm\(^{-1}\) band) and not so greatly in the dissolved lignins (42 to 35 (16,7 \%) for the 1708 cm\(^{-1}\) band and from 33 to 28 (15,2 \%) for the 1656 cm\(^{-1}\) band).

The intensity of the absorption band at 1597 cm\(^{-1}\), caused by vibration of aromatic ring, increases during the cooking (from 45 to 51 (13,3 \%) for residual lignin and from 42 to 54 (28,6 \%) for dissolved lignin).

From the tables, it can be concluded that the changes in relative absorbencies for the bands discussed above seem to have relatively large uncertainties.

3.6 Comparison of changes in lignin functional structure and changes in lignin spectra during cooking

Comparisons were subsequently made between the following absorption bands and functional groups:

- total acid groups (OH + COOH) and absorption band assigned to OH stretching vibrations (3420 cm\(^{-1}\));
- carbonyl groups and absorption band assigned to stretching vibrations of C=O bands at \(\alpha\)- and \(\gamma\)- positions (1656 cm\(^{-1}\))
- carboxyl groups and absorption band assigned to stretching vibrations of C=O bands at \(\beta\) – position and in COOH groups (1708 cm\(^{-1}\))
SODA COOKING

By comparing the changes in the amount of total acid groups determined by chemical methods to the changes in intensity in the corresponding absorption band, it was found that the amount of total acid groups increased whereas the relative absorbance decreased. Thus, similar changes was not observed.

In the comparison of changes in the amount of carbonyl groups and the changes in the respective absorption band, it was observed that the amount of carbonyl groups increased whilst the relative absorbance decreased. Hence, similarity in changes was not observed.

When comparing the changes in the amount of carboxyl groups to the changes of the respective absorption bands for residual lignin, it was found that the number of carboxyl groups decreased, as did the relative absorbance. Thus, similarity in changes was observed.

ORGANOSOLV COOKING

Comparison of the changes in the amount of total acid groups to the changes of respective absorption band revealed that the amount of total acid groups increased whilst the relative absorbance does not change. Hence, similarity in changes was not observed.

When comparing the changes in the amount of carbonyl groups to the changes in the corresponding absorption band it was found that the amount of carbonyl groups increased continuously whereas the corresponding absorption band did not. Thus, similarity in changes was not observed.

Some similarities in behaviour and some totally different results for some of the points was observed when comparing the changes in the amount of carboxyl groups to the changes in relative absorbance of the absorption bands. Thus, it is impossible to use the IR-spectroscopy with used method of samples preparation (lignin-in-liquid paraffin emulsion between two KBr windows) instead of chemical analysis to characterize the lignin’s functional structure changes.
CONCLUSIONS

1) An electronic library of lignin IR-spectra was created. The library can be used to identify and compare lignin spectra.

2) Comparison of the functional structure of the lignins obtained at different conditions shows:
   - that for the soda cooking conditions dissolved lignin is more oxidized than residual lignin;
   - that for organosolv cooking conditions dissolved lignin is less oxidized than residual lignin;
   - dissolved lignin obtained at the soda cooking conditions is more oxidized than dissolved lignin obtained at the organosolv cooking conditions;
   - residual lignin obtained at the organosolv conditions is more oxidized than dissolved lignin obtained at the soda cooking conditions.

3) Comparison between changes of the functional groups amount and changes of the lignin spectra shows that it is impossible to use the IR-spectroscopy with the used method of samples preparation instead of chemical analysis to characterize the lignin’s functional structure changes.
REFERENCES

Appendix 1 *Lignin IR-spectra library*
Figure 1 – IR spectrum of spruce dioxanelignin
Figure 2 – IR spectrum of larch dioxanelignin
Figure 3 – IR spectrum of hardwood sulphate lignin
Figure 4 – IR spectrum of spruce Bjorkman lignin
Figure 5 – IR spectrum of pine dioxanelignin
Figure 6 – IR spectrum of birch dioxanelignin (1)
Figure 7 – IR spectrum of oat stem dioxanelignin
Figure 8 – IR spectrum of rye stem dioxane lignin
Figure 9 – IR spectrum of birch dioxanelignin (2)
Figure 10 – IR spectrum of aspen dioxan lignin
Figure 11 – IR spectrum of softwood dioxanelignine
Figure 12 – IR spectrum of residual soda lignin
Figure 13 – IR spectrum of dissolved soda lignin
Figure 14 – IR spectrum of residual organosolv lignin
Figure 15 – IR spectrum of dissolved organosolv lignin