

Lignin fractionation from waste wood using organosolv treatment combined with membrane filtration

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Abstract. The purpose of this study was to investigate the characteristics of lignin fractionated from waste wood (WW) using a two-step process of ethanol organosolv pretreatment followed by ultrafiltration with membranes of different molecular weight cut-offs (1, 5 and 20 kDa). The different permeates obtained were characterized by fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (NMR), thermogravimetric analysis (TGA) and gel permeation chromatography (GPC). The analysis by FT-IR and NMR of these lignins showed that the lignin core was successfully separated from WW. TGA curves confirmed that the thermal properties of lignin fractionated by ultrafiltration were almost identical to each other. The results from GPC confirmed that fractionating of lignin was achieved by ultrafiltration. For the membrane fractionation process, values of molecular weight decreased as the cut-offs used to obtain the fractions became smaller. As a result, fractionating lignin by a two-step process allowed separating different fractions of lignin of different molecular weights yielded high purity without interference from existing pollutants in WW. The two-step process offers the possibility of using fractionated WW as an untapped source of lignin.

Keywords: waste wood; lignin; ultrafiltration; fractionation; characterization

1. Introduction

Lignin, along with cellulose and hemicellulose, represents one of three major constituents of lignocellulosic biomass. Cellulose isolated from lignocellulosic biomass has long been utilized to create various organic acids or biofuels, while most lignin has been simply burned as a waste byproduct until recently (Laurichesse and Avérous 2014). However, lignin having several functional groups including aliphatic hydroxyl, carboxyl, and phenol groups can be applied in different fields yielding products such as emulsifiers, adhesives, resins, dispersants, paints and fuels (Mousavioun and Doherty 2010). Because of its functional groups, lignin can be used as a precursor for carbon fiber, vanilla, phenol, and ethylene (Reddy and Yang 2005). Practically, separating lignin from various lignocellulosic biomasses in biorefineries has been carried out in high-

value applications (Lee *et al.* 2019, Norgren and Edlund 2014).

Wood is wasted in the order of 1.6-2.0 million tons per year in the Republic of Korea. Approximately 70% of waste wood results from industrial and construction sites in urban areas (Lee *et al.* 2018). Currently, large amounts of waste wood contaminated by paints, oils, preservatives, halogenated organic chemicals and heavy metals during processing and transport are improperly handled, producing environmental pollution via incineration and contaminating landfills. Waste wood, one of the lignocellulosic biomasses, can be considered good feedstock for available technologies, yielding useful chemicals and fuels as well as preventing environmental pollution.

To extract lignin from lignocellulosic biomass, various pretreatments such as acid hydrolysis, alkali hydrolysis and organosolv have been applied. Organosolv treatment is a chemical process, using both an organic solvent and catalyst at high temperature to fractionate biomass (Blanch *et al.* 2011). After organosolv treatment, the lignin remaining in liquid fractions must be further processed to obtain relevant target compounds which are sulfur-free, high purity and high-quality (Sannigrahi *et al.* 2010). Membrane filtration for further processing the liquors from organosolv treatment has been applied (Moniz *et al.* 2018, Toledano *et al.* 2010). Application of the membrane process as the final step allows obtaining lignin fractions with defined molecular

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weight distributions as well as removing non-lignin derived compounds from the organosolv liquor (Moniz *et al.* 2018). Ultrafiltration (UF) membranes, nanofiltration (NF) or using the UF-NF process have been studied for separating lignin fractions of different molecular weights from black liquor, showing their applicability and various effectiveness (Toledano *et al.* 2010, Oriez *et al.* 2019).

In this study, the potential of using hydrothermally treated waste wood as a feedstock for lignin-derived biomass was evaluated. As the first step, ethanol organosolv treatment of waste wood was carried out to fractionate lignin. The black liquor resulting from the organosolv treatment was processed using UF and NF membranes to obtain several lignin fractions with specific molecular weight distributions. The physicochemical properties and structures of each resulting lignin fraction were analyzed using comprehensive methods.

2. Materials and methods

2.1 Organosolv pretreatment

Ethanol organosolv treatment was performed in a 1 L batch reactor with a magnetic stirrer (CHEMRE SYSTEM Inc., Anyang, Republic of Korea). Biomass loading was 10 % (30 g in 300 g total mass of the mixture). Waste wood (WW) as biomass was sampled from a waste recycling company in Gwangju, where WW weighing 30-80 tons was collected daily. All samples were air-dried and milled by a disintegrator and then using sieves was separated into particles of 0.15-0.85 mm. Treatment was performed at 178.2°C and 2.32 % H₂SO₄ and 65 % (v/v) concentration of ethanol with a reaction time of 60 min., based on optimal conditions reported to yield the maximum lignin from dry wood (Lee *et al.* 2018). After treatment, the mixture was filtered under a vacuum using Whatman grade 1 filter paper to separate the liquid from solids (pulp). The resultant organosolv black liquor was used for membrane separation.

2.2 Membrane separation

Membranes were tested using three different molecular weight cut-offs of 1 kDa, 5 kDa and 20 kDa (Synder Filtration, CA, USA). These membranes made of polyethersulfone (PES) were of a flat sheet type with an active area of 20.6cm². A cross flow cell for UF and NF (CF016D, Steritech) was used. In the cross-flow filtration process (Fig. 1), cross flow velocity (CFV) and transmembrane pressure (TMP) were controlled manually by adjusting three valves at the inlet and outlet of the membrane module and on the permeate side. Permeate flow was weighted with a balance (PAG 2102, OHAUS, USA). All the weight data was transmitted to a computer using software of SPDC Data collection V2.01 (OHAUS, USA).

The black liquor solution was first filtered by membrane with a cut-off of 20 kDa to remove any suspended solids or high molecular weight chemicals. Operating conditions were constantly controlled at 300 g of feed weight, 5 bar of feed pressure and 50 L/h of flow rate, respectively. The 20

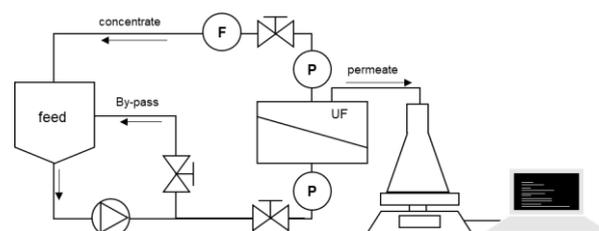


Fig. 1 Set-up of the membrane filtration process for separating black liquor resulting from the organosolv treatment

kDa permeate was then concentrated by a 1 kDa cut-off, removing lower molecular weight sugars or other organic acids. After filtration by membrane with a cut-off of 1 kDa, the resulting concentrated solution was separated using a 5 kDa membrane. Separated solutions were added with distilled water to make 3 times the volume of the solutions to obtain the precipitated lignin. The mixture was then separated by centrifugation at 4000 rpm for 20 min. The supernatant was removed and the solid part was dried at 40°C to recover the lignin. Lignin recovery from total extractable lignin in the black liquor was approximately 0.5 % and 33 % from the 1-5 kDa and 5-20 kDa membranes, respectively. The filtration system was rinsed with 0.5 M NaOH solution to remove any remaining compounds in the system.

2.3 Lignin characterization

Average molecular weight distributions of separated lignin were determined by gel permeation chromatography (GPC) analysis with an Ultimate 3000 GPC system (Thermo, MA, US) at 1 mL/min flow rate and 40°C column temperature. A fourier transform infrared spectroscopy (FT-IR) spectra study was carried out in a Nicolet 6700 FT-IR spectrophotometer (Thermo, MA, US). The lignin samples were recorded with a resolution of 2 cm⁻¹ in the region of 4000-400 cm⁻¹. Thermal properties of the lignin samples were determined by a Discovery (thermogravimetric analysis) TGA analyzer (TA Instruments, DE, US) making scans of temperatures from 25 to 800°C with a heating rate of 10°C/ min. ¹H-nuclear magnetic resonance (NMR) spectra were recorded using an AVANCE 600 MHz High Resolution NMR Spectrometer (Bruker, MA, US) with 128 scans and an acquisition time of 1.36 s. The chemical shifts of the ¹H-NMR spectrum were calibrated with reference to DMSO-d₆ at 2.49 ppm. All analyses were performed in duplicate.

3. Results and discussion

3.1 Structural characterization of the obtained lignin

The physicochemical structure of the different fractions (black liquor: OSL1; 1-5 kDa fraction: OSL2; 5-20 kDa: OSL3) obtained from the membranes process was characterized for comparison. The FT-IR spectra of different fractions obtained are shown in Fig. 2. All samples

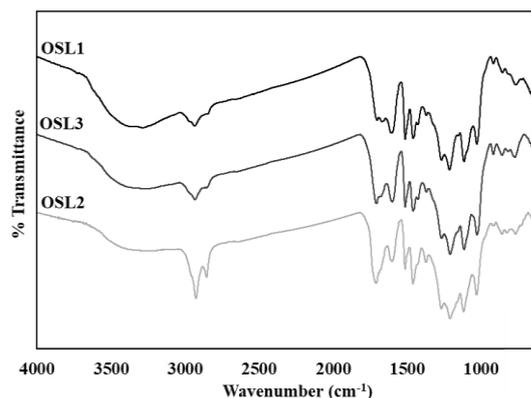


Fig. 2 FT-IR spectra of the fractions obtained by membrane filtration

yielded characteristic absorbance at 3200 cm^{-1} indicating aromatic and aliphatic O-H stretching (Table 1). The peaks at 2935 cm^{-1} (OSL1), 2924 and 2853 cm^{-1} (OSL2) and 2932 cm^{-1} (OSL3) correspond to C-H stretching of methyl, methylene and methoxy groups (Delgado *et al.* 2018). Peaks from 1701 cm^{-1} (OSL1), 1708 cm^{-1} (OSL2) and 1707 cm^{-1} (OSL3) were attributed to conjugated carbonyl groups in ketones and aliphatic acetate presenting a quinonic structure (Hage *et al.* 2009). Peaks at $915\text{-}1212\text{ cm}^{-1}$ in all samples represent C-H stretching of the syringyl (S) and guaiacyl (G) units (Table 1): the aromatic C-H deformation of the S units was represented at 1114 cm^{-1} (OSL1 and OSL3) and 1116 cm^{-1} (OSL2) (de Carvalho Oliveira *et al.* 2018), while aromatic C-H deformation of the G units was represented at 1212 cm^{-1} (OSL1), 1209 cm^{-1} (OSL2) and 1208 cm^{-1} (OSL3). Additionally, G units were distributed to peaks at 1511 cm^{-1} , 1266 cm^{-1} and $1027\text{-}1029\text{ cm}^{-1}$ in all lignin fractions corresponding to C-C stretch of aromatic skeletal vibration, C=O stretching units and aromatic C-H deformation, respectively (Hage *et al.* 2009, Rashid *et al.* 2018). Meanwhile, a peak at 1669 cm^{-1} occurred only in OSL1 and was assigned to conjugated C=O groups in the *p*-aryl ketone (de Carvalho Oliveira *et al.* 2018). Signal intensity seemed to decrease after ultrafiltration. This phenomenon indicates reduction of ketones of unbroken hemicellulose and lignin (Grabber 2005). Based on FT-IR spectra, however, no significant differences were observed (Fig. 2).

Characterization of signal intensity using $^1\text{H-NMR}$ provides an adequate method of monitoring the purity of the separated lignin structure. $^1\text{H-NMR}$ spectra of OSL1, OSL2 and OSL3 are shown in Fig. 3a. Signals in the range of $6.0\text{-}8.0\text{ ppm}$ correspond to aromatic H of lignin obtained. In this range, signals between 6.8 and 7.25 ppm are associated with protons on the aromatic ring of the G unit (Zhang *et al.* 2017), while signals at $6.6\text{-}6.7\text{ ppm}$ indicate protons on the aromatic ring of the S unit (Yang *et al.* 2017). The signal at 5.3 ppm is attributed to the H- α of $\beta\text{-}5$ structure (Yang *et al.* 2017). Amplification of signals between 4.0 and 4.5 ppm indicates H- γ bonds (Toledano *et al.* 2010). The sharp peak at 2.5 ppm is assigned to the solvent (DMSO- d_6) used to prepare the samples (Xu *et al.* 2006). The signals at $0.8\text{-}1.5\text{ ppm}$ are related to aliphatic OH of side chains of lignin or acetyl groups in xylan (Xu *et al.* 2006).

Table 1 Assignment of FT-IR spectra

Wavenumber (cm^{-1})			Assignment
OSL1	OSL2	OSL3	
3285	-	3265	Phenolic and aliphatic O-H stretch
2935	2924	2932	C-H stretch
-	2853	-	C-H stretch methoxy groups
1701	1708	1707	C=O stretch unconjugated
1669	-	-	C=O stretch conjugated
1605	1601	1599	C-C stretch (aromatic skeletal vibration)
1511	1511	1511	C-C stretch (aromatic skeletal vibration), G
1458	1459	1459	C-H deformation methyl and methylene
1426	-	-	C-H deformation (aromatic skeletal vibration)
1369	1372	1369	Phenolic O-H and aliphatic C-H stretch methyl groups
1266	1267	1266	C-O stretch, G
1212	1209	1208	Aromatic C-H deformation, G
1114	1116	1114	Aromatic C-H deformation, S
1028	1029	1027	Aromatic C-H deformation, G+ S
916	915	917	Aromatic C-H deformation
855	850	858	C-H deformation, G
-	824	816	C-H deformation, G
767	766	770	C-C stretch ring of the sugar and lignin

To obtain further information about the lignin structures, $^{13}\text{C-NMR}$ analysis was conducted. As shown in Fig. 3b, all three samples had similar features. There were no signals at $90\text{-}102\text{ ppm}$, indicating low contamination by residual sugars in the lignin fraction (Hage *et al.* 2009). Signals between 160 and 102 ppm are assigned to aromatic C in lignin samples. The signals at 152.6 and 148.3 ppm correspond to the S unit, while signals at 147.2 , 119.4 and 112.0 ppm represent the G unit (Yang *et al.* 2017). Additionally, a small amount of *p*-coumaric esters was found from the signals at 159.9 ppm and 130.1 ppm . The signals at 85.0 ppm (C- β), 73.1 ppm (C- α) and 60.0 ppm (C- γ) are due to $\beta\text{-O-}4'$ structure and the signal at 56.4 ppm is attributed to methoxyl groups (Yang *et al.* 2017). From the comparison, the core of lignin was similar, indicating lignin was successfully separated from WW.

TGA was used to reveal how organic polymers decompose. TG curves represent the weight loss of substances with increasing temperature, while the differential thermal gradient (DTG) curve demonstrates the corresponding rate of weight loss. Results from lignin samples fractionated by ultrafiltration are shown in Fig. 4. A peak corresponding to the first weight loss was observed around 60°C , reflecting evaporation of residual moisture on the lignin surface. The second peak at around 270°C , which appeared only in OSL2, can be attributed to degradation of small phenolic compounds from $\beta\text{-ether}$ cleavage of the side chains of lignin (Zhou *et al.* 2016). In all samples, maximum degradation appeared at 380°C , attributable to

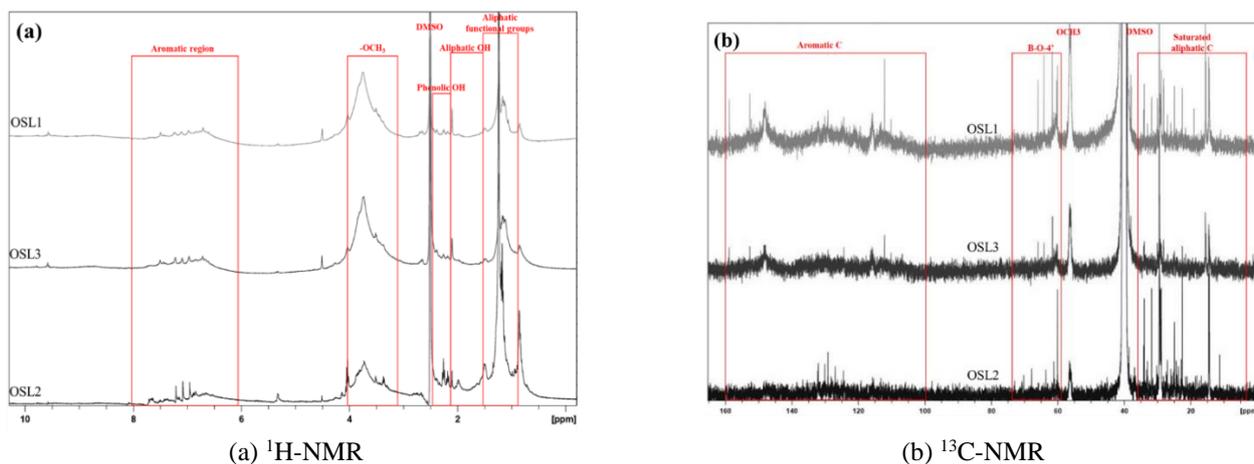
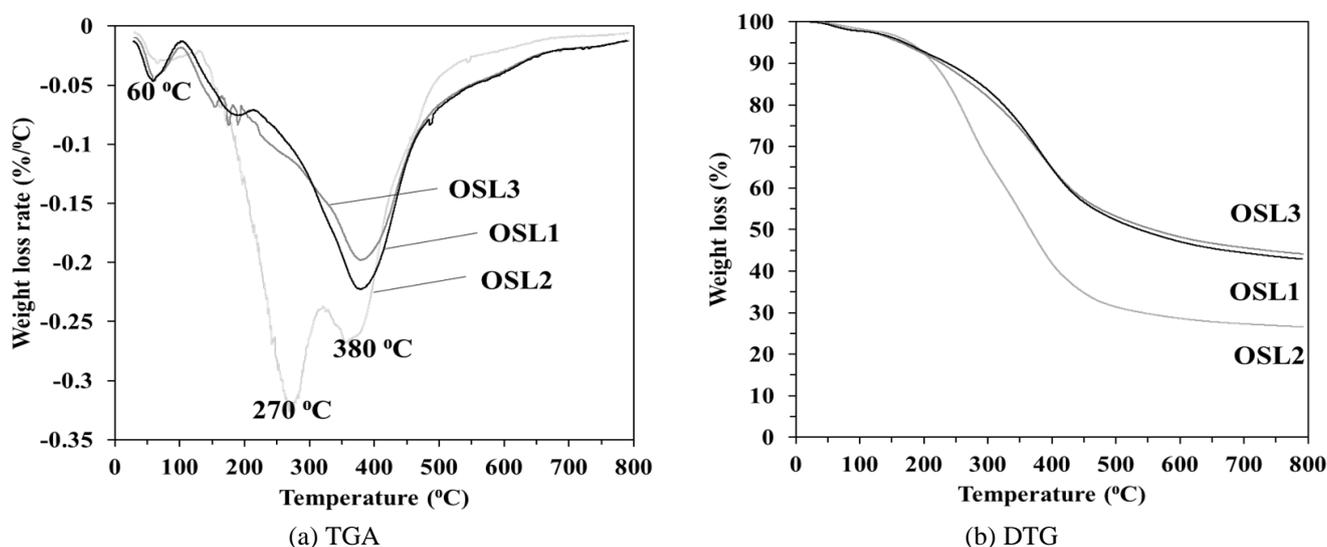
Fig. 3 $^1\text{H-NMR}$ (a) and $^{13}\text{C-NMR}$ (b) spectra of the obtained fractions

Fig. 4 TGA and DTG curves

Table 2 Molecular weight and polydispersity

Sample	$M_n(\text{g mol}^{-1})$	$M_w(\text{g mol}^{-1})$	$\text{PDI}(M_w/M_n)$
OSL1	483	1220	2.52
OSL2	337	516	1.53
OSL3	412	791	1.92

lignin degradation. Thermal degradation of lignin occurs from 185 to 500°C, being associated with complex lignin structures of benzylic OH, phenolic OH, and carbonyl groups (Domínguez *et al.* 2008): the first decomposition of lignin starts with the dehydration of benzyl group at a temperature of 150-275°C, along with the decomposition of α - and β -aryl-alkyl-ether linkages at 150-300°C. Thereafter, decomposition of aliphatic side chains in the aromatic compounds occurs at around 300°C, while cleaving C-C in lignin structures appears between 370-400°C. Finally, at a temperature of 500°C, volatile products are released slowly with small weight loss, resulting in 30-50% char production (Laurichesse and Avérous, 2014). In our study, 43% of OSL1 and OSL3 and 26% of OSL2 remained as char residue. Based on both TGA and DTG curves, the thermal

properties of lignin fractionated by ultrafiltration were almost identical to each other.

The average molecular weight (M_w), average molecular number (M_n) and polydispersity (PDI) of the different acetylated fractions of lignin fractionated by ultrafiltration were analyzed by GPC (Table 2). The results show that fractionating lignin was achieved by ultrafiltration. For the membrane fractionation process, values of M_w decreased as the cut-offs used to obtain the fractions became smaller. As a result, the PDI also decreased with pore size: OSL2 (1-5 kDa fraction) with a PDI of 1.53 had a more homogeneous value than OSL3 (5-20 kDa) with a PDI of 1.92. All obtained fractions indicated a relatively low PDI, possibly resulting from a high fraction of low M_w possibly forming C-C bonds related to the structures involving C5 in the aromatic ring, the G unit and S unit (Toledano *et al.* 2010).

4. Conclusions

A process combining an ethanol organosolv treatment followed by membrane filtration was found to be effective fractionating lignin from WW in this study:

- The physicochemical characterization of lignin was performed by FT-IR, TGA, GPC, and ¹H-NMR.
- These results support separation of lignin with high purity without interference from existing pollutants in WW.
- This study demonstrates the possibility of using WW for lignin valorization.

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