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

## Karakterizacija i odvajanje lignina iz crnog luga dobivenog kraft metodom uz primjenu različitih alkohola

### ORIGINAL SCIENTIFIC PAPER

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**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  $(170 \pm 2)$  °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  $170 \pm 2$  °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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(XRD) i termogravimetrijskom analizom (TGA). Za usporedbu svojstava lignina dobivenog iz crnog luga poslužio je komercijalni lignin (cml-lignin). SEM slike pokazale su da su veličine čestica lignina dobivenog uz pomoć EtOH i MeOH bile slične. FT-IR analizom utvrđeno je da izdvojeni tipovi lignina imaju slične funkcionalne grupe te da su se pojavile neke razlike u intenzitetu pikova. Rezultati XRD-a otkrili su da svi tipovi lignina imaju sličnu strukturu kao i cml-lignin i da vrsta alkohola upotrijebljenog tijekom procesa izdvajanja lignina nema bitan učinak na strukturalna svojstva lignina. Rezultati TGA analize pokazali su da je toplinska stabilnost izdvojenog lignina bolja od toplinske stabilnosti cml-lignina. Prema rezultatima istraživanja može se zaključiti da je izdvojeni lignin sličan komercijalnom ligninu, da može biti izdvojen iz tekućine koja je preostala od proizvodnje celuloze opisanom kraft metodom te da se može rabiti u industriji.

**KLJUČNE RIJEČI:** proizvodnja celuloze kraft metodom; crni lug; lignin; recikliranje; karakterizacija lignina

## 1 INTRODUCTION

### 1. UVOD

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 pulping 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 deter-

mined 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. MATERIJALI I METODE

#### 2.1 Materials

##### 2.1. Materijali

Scots pine (*Pinus sylvestris* L.) and European aspen (*Populus tremula* L.) woods were supplied from a local mill in Bartın 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.

**Table 1** Cooking parameters**Tablica 1.** Parametri kuhanja

Wood Type <i>Vrsta drva</i>	Wood / liquor <i>Drvo / lug</i>	Active alkali (NaOH), % <i>Aktivna lužina (NaOH), %</i>	Sulfidity (Na <sub>2</sub> S), % <i>Sulfidnost (Na<sub>2</sub>S), %</i>	Cooking temperature, °C <i>Temperatura kuhanja, °C</i>	Reach time to cooking temperature, min <i>Vrijeme doseganja temperature kuhanja, min</i>	Cooking time, min <i>Vrijeme kuhanja, min</i>
Pine / <i>borovina</i>	4/1	18	25	170±2	90	75
Aspen / <i>jasikovina</i>	4/1	18	25	170±2	90	75

**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

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

### 2.2. Proces izdvajanja lignina

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).

## 2.3 Characterization technics

### 2.3. Tehnike karakterizacije

#### 2.3.1 Morphological analysis

##### 2.3.1. Morfološka analiza

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)

##### 2.3.2. Infracrvena spektroskopija s Fourierovom transformacijom (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<sup>-1</sup> and 4000 cm<sup>-1</sup> wavenumbers at a resolution of 4 cm<sup>-1</sup>. Three specimens for each formulation were scanned and the average spectra were used.

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

##### 2.3.3. Analiza difrakcije X-zraka (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:

$$CI = \frac{\Sigma A_c}{\Sigma(A_c + A_a)} (\%) \quad (1)$$

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

#### 2.3.4. Termogravimetrijska analiza

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

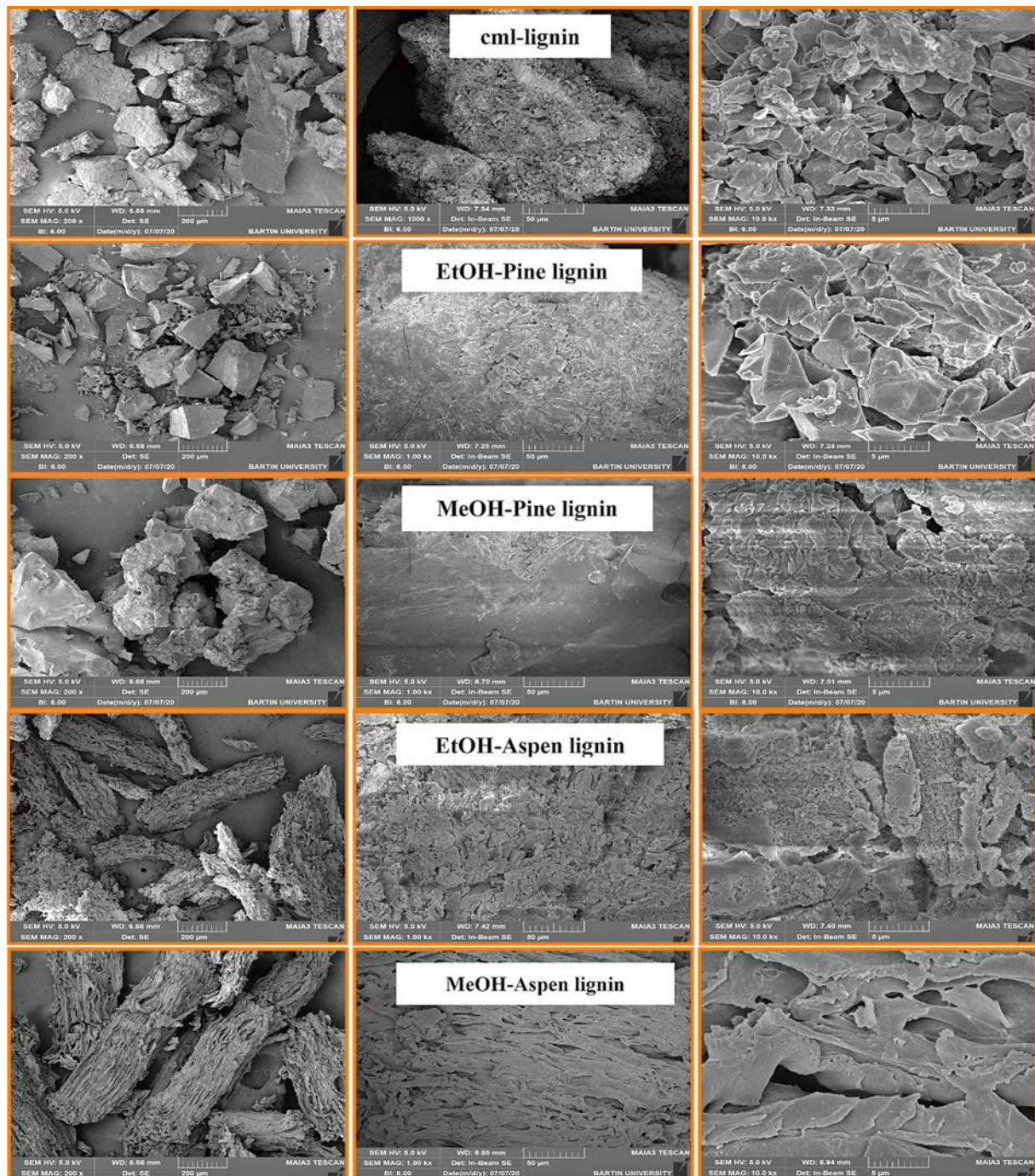


Figure 2 SEM images of lignin particles recovered from black liquor and cml-lignin  
Slika 2. SEM slike čestica lignina izdvojenoga iz crnog luga i cml-lignina

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 ( $DTG_{max}$ ). Finally, the mass loss of the samples was calculated.

### 3 RESULTS AND DISCUSSION

#### 3. REZULTATI I RASPRAVA

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.

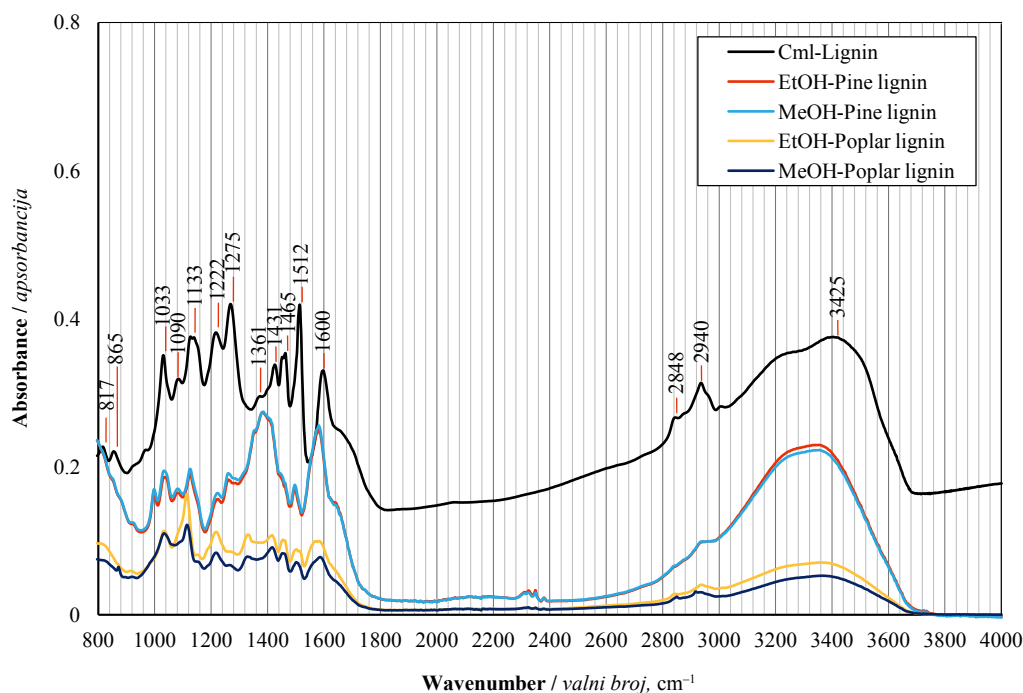
In a study, Haz *et al.* (2015) investigated the size distribution of lignin precipitated with sulphuric acid and the obtained results showed that lignin has a bimodal distribution, and contains nano- and micro-sized

particles. The average diameter of the particles was found to range from 353 nm to 5.5  $\mu\text{m}$ . 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

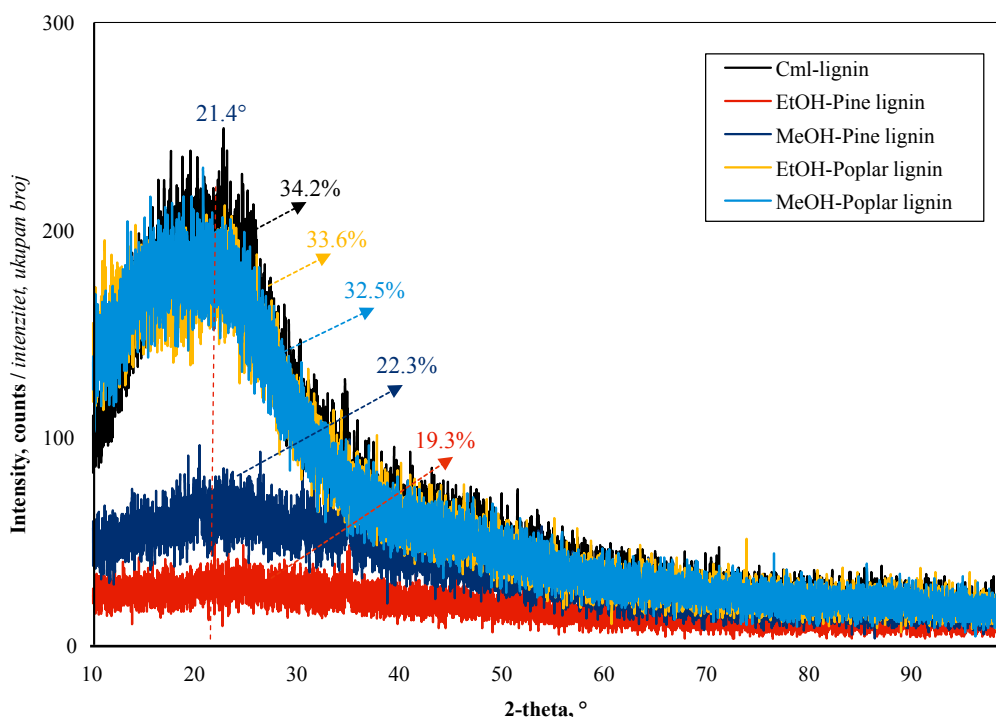
XRD was used for the structural analysis of the recovered lignin and the obtained results are given in Figure 4.



**Figure 3** FT-IR spectra of lignin particles recovered from black liquor  
**Slika 3.** FT-IR spektar čestica lignina izdvojenoga iz crnog luga

**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)**Tablica 2.** FT-IR spektar različitih uzoraka lignina (Sun *et al.*, 1999.; Zhao *et al.*, 2009.; Hermiati *et al.*, 2017.; Hidayati *et al.*, 2018.)

cm <sup>-1</sup> , cm <sup>-1</sup>	Pine / Borovina, cm <sup>-1</sup>		Aspen / Drvo jasike, cm <sup>-1</sup>		Band position / Pozicija vrpce, cm <sup>-1</sup>	Assignments / Vrsta grupe i vibracije
	EtOH	MeOH	EtOH	MeOH		
3425	3400		2950	2940	3450-3400	O-H stretching (phenolic OH and aliphatic OH)
2940	2933	2928	2830	2833	2940-2820	C-H stretching (CH <sub>3</sub> and CH <sub>2</sub> )
2848	-		2835	2840	2850-2840	C-H stretching (OCH <sub>3</sub> )
					1715-1710	C=O stretching (unconjugated ketone, carbonyl and ester groups)
	1655	1655			1675-1660	The C = O range is unconjugated with an aromatic ring
1600	1595	1595	1589	1593	1605-1595	C-C stretching (aromatic ring)
1512	1505	1502	1508	1510	1515-1505	C-C stretching (aromatic ring)
1465	1450	1456	1464	1462	1470-1461	C-H deformation (asymmetric in -CH <sub>3</sub> and -CH <sub>2</sub> )
1431			1421	1422	1430-1422	C-C stretching (aromatic ring) with C-H in-plane deformation
1361	1375	1368			1370-1365	In-plane deformation vibration of phenolic OH
	1335	1333	1335	1338	1330-1325	C-O stretching (syringil)
					1328 and 1215	C <sub>aryl</sub> -O vibration in syringyl derivatives
1275	1273	1271	1280	1278	1270-1275	Vibration of guaiacyl rings
1222	1225	1227	1222	1224	1220	C-O(H) + C-O(Ar) (phenolic OH and ether in syringil and guaiacyl)
			1116	1118	1115	Ar-CH in-plane deformation (syringil)
1133	1132	1130			1123 and 1028	Aromatic C-H inplane deformations in syringyl-type and guaiacyl-type lignin
1090	1095	1095	1035	1040	1085-1030	C-O(H) and C-O(C) (first order aliphatic OH and ether)
1033	1035	1035			1030	C-O of syringyl and guaiacyl ring, C-H bond in guaiacyl ring
930	931	931	920	922	915	C-H out of plane (aromatic ring)
865, 825				875	838-875	aromatic C-H out-of-plane bending

**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

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

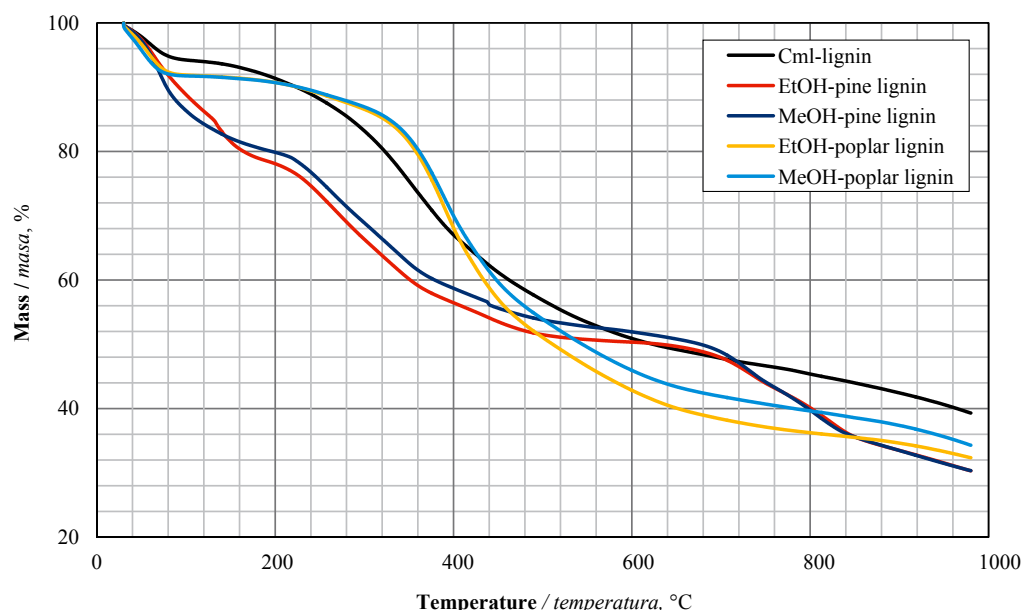


Figure 5 TGA curves of lignin particles recovered from black liquor  
Slika 5. TGA krivulje čestica lignina izdvojenoga iz crnog luga

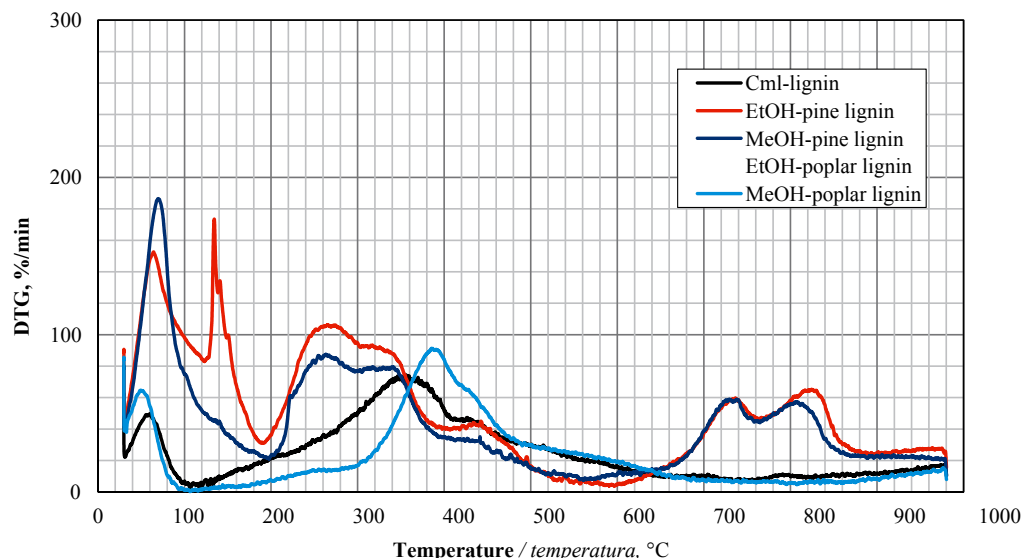


Figure 6 DTG curves of lignin particles recovered from black liquor  
Slika 6. DTG krivulje čestica lignina izdvojenoga iz crnog luga

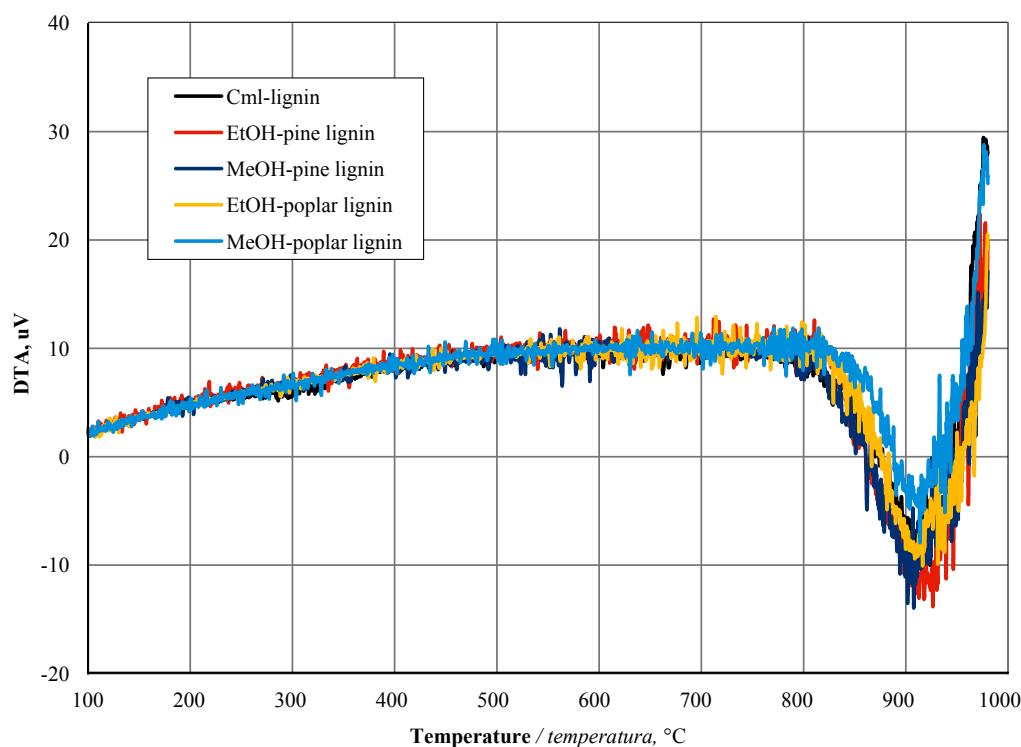


Figure 7 DTA curves of lignin particles recovered from black liquor

Slika 7. DTA krivulje čestica lignina izdvojenoga iz crnog luga

Table 3 Summary of TGA/DTG curves of lignin particles recovered from black liquor

Tablica 3. Sažetak za TGA/DTG krivulje čestica lignina izdvojenoga iz crnog luga

Samples / Uzorci	$T_{10\%}, ^\circ\text{C}$	$T_{50\%}, ^\circ\text{C}$	$\text{DTG}_{\text{max}}, ^\circ\text{C}$	$T_d, ^\circ\text{C}$	Weight loss, % Gubitak mase, %
cml-lignin	223.7	623.7	354.5	923.7	60.7
EtOH-pine lignin	91.7	632	134.4	922.5	69.7
MeOH-pine lignin	78.1	676.2	59.5	907.7	69.7
EtOH-aspen lignin	224.9	511.1	388.9	916.4	67.6
MeOH-aspen lignin	226.6	544.3	385.4	913.8	65.7

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.  $\text{DTG}_{\text{max}}$  of all the recovered lignin was found to be lower than that of cml-lignin and the highest and lowest  $\text{DTG}_{\text{max}}$  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

### 4. ZAKLJUČAK

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.



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