Characterization and Separation of Lignin from Kraft Black Liquor with Different Alcohols

ABSTRACT • The aim of this study was to investigate the properties of lignin obtained from black liquors of Scots pine (Pinus sylvestris L.) and European aspen (Populus tremula L.) woods cooked by Kraft method. In the study, the cooking process was carried out according to parameters such as: 1/4 of wood/liquor ratio, cooking temperature at (170±2) °C, and cooking time of 90 min. After the cooking process, the black liquor was taken to a beaker from the digester, and lignin was recovered in different ways from the black liquor with methyl alcohol (MeOH) and ethyl alcohol (EtOH). The material properties of the recovered lignin were analyzed by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), x-ray diffraction (XRD), and thermogravimetric analysis (TGA). Commercial lignin (cml-lignin) was used to compare the properties of lignin obtained from black liquor. SEM images showed that the particle sizes of lignin obtained with EtOH and MeOH were similar. In FT-IR, it was detected that the recovered lignin types have similar functional groups, while some differences were observed in intensities of the peaks. XRD results revealed that all lignin types were found to have a similar structure with the cml-lignin, and that alcohol types used during the recovery process of lignin do not have an important effect on the structural properties of lignin. The TGA results indicated that the thermal stability of recovered lignin has better thermal stability than cml-lignin. The results showed that the recovered lignin was similar to commercial lignin and that it can be recovered from the liquor leftover from Kraft pulping by the method described and used in industry.

KEYWORDS: Kraft pulping; black liquor; lignin, recycling; lignin characterization

SAŽETAK • Cilj rada bio je istražiti svojstva lignina dobivenog od crnog luga drva bijelog bora (Pinus sylvestris L.) i jasike (Populus tremula L.), kuhanoga kraft metodom. Proces kuhanja u ovom je istraživanju proveden uz ove parametre: omjer drva i luga 1 : 4, temperatura kuhanja 170 ± 2 °C, vrijeme kuhanja 90 min. Nakon procesa kuhanja crni je lug premješten iz digestora u čašu te je lignin metilnim alkoholom (MeOH) i etilnim alkoholom (EtOH) na različite načine izdvojen iz crnog luga. Svojstva izdvojenog lignina analizirana su skenirajućim elektronskim mikroskopom (SEM), infracrvenom spektroskopijom s Fourierovom transformacijom (FT-IR), difrakcijom X-zraka

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1 INTRODUCTION

The pulp and paper industry is an important sector that produces paper and paper-based materials from biomaterials such as wood, vegetable plants, and other biomass. In the world, many paper mills have manufactured paper products with a chemical pulping technique in huge amounts (Sasaki and Goto, 2008; Zhang et al., 2019; Do et al., 2020). Large amounts of energy, water, and biomass have been used to obtain the pulp/paper, generally without recovering the chemicals after the production of pulp or using recovering systems that are not sufficient to clean the chemical wastes such as black liquor, other cooking solvents, etc. After the pulping process, the chemical wastes are generally discharged to water resources such as rivers, seas, oceans, etc. In order to reduce the waste, they were burned for heat because of the great amount of lignin in chemical wastes (Lateef et al., 2009; Zainab et al., 2018) causing major environmental pollution in many developing countries. The wastewater contains several biomaterials such as lignin, hemicellulose, etc. and efforts have been made to recover the biomaterials in different ways; lignin, as one of the biomaterials, is a commercially important biopolymer (Rydholm, 1965; Sun et al., 1999; Lake and Blackburn 2014).

Lignin is an aromatic amorphous polymer, which is composed of 5 – 500 phenylpropan units and it has a cross-linked structure both with itself and with other elements such as hemicellulose and cellulose. Lignin has several monomers such as sinapyl, coniferyl and coumaryl alcohols according to the wood species (Tomani, 2010; Gordobil et al., 2016; Hubbe et al., 2019). Previous research has been conducted on the recovery of lignin from black liquor with different methods such as alkaline or acidic methods by Sun et al. (1999), Kouisni et al. (2011), Lubis et al. (2012), Kouisni et al. (2012), Ragauskas et al. (2014). Kamble and Bhattacharyulu (2015) investigated the separation and characterization of lignin from black liquor waste by inorganic and organic acids. The obtained results showed that the mixture of phosphoric acid and acetic acids at the reaction temperature of 50 °C was determined as the best chemical for lignin separation. Thermogravimetric analysis results of the obtained lignin showed that lignin from different acids differs significantly in thermal decomposition. In another study, Maitz et al. (2020) studied the preparation and characterization of lignin obtained from black liquor by two methods such as water-washed and acid-washed process. According to the results obtained in previous studies, it was found that acid-washed lignin has a higher molecular weight than water-washed lignin; however, the content of hydroxyl and methyl groups of each lignin was similar to each other. In another study, Sameni et al. (2016) investigated the characterization of lignin isolated from Kraft black liquor. The obtained results showed that the amount of lignin isolated was 27 % of black liquor solids and all types of lignin obtained in different ways were found to exhibit similar physicochemical properties. As a result, the literature review showed that the recovery of lignin, as by-products to value-added materials, is an important issue in obtaining eco-friendly materials and reducing the global warming problems. Consequently, the aim of this research is to isolate the lignin from chemical wastes (named black liquor) of two types of biomass, Scots pine and European aspen woods, with two different solvents such as EtOH and MeOH. The material properties such as thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), x-ray diffraction analysis (XRD), and scanning electron microscopy (SEM) of the recovered lignin were investigated.

2 MATERIALS AND METHODS

2.1 Materials

Scots pine (Pinus sylvestris L.) and European aspen (Populus tremula L.) woods were supplied from a local mill in Bartin City, Turkey. Wood materials were chipped by hand using a hammer and knife. The obtained chips of about 4 cm × 2.5 cm × 1 mm were dried under room conditions (about 25 °C). The cooking process was done in an electrically heated rotary digester. The cooking parameters are given in Table 1.
After kraft pulping, the black liquor was taken from the digester with a beaker as visually presented in Figure 1(A). After Kraft pulping process, the black liquor was taken with a beaker from the digester as shown in Figure 1(A). The top surface of the beaker was covered with a paraffin film and stored in a dark cabinet.

Commercial lignin (cml-lignin) was supplied from Canadian Lignin Inc. for comparison with lignin from black liquor.

### 2.2 Recovery process of lignin

In this study, lignin was obtained by precipitating with MeOH and EtOH. 10 mL black liquor was added to 50 ml beaker, and four different beakers were prepared to isolate the lignin from Kraft black liquor of pine and aspen wood with MeOH and EtOH. The solutions were put on a heater plate at 100 °C for 30 min. All water content was meant to evaporate, and the solid residue of black liquor was obtained for the next processing. The solid residues of black liquor were solved with 60 % MeOH and EtOH in 50 mL beakers, respectively, and then three drops of hexane were added to the solutions. The resulting solution was kept under laboratory conditions for one day, and then it was filtered with a special filter paper for the analysis as given in Figure 1(B).

### Table 1 Cooking parameters

<table>
<thead>
<tr>
<th>Wood Type</th>
<th>Wood / liquor</th>
<th>Active alkali (NaOH), %</th>
<th>Sulfdity (Na₂S), %</th>
<th>Cooking temperature, °C</th>
<th>Reach time to cooking temperature, min</th>
<th>Cooking time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pine / borovina</td>
<td>4/1</td>
<td>18</td>
<td>25</td>
<td>170±2</td>
<td>90</td>
<td>75</td>
</tr>
<tr>
<td>Aspen / jasikovina</td>
<td>4/1</td>
<td>18</td>
<td>25</td>
<td>170±2</td>
<td>90</td>
<td>75</td>
</tr>
</tbody>
</table>

### Figure 1

Obtaining (A) and recovery process (B) of lignin from black liquor

Slika 1. Dobivanje (A) i proces izdvajanja (B) lignina iz crnog luga

### 2.3 Characterization techniques

#### 2.3.1 Morphological analysis

The samples were morphologically characterized with TESCAN MAIA3 scanning electron microscopy (SEM). First, the samples were covered with gold nanoparticles by using a coater, and SEM analysis was conducted at an accelerating voltage of 15 kV.

#### 2.3.2 Fourier Transform Infrared Spectroscopy (FT-IR)

A Shimadzu IRA Affinity-1 spectrometer was used for the chemical characterization of the samples. The device included a single-reflection ATR pike MIR-acle sampling attachment. Spectra of FT-IR was between 800 cm⁻¹ and 4000 cm⁻¹ wavenumbers at a resolution of 4 cm⁻¹. Three specimens for each formulation were scanned and the average spectra were used.

#### 2.3.3 X-Ray Diffraction Analysis (XRD)

A high-resolution X-ray diffractometer (Model Model Rigaku SmartLab, PAN Analytical, Netherlands) with Ni-filtered Cu Ka (1.540562 Å) radiation
source operated at 45 kV voltage and 40 mA electric current was used in the structural characterization. The specimens were scanned in the range from 5° to 90° 2θ with 0.02° steps. A silicon zero-background plate was used to make sure that there was no peak associated with the sample holder. The same sample holder and the same position of the holder were used for all tests. The crystallinity index (CI) of the powdered samples was calculated as the ratio of the total area under the resolved crystalline peaks to the total area under the unresolved X-ray scattering curve (Rabiej, 2003). CI values were found using the formulation given below:

$$\text{CI} = \frac{\sum A_c}{\sum (A_c + A_a)} \times 100$$  \hspace{1cm} (1)$$

Where $A_c$ is the integrated area under the respective crystalline peaks, and $A_a$ is the integrated area of the amorphous halo.

2.3.4 Thermogravimetric analysis

The thermal stability of lignin is an important issue in many applications; therefore, the thermal properties of the lignin particles were investigated using a thermogravimetric analyzer (TGA/Q6 DTG) (Perkin

![Figure 2 SEM images of lignin particles recovered from black liquor and cml-lignin](image)

**Figure 2** SEM images of lignin particles recovered from black liquor and cml-lignin

**Slika 2**. SEM slike čestica lignina izdvojenoga iz crnog luga i cml-lignina
Elmer, TA Instruments). The particles were heated from 25 °C to 1000 °C at a heating rate of 20 °C/min and a nitrogen flow of 20 ml/min. After TG analysis, the degradation temperatures of the samples at 10 % weight loss ($T_{10\%}$), 50 % weight loss ($T_{50\%}$), and 75 % weight loss ($T_{75\%}$) were determined, as well as the maximum degradation temperature in the derivative thermogravimetric peaks (DTG$_{\text{max}}$). Finally, the mass loss of the samples was calculated.

3 RESULTS AND DISCUSSION

After the recovery process, the morphological analysis of commercial and recovered types of lignin including cml-lignin, lignin recovered with MeOH and EtOH from the black liquor of both pine and aspen wood, was conducted with SEM. The obtained SEM images are given in Figure 2.

The morphological structure and particle size of both MeOH-pine and EtOH-Pine lignin were similar compared to Cml-lignin, and the particle size was generally determined as a circle, sphere, or polygon. However, MeOH-aspen and EtOH-aspen lignin had layered structures and it was determined that they were similar to a long and wide bar. As a result, it can be said that the structure of lignin depends on the wood type, and that the particle sizes of lignin obtained with EtOH and MeOH alcohols were generally similar.

In a study, Haz et al. (2015) investigated the size distribution of lignin precipitated with sulphuric acid and the obtained results showed that lignin has a bi-modal distribution, and contains nano- and micro-sized particles. The average diameter of the particles was found to range from 353 nm to 5.5 µm. In another study, Hermiati et al. (2017) studied the morphological structure of lignin obtained from Kraft pulping black liquor with 2 different hydrochloric acid solutions/ethanol and SEM images showed that the surface morphology of lignin was generally similar and lignin surface was determined to have some impurity and pores. Ibrahim et al. (2011) found similar results.

The chemical structure of lignin was investigated with FT-IR and the obtained spectra are given in Figure 3.

The FT-IR spectra of the lignin types obtained in two different ways from the black liquor of pine and aspen chips are given in Table 2. The spectra of the recovered lignin appear to be generally similar to cml-lignin. However, some spectra shifted to lower or higher wavenumbers. Fifteen peaks of commercial lignin and other lignin types were clearly detected as given in Figure 3 and Table 2. The FT-IR spectra revealed that the recovered lignin types had similar functional groups but some differences in intensities of the peaks were observed. It has also been stated that the FT-IR spectra of the four lignin fractions from the black liquor appear to be rather similar to typical lignins, indicating that the “core” of the lignin does not change dramatically and that the recovered lignin isolates had similar functional groups (Sun et al., 1999; Hermiati et al., 2016; Sameni et al., 2016; Santos et al., 2015). As a result, it can be said that the recovered lignin types were similar to the cml-lignin.

XRD was used for the structural analysis of the recovered lignin and the obtained results are given in Figure 4.
Table 2 FT-IR spectra of different lignin samples (Sun et al., 1999.; Zhao et al., 2009.; Hermiati et al., 2017.; Hidayati et al., 2018.)

<table>
<thead>
<tr>
<th>cm-l, cm⁻¹</th>
<th>Pine / Borovina, cm⁻¹</th>
<th>Aspen / Drvo jasike, cm⁻¹</th>
<th>Band position / Pozicija vrpce, cm⁻¹</th>
<th>Assignments / Vrsta grupe i vibracije</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EtOH MeOH</td>
<td>EtOH MeOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3425</td>
<td>3400</td>
<td>2950 2940</td>
<td>3450-3400</td>
<td>O-H stretching (phenolic OH and aliphatic OH)</td>
</tr>
<tr>
<td>2940</td>
<td>2933 2928</td>
<td>2830 2833</td>
<td>2940-2820</td>
<td>C-H stretching (CH₃ and CH₂)</td>
</tr>
<tr>
<td>2848</td>
<td>-</td>
<td>2835 2840</td>
<td>2850-2840</td>
<td>C-H stretching (OCH₃)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1715-1710</td>
<td>C=O stretching (unconjugated ketone, carbonyl and ester groups)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1675-1660</td>
<td>The C = O range is unconjugated with an aromatic ring</td>
</tr>
<tr>
<td>1600</td>
<td>1595 1595</td>
<td>1589 1593</td>
<td>1605-1595</td>
<td>C-C stretching (aromatic ring)</td>
</tr>
<tr>
<td>1512</td>
<td>1505 1502</td>
<td>1508 1510</td>
<td>1515-1505</td>
<td>C-C stretching (aromatic ring)</td>
</tr>
<tr>
<td>1465</td>
<td>1450 1456</td>
<td>1464 1462</td>
<td>1470-1461</td>
<td>C-H deformation (asymmetric in –CH₃ and –CH₂)</td>
</tr>
<tr>
<td>1431</td>
<td>1421 1422</td>
<td>1430-1422</td>
<td></td>
<td>C-C stretching (aromatic ring) with C-H in-plane deformation</td>
</tr>
<tr>
<td>1361</td>
<td>1375 1368</td>
<td>1370-1365</td>
<td></td>
<td>In-plane deformation vibration of phenolic OH</td>
</tr>
<tr>
<td>1335</td>
<td>1333 1335 1338</td>
<td>1330-1335</td>
<td></td>
<td>C-O stretching (syringil)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1328 and 1215</td>
<td>C₅₇₋₇₋O vibration in syringyl derivatives</td>
</tr>
<tr>
<td>1275</td>
<td>1273 1271 1280 1278</td>
<td>1270-1275</td>
<td></td>
<td>Vibration of guaiacyl rings</td>
</tr>
<tr>
<td>1222</td>
<td>1225 1227 1222 1224</td>
<td>1220</td>
<td></td>
<td>C-O(H) + C-O(Ar) (phenolic OH and ether in syringil and guaiacyl)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1116 1118</td>
<td>Ar-CH in-plane deformation (syringil)</td>
</tr>
<tr>
<td>1133</td>
<td>1132 1130</td>
<td>1123 and 1028</td>
<td></td>
<td>Aromatic C-H inplane deformations in syringyl-type and guaiacyl-type lignin</td>
</tr>
<tr>
<td>1090</td>
<td>1095 1095 1035 1040</td>
<td>1085-1030</td>
<td></td>
<td>C-O(H) and C-O(C) (first order aliphatic OH and ether)</td>
</tr>
<tr>
<td>1033</td>
<td>1035</td>
<td>1030</td>
<td></td>
<td>C-O of syringyl and guaiacyl ring, C-H bond in guaiacyl ring</td>
</tr>
<tr>
<td>930</td>
<td>931 931 920 922</td>
<td>915</td>
<td></td>
<td>C-H out of plane (aromatic ring)</td>
</tr>
<tr>
<td>865, 825</td>
<td></td>
<td>875 838-875</td>
<td></td>
<td>aromatic C-H out-of-plane bending</td>
</tr>
</tbody>
</table>

Figure 4 XRD pattern of lignin particles recovered from black liquor

Slika 4. XRD uzorak čestica lignina izdvojenoga iz crnog luga
According to Figure 4, the peak point for the recovered lignin and control lignin was detected at 21.4°. While the peak for the EtOH-aspen and MeOH-aspen has high intensity, the intensity of the EtOH-pine and MeOH-pine was detected to be lower. In CI, the highest and lowest CI for the samples was calculated as 34.2 % and 19.3 % for control lignin and for EtOH-pine, respectively. As a result, the lignin recovered from pine was found to have a similar structure as the control lignin and it can be said that the lignin structure changed according to the wood type, while the alcohol type used during the lignin recovery process had no significant effect on the structural properties of lignin.

The thermal analysis of the recovered lignin was conducted from 25 °C to 1000 °C. The obtained TG curves are given in Figure 5 - 7, and Table 3 shows the

![Figure 5 TGA curves of lignin particles recovered from black liquor](image)

Figure 5 TGA curves of lignin particles recovered from black liquor
Slika 5. TGA krivulje čestica lignina izdvojenoga iz crnog luga

![Figure 6 DTG curves of lignin particles recovered from black liquor](image)

Figure 6 DTG curves of lignin particles recovered from black liquor
Slika 6. DTG krivulje čestica lignina izdvojenoga iz crnog luga

summary of TG curves of the recovered lignin and cml-lignin. The thermal decomposition of the recovered lignin and the cml-lignin consists of degradation peaks at different areas occurring between 75 °C and 900 °C (Figure 5). The DTG curves showed many decomposition peaks of lignin at the same temperatures (Figure 6) due to hydrolysis, decomposition (at temperatures between 200 °C and 500 °C) and oxidative chain scission (at temperatures above 600 °C) of lignin as shown by the DTG curves. According to Figure 5 and 6, it can be said that pine lignin exhibited a different behavior than aspen lignin.

The thermal stability of the recovered lignin was found to be generally similar compared to cml-lignin as shown in Table 3. \( T_{10\%} \) of the cml-lignin and lignin from aspen were similar to each other. However, \( T_{10\%} \) of lignin
from pine was found very low due to possible impurities. $T_{50\%}$ of the recovered lignin was found to change from 511.1 °C to 676.2 °C. The highest and lowest weight loss was calculated as 69.7 % and 60.7 % for lignin from pine and for cml-lignin, respectively. DTG$_{\text{max}}$ of all the recovered lignin was found to be lower than that of cml-lignin and the highest and lowest DTG$_{\text{max}}$ was found as 388.9 °C and 59.5 °C for EtOH-aspen lignin and for MeOH-pine lignin, respectively. $T_d$ of lignin was determined to range from 907.7°C (MeOH-pine lignin) to 923.7°C (cml-lignin). As a result, it can be concluded that the recovered lignin generally has similar thermal stability as cml-lignin.

### 4 CONCLUSIONS

In this study, lignin from black liquors obtained from Scots pine (Pinus sylvestris L.) and European aspen (Populus tremula L.) wood cooked by the Kraft method was recovered with methyl and ethyl alcohols, and the material properties of the recovered lignin were analyzed by SEM, FT-IR, XRD, and TGA. According to the obtained results, SEM images showed that the particle sizes of lignin obtained with ethyl and methyl alcohols were generally similar to each other. FTIR showed that the recovered lignin types had similar functional groups, while some differences were observed in intensities of the peaks. XRD results revealed that the lignin recovered from pine was found to have a similar structure as the control lignin and that the alcohol type used during the lignin recovery process had no significant effect on the structural properties of lignin.

TGA results show that the recovered lignin generally has thermal stability comparable to cml-lignin. The results indicated that the lignin structure change according to the wood type but the structure of lignin is not significantly changed by the recovery process described. The results revealed that the recovered lignin was similar to commercial lignin. Based on the obtained results, it can be concluded that lignin can be recovered from the liquor leftover from pulping and/or paper production by the method described and that it can be used in industry.
5 REFERENCES

5. LITERATURA


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