



Pretreatment of lignocellulosic biomass at atmospheric conditions by using different organosolv liquors: a comparison of lignins

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Abstract

In order to strengthen the bio-based economy, it is necessary to produce value-added products by processing all fractions of the biomass, especially lignin. Isolation of lignin at atmospheric pressure and lower temperature will make it possible to recover lignin and use it for different purposes. In the present study, lignins were recovered from wood sawdust by applying six different organosolv treatments at atmospheric pressure. The lignins (ethanol organosolv lignin (EOL), alkaline glycerol organosolv lignin (AGOL), acetic acid organosolv lignin (AAOL), formic acid/acetic acid/water organosolv lignin (FAWOL 1 (40/40/20, v/v/v), FAWOL 2 (50/30/20, v/v/v), FAWOL 3 (30/50/20, v/v/v)) were compared in terms of yield, thermal properties, weight-average molecular weight, and fast pyrolysis properties. The effect of isolation method on lignin yield and structure was remarkable. Organosolv treatments at atmospheric conditions resulted in precipitation yields between 6.6% (ethanol organosolv) and 42% (alkaline glycerol organosolv). The lignin precipitated with the highest yield (AGOL) actually had the highest ash content (3.9%) and the lignin precipitated with the lowest yield (EOL) had the lowest ash content (1.2%). According to FTIR analysis, all lignins exhibited peaks at similar wavelengths but with different intensities. The weight-average molecular weight of lignins ranged between 1373 g/mol (AGOL) and 7400 g/mol (FAWOL 1). The polydispersity index of lignins ranged between 7.3 (FAWOL 1) and 2.5 (EOL and AAOL), where the lignins isolated from formic acid/acetic acid/water liquors showed higher polydispersity index compared to other lignins. Pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) revealed that pyrolysis product distribution was strongly affected from the isolation method. The most abundant phenolic compound, which was observed in all lignins, was 2-methoxy-4-methylphenol (4-methylguaiacol), which was followed by 2-methoxy-4-(2-propenyl) phenol (eugenol) and guaiacol, respectively. It has been observed that each lignin is a good candidate for a different end-use due to their own characteristics.

Keywords Lignin recovery · Organosolv treatment · Biorefinery

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1 Introduction

The most abundant source of carbon on earth is lignocellulosic biomass, which is a complex composite material mainly consisting of cellulose, hemicellulose, and lignin [1]. Agricultural wastes and residues (straws, stovers, seeds, pomace, etc.), forestry wastes and residues (wood shavings, wood sawdust, leaves, etc.), wood (hardwood, softwood), energy crops (switchgrass, *Miscanthus*, etc.), organic fraction of municipal solid waste, and wastes from food industry are very well known sources of lignocellulosic biomass. The structure and the composition of hemicellulose, cellulose, and lignin vary depending on biomass type, season of harvest, maturity, and geographic location [2, 3].

Biorefining of lignocellulosic biomass includes several conversion processes and it is a good alternative for producing

fuels, bio-based chemicals, and biomaterials [4, 5]. In a bioethanol-based biorefinery, cellulose and hemicellulose are hydrolyzed to produce fermentable sugar for further biofuel production. However, lignin, which remains, is combusted (most convenient way) or dumped as a waste [6]. Actually, lignin is not a waste, mainly because it has several end-uses if properly isolated. Products, which can be derived or produced from lignin, can be used for different purposes including fuels, fuel additives, chemicals, biopolymers, adhesives, lubricant additive, carbon fiber, biomaterials for drug release, flocculants, dispersants, and polymer fillers [7–13]. Due to its high carbon content, lignin is also used as a precursor for the production of activated carbon [14]. An economically viable integrated biorefinery should recover hemicellulose and lignin as much as possible [15, 16]. The degree of separation, isolation, and recovery of each structural unit depends on the biomass pretreatment methods, which include steam explosion, hot water treatment, ionic liquid pretreatment, organosolv, and ammonia fiber explosion [3, 17, 18].

Lignin is a complicated natural and phenolic biopolymer, which is bound to hemicellulose by ether or ester bonds [19]. With a 15–40% of mass fraction, lignin is one of the main components of lignocellulosic biomass [20]. The amount and placement of phenyl propanoid units (viz., *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units) make the lignin structure complex and heterogeneous [10]. In softwoods, lignin is comprised of mainly G units (90–95 wt%) and S units with less contribution (5–10 wt%) [16]. In hardwood lignin, the average percentage of G units and S units are 50 wt% for each. In herbaceous biomass, lignin also includes H units with a small percentage (5 wt%) [16]. The method of lignin isolation strongly affects the lignin structure and properties (including average molecular weight, polydispersity index, functional groups, purity, etc.) [10, 11, 21].

Among the isolation methods, organosolv pretreatment is the one which enables the separating of cellulose with minor degradation and obtaining high-quality lignin [22, 23]. It is well documented that organosolv lignin is fairly pure with a very low ash content [8, 24, 25]. In organosolv process, lignocellulosic biomass is treated with an organic solvent (such as ethanol, methanol, acetone, ethylene glycol, formaldehyde, formic acid, acetic acid, glycerol, etc.) at a defined temperature (77–220 °C) and pressure (dependent on the selected solvent) for a period of time [22, 24]. Based on organic solvent, catalysts might also be used in the process. The most preferred catalysts in the organosolv process carried out in the presence of catalyst are acids (such as H₂SO₄, HCl), Lewis acids (FeCl₃·6H₂O), bases (NaOH, KOH), and ionic liquids (1-butyl-3-methylimidazolium hydrogen sulfate ([Bmim] HSO₄)) [8, 18, 22, 23]. The most important parameters affecting the lignin delignification and lignin structure are temperature, presence of catalyst and

solvent concentration [4]. According to the studies, the effect of reaction time and particle size is quite limited [26]. In a typical organosolv method, hemicellulose and most of the lignin are dissolved in organic medium, leaving the majority of cellulose in solid fraction. Cellulose-rich solid fraction is separated for further processes such as hydrolysis and fermentation. Precipitation is the most preferred method of separating lignin from organosolv solution. To precipitate the lignin, either water is added to the organosolv solution or some of the solvent is evaporated before adding water [27]. Dilution with water reduces the solubility of lignin, which causes lignin to precipitate. There is also a possibility to recover hemicellulose via two-stage organosolv pretreatment, where the hemicellulose is solubilized first and precipitated prior to lignin extraction [16].

Selection of organic solvent is an important issue due to its critical effect on process conditions and lignin properties. Low boiling point organic solvents such as ethanol, acetone, and methanol require pressurized vessels, which increase the cost of process [28]. The high volatility of the low boiling solvents is an advantage for the recovery of the solvent, while the high flammability is a disadvantage for high-pressure processes [29]. Since the solvent recovery is easy and requires less energy, organosolv treatments by using low boiling point solvents (especially ethanol) were also tested under atmospheric conditions [28, 30, 31]. High boiling point organic solvents such as glycerol take advantage of low operating pressure [23]. There is no need to use pressurized vessels, but solvent recovery demands high energy [22, 32]. The organic solvents such as acetic acid and formic acid, which have boiling points in between low and high temperatures, enable lignin degradation at mild temperatures and at atmospheric pressure [22, 33].

In many studies, lignin isolation was performed in pressurized systems. The risk of the high-pressure reactor and the cost of the entire process limit the recovery of each biomass component. To develop the bio-based economy, there is a need to decrease the cost of biomass fractionation by changing the pretreatment options. This study investigated the recovery of lignin from a single source of biomass under atmospheric conditions by organosolv method. As the forestry and wood processing wastes have an important role in the development of the biorefineries, wood sawdust was used in the present study. Ethanol, acetic acid, glycerol, and formic acid/acetic acid/water mixture (in different proportions) were used separately as organosolv liquor. Thus, by using the same biomass, it was possible to compare the precipitation yield of each organosolv method and properties of isolated lignins. The lignins were characterized by gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and pyrolysis gas chromatography/mass spectrometry (Py-GC/MS).

2 Experimental

2.1 Materials

The biomass used in this study was the sawdust, which was the residue from the sawmill of a wood processing industry in East-Marmara Region, Turkey. Sawdust was in the form of a mixture, mainly softwood, obtained from the processing of different types of trees (in order of use: pine (*Pinus sylvestris*), yellow pine (*Pinus sylvestris* Lipsky), red pine (*Pinus brutia*), cedar (*Cedrus libani*), hornbeam (*Carpinus betulus*)).

Before the experiments, wood sawdust was sieved (60 mesh, 250 μm) and stored in closed bags. Moisture content was determined by using American Society for Testing and Materials (ASTM) E871–82 method [34]. Ash content was determined by using ASTM E1755–01 method [35]. Extractive content was determined according to ASTM E1690–08 Standard Test Method for Determination of Ethanol Extractives in Biomass [36]. Klason lignin in biomass was determined according to TAPPI Test Method T 222 om-02-Acid insoluble lignin in wood and pulp [37]. The C, H, and N analyses were carried out in an elemental analyzer (LECO CHN628). Based on the analysis, moisture content and ash content of wood sawdust were 2.3% and 7.4%, respectively. C, H, and N content (on dry basis) were 45.6%, 6.1%, and 0.09%, respectively. Ethanol extractives content and Klason lignin content (on dry basis) were 1.9% and 28.5%.

2.2 Organosolv treatment methods

2.2.1 Ethanol organosolv treatment

This method was adapted from [31]. Twenty grams of dry wood sawdust was mixed with 200 mL of 95% ethanol (v/v) solution in a round bottom glass flask. Ten milliliters of 0.1 M HCl was added as catalyst. The mixture was continuously stirred and refluxed at 77 °C for 8 h. The mixture was then filtered, and the pulp was washed 3 times with 50 mL of ethanol. To recover ethanol and concentrate the solution, the filtrate (filtrate and the washings) was distilled to 90–100 mL. Concentrated solution was diluted to 1 L with cold deionized water. The precipitated ethanol organosolv lignin (EOL) was filtered and dried at atmospheric conditions.

2.2.2 Acetic acid organosolv treatment

Twenty grams of dry wood sawdust was mixed with 200 mL of 93% aqueous acetic acid solution (v/v) and 0.1% (w/w) HCl (as catalyst) in a round bottom glass flask [38]. The mixture was continuously stirred and refluxed at 107 °C for 3 h. The mixture was filtered, and the pulp was washed 3 times with 50 mL of acetic acid. To concentrate the solution, the filtrate (filtrate and the washings) was distilled until the

concentrated solution was 90–100 mL. Concentrated solution was diluted to 1 L with cold deionized water. The precipitated acetic acid organosolv lignin (AAOL) was filtered and dried at atmospheric conditions.

2.2.3 Alkaline glycerol organosolv treatment

This procedure was modified from Guragain et al. [39]. Twenty grams of dry wood sawdust was mixed with 200 mL of glycerol solution in a round bottom glass flask. As a catalyst, 0.8 g NaOH was added into the mixture. The mixture was continuously stirred under reflux at 170 °C for 2 h. At the end of the treatment, the mixture was immediately filtered. The pulp was washed, and the filtrate was diluted with cold deionized water to 1 L. The precipitated alkaline glycerol lignin (AGOL) was washed, filtered, and dried at atmospheric conditions.

2.2.4 Formic acid/acetic acid/water organosolv treatment

In this procedure, organosolv liquor is a mixture of formic acid, acetic acid, and water in varying volumetric ratios: 40/40/20, 50/30/20, and 30/50/20. Twenty grams of dry wood sawdust was mixed with 200 mL of solvent mixture in a round bottom glass flask. The mixture was continuously stirred and refluxed at 107 °C for 3 h. At the end of the treatments, the pulp was washed with acetic acid and formic acid solution. The filtrate was concentrated to 90–100 mL. Concentrated solution was diluted to 1 L with cold deionized water. The precipitated lignin was filtered and dried at atmospheric conditions. The lignins recovered from the spent liquors were named as: formic acid/acetic acid/water (40/40/20) organosolv lignin (FAWOL 1), formic acid/acetic acid/water (50/30/20) organosolv lignin (FAWOL 2), and formic acid/acetic acid/water (30/50/20) organosolv lignin (FAWOL 3).

Each organosolv process was repeated at least six times. To calculate the precipitation yield of each treatment, the amount of precipitate was divided by the Klason lignin content of the wood sawdust.

2.3 Analyses

FTIR spectra of lignins were obtained using a Perkin Elmer Spectrum 100 spectrometer equipped with a Universal ATR sampling device with a diamond crystal. The spectra were recorded in the range from 400 to 4000 cm^{-1} , with a resolution of 4 cm^{-1} .

Thermogravimetric analysis (TGA) of each lignin sample was performed using a thermogravimetric analyzer (Seiko, TG/DTA 6300) under a constant nitrogen flow (200 mL/min). Each sample was heated to 105 °C with a heating rate of 10 °C/min. The sample (10 mg) was kept at this

temperature for 10 min. It was then heated to 900 °C at a heating rate of 15 °C/min, and kept at this temperature for 7 min.

Ash content of lignins was also determined by using TGA. The samples (10 mg) were heated to 900 °C at a heating rate of 15 °C/min in the air atmosphere (200 mL/min), and kept at this temperature for 7 min.

The molecular weight distribution of each lignin sample was determined by using gel permeation chromatography (GPC) (Shimadzu, Japan), which has a liquid chromatograph (Shimadzu LC-20 AD), degassing unit (DGU-20A 3R), column oven (CTO 10AS VP, with three columns 8 × 300mm, PSS SDV 3 μm, oven temperature: 30 °C), and a refractive index detector (RID-10A, wavelength: 280 nm). Each lignin sample was first dissolved in HPLC-grade tetrahydrofuran (THF) (1 mg/mL) and then filtered through Teflon syringe filter. THF was used as eluent at a flow rate of 1 mL/min. Standard calibration was performed with ReadyCal polystyrene kit (Sigma-Aldrich, M_p 266-66,000 Da). Number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (M_w/M_n) were determined by LabSolutions GPC software (Shimadzu). Analyses were done twice.

Fast pyrolysis analyses were performed in a pyrolyzer (Frontier/PY2020is), which was connected to a GC/MS instrument (Shimadzu/QP 2010 Ultra). Each pyrolysis reaction was performed at 550 °C for 10 s. Pyrolysis products were purged with He into a GC capillary column (Teknokroma, 30 m*0.25 mm*0.25 μm). The oven temperature was programmed from 40 to 320 °C at a heating rate of 8 °C/min. The MS was operated by electron impact ionization at 70 eV with the mass scan range of m/z 35–600. Peaks were identified by NIST mass spectral library. Py-GC/MS analyses were repeated three times to see the consistency of the results.

3 Results and discussion

3.1 Lignin precipitation yield

The precipitation yields of the lignins recovered after atmospheric organosolv treatments are shown in Fig. 1. As seen in Fig. 1, there is a remarkable difference between the precipitation yields of lignins isolated with different solvents. This is mainly due to the solubility of lignin [40], which is affected from the treatment temperature (for EOL, 77 °C; AAOL and FAWOL, 107 °C; AGOL, 170 °C) [41] and solution medium (for EOL, ethanol, and HCl; for AAOL, acetic acid, and HCl; for AGOL, glycerol, and NaOH; for FAWOL, formic acid, acetic acid, and water) [42].

Organosolv treatments at atmospheric conditions resulted in precipitation yields between 6.6% (ethanol organosolv) and 42% (alkaline glycerol organosolv).

As seen in Fig. 1, the lowest precipitation yield was obtained via ethanol organosolv treatment. Apart from its low yield, EOL had a sticky structure that made the separation difficult. In the lignin precipitation process, the evaporation of the ethanol followed by the addition of water has been reported to cause the formation of a sticky lignin [41, 43, 44]. However, in the present study, a sticky lignin formation was observed in organosolv treatment with ethanol whether the organosolv solution was directly diluted with water or the ethanol was recovered prior to dilution. Fernando et al. investigated the best applicable method of lignin precipitation (direct dilution or evaporation prior to dilution) from ethanol-water organosolv liquor of sugarcane bagasse (H_2SO_4 was used as catalyst) [45]. Best method (based on lignin recovery percentage) was found as the evaporation of organosolv liquor in a flash evaporator to 30% (ethanol content, v/v), and then dilution of the liquor (liquor/water ratio, 1:1) at 40 °C. After centrifugation, the percentage yield of precipitation was 45% with a 94% of lignin purity. According to the experimental study of Rohde et al., the lignin yield in ethanol-based organosolv treatment (biomass/ethanol-water solution, 1/7 (w/w); catalyst: H_2SO_4 (0.5 wt% of biomass); temperatures, 160, 175, 190 °C; reaction periods, 120, 180, 240 min; ethanol concentrations, 35, 55, 75 wt%) ranged between 14 and 43% [46]. In the study of Bauer et al. (biomass/organosolv liquor, 25 g *Miscanthus giganteus*/175 mL ethanol solution; ethanol concentrations, 65, 75, 85, 95%; catalyst: HCl; refluxing at atmospheric conditions for 2–8 h), lignin recovery was reported to vary between 13% (65% ethanol solution, 4 h reaction period) and 44% (95% ethanol solution, 8 h reaction period) depending on ethanol concentration and reaction period [31]. The comparatively low precipitation yield obtained in ethanol organosolv treatment (6.6%) could be due to low temperature of treatment and formation of small-sized lignin fragments that suspended in solution as colloids [31, 47].

As seen in Fig. 1, the highest yield of precipitation was observed after alkaline glycerol organosolv treatment. Although the yield was high, the difficulty in filtering the pulp was the main problem. In many of the studies related with the

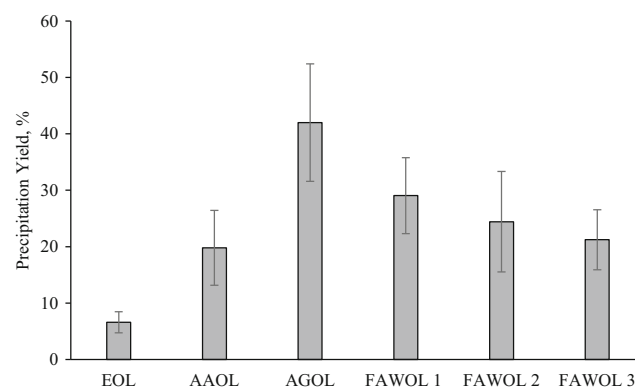


Fig. 1 Precipitation yield of lignins

alkaline glycerol treatment, mainly delignification and the hydrolyzability of cellulose have been investigated. Since this study aimed to recover lignin by precipitation, the delignification rate was not investigated. Therefore, it was quite difficult to compare the lignin yield found by this method with other data. Still, the comparison of experimental data from other studies that applied the alkaline glycerol method gave an idea of the effectiveness of the method. Sun et al. showed that glycerol was an effective solvent (yield ranging between 16 and 35%), which was used to produce cellulose rich organosolv pulp with very low lignin and hemicellulose content [48, 49]. According to Meighan et al., pretreatment of sugarcane bagasse with glycerol (80%, (v/v)) was strongly influenced from the reaction period [50]. As the reaction period changed from 40 to 120 min, the delignification extent increased from 47.9 to 84.6%. Romani et al., who used glycerol-water liquor for the pretreatment of *Eucalyptus globulus* wood, found out the maximum lignin removal as 77% (200 °C, glycerol/water solution: 80%, 65 min) [51]. A similar study, which was done by Novo et al., showed that 79.9% of delignification was possible (feedstock: wheat straw, glycerol/water solution: 80%, 190 °C, 240 min). It was observed that not only crude glycerol was effective in pretreatment [32]. Todaka et al. used glycerol byproduct of biodiesel production (which includes fatty acid sodium soap) and successfully pretreated the softwood samples [52]. The reason why glycerol is a good solvent is that it can easily diffuse into the biomass due to its highly polar triol structure [53, 54]. However, none of the studies listed above indicated how much lignin was recovered from the solution.

Based on the results, it can be concluded that formic acid-acetic acid-water mixtures provide a higher precipitation yield than acetic acid. Shui et al. compared the pretreatment of corn stalk by using the formic acid, acetic acid, and formic acid/acetic acid/water liquors separately [24]. They reported a lignin yield of 31–36% in the case of organic acid mixture, which was higher than only acetic acid or formic acid.

Ash in lignin is an important impurity [55, 56]. On the other hand, organosolv treatment is also known to produce lignin with lowest amount of impurities. The ash contents of the obtained EOL, AAOL, AGOL, FAWOL 1, FAWOL 2, and FAWOL 3 lignins were 1.2%, 3.8%, 3.9%, 1.3%, 1.2%, and 2.8%, respectively. When the ash contents of the lignins were examined, it was seen that AGOL had the highest ash content and EOL had the lowest ash content. The high impurity in AGOL was expected due to the reason that lignin, which is isolated by alkaline process, is reported to be less pure and highly condensed [57]. The ash content of all lignins in this study were higher than that reported by Bauer et al. [31] (the ash content of lignin was between 0.04 and 0.05% after ethanol organosolv treatment, 0.11% after dioxane organosolv treatment) and Hosseinaci et al. [13] (the ash content ranged between 0.07 and 0.19% (depending on the severity of the

treatment) after methyl isobutyl ketone and ethanol treatment). On the other hand, the ash content of all lignins in this study were lower than that reported by Panamgama and Peramune [47] (ash content of lignin was 6% after acetic acid-formic acid treatment) and Espinoza-Acosta et al. [57] (ash content of organosolv lignin was between 1.13 and 4.9).

3.2 Lignin structure

FTIR spectra of organosolv lignins, which were recorded in the 4000–400 cm^{-1} region, are shown in Fig. 2. The functional groups were identified based on reference studies [47, 58–63]. As the FTIR spectra of EOL, AAOL, AGOL, FAWOL 1, FAWOL 2, and FAWOL 3 were compared with the spectra given in the reference studies, it was seen that the peak intensities and the wavelengths corresponding to the peaks differed slightly. This could be explained by the fact that the biomass used and lignin isolation methods were not exactly the same with the reference literature.

Based on the FTIR spectra, all organosolv lignins represented the same functional groups at similar wavelength regions, but with different intensities.

The broad stretching vibration observed at (3300–3400) cm^{-1} is assigned to phenolic and aliphatic O–H stretching [64]. Among the organosolv lignins, AGOL represented the highest intensity at this region, specifically at 3306 cm^{-1} , due to O–H stretching of glycerol. All of the organosolv lignins represented the stretching vibration of C–H in $-\text{CH}_3$ and $-\text{CH}_2-$ groups at 2926–2936 cm^{-1} , 2851–2856 cm^{-1} , and 1452–1463 cm^{-1} . The intensity of the stretching vibration of C–H (due to side chain methyl and methylene group in lignin) was clearly higher in EOL as compared with the other lignins. In all studies in which lignin is isolated, this vibration is observed in different intensities. The reason why the intensity of this vibration was higher could be explained by the fact that ethanol might also be carried by the EOL, like observed in the

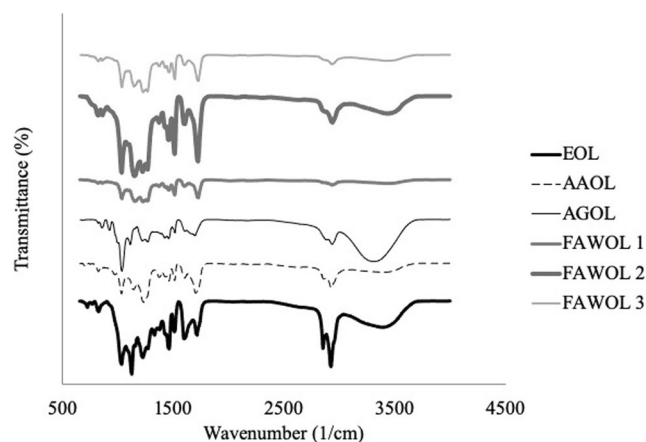


Fig. 2 FTIR spectra of EOL, AAOL, AGOL, FAWOL 1, FAWOL 2, and FAWOL 3

case of AAOL. AAOL showed a strong peak at 1698 cm^{-1} due to C=O stretch of carboxylic acids [65]. The presence of acetic acid adsorbed by AAOL could be the reason for the strong carboxylic acid C=O stretch, which was also confirmed by Py-GC/MS. Unlike other lignins, FAWOL 1, FAWOL 2, and FAWOL 3 showed a strong C=O stretch, which is originated from unconjugated ketones, carbonyls, and esters, at 1720 cm^{-1} [65]. All of the lignins showed stretching vibration of C=C in aromatic skeleton, which was observable at $1596\text{--}1603\text{ cm}^{-1}$, $1509\text{--}1512\text{ cm}^{-1}$, and $1422\text{--}1433\text{ cm}^{-1}$. Aromatic skeleton vibration, which was observed at $1596\text{--}1603\text{ cm}^{-1}$, was more intense in EOL. AGOL is the one, which represented the all peaks of stretching vibration of C–C in aromatic skeleton in the lowest intensity. In all of the lignins (except EOL and AGOL), more intensely in the spectra of AAOL and FAWOL 3, in-plane deformation vibration of O–H in phenolic structure was observable at $1365\text{--}1368\text{ cm}^{-1}$. This shows that acetic acid and formic acid and their combination worked well for the cleavage of $\beta\text{-O-4}$ linkages to form phenolic hydroxyl and carbonyl (1720 cm^{-1}) groups [62].

Stretching vibration of C–O, which denotes the S-ring breathing at 1328 cm^{-1} was only observable in the spectra of EOL. Stretching vibration of C–O of guaiacyl unit, which was observed at $1265\text{--}1268\text{ cm}^{-1}$, was detected in all organosolv lignins. Stretching vibration of C–O–C in aromatic ether group was observable in all lignins, except AGOL, at $1138\text{--}1153\text{ cm}^{-1}$. In-plane deformation of C–H in guaiacyl unit (at 1122 cm^{-1}) was only observable in the spectra of EOL. The peaks representing the stretching vibration of secondary alcohols and aliphatic ethers and stretching vibration of C–O in the primary alcohols were observed at 1082 cm^{-1} and 1030 cm^{-1} , respectively. Only AAOL, FAWOL 1, FAWOL 2, and FAWOL 3 represented a peak at 967 cm^{-1} , denoting the out of plane deformation vibration of trans double bonds in –HC=CH– . Except EOL, all lignins represented the stretching vibration of C–H in guaiacyl unit at $853\text{--}855\text{ cm}^{-1}$.

The lignins were also compared semiquantitatively using the data obtained from the FTIR results and shown graphically in Fig. S1 in the Supplementary Material. Semiquantitative FTIR analysis was based on the relative absorbance intensity of the peaks (A_x) with reference to the absorbance intensity of the peak at 1511 cm^{-1} (A_{1511}), which was the stretching vibration of C=C in aromatic skeleton of lignin. As seen from Fig. S2, the presence of guaiacyl unit for all lignins were high, which was observable from A_{1267}/A_{1511} ratio (1.66 for EOL, 2.35 for AAOL, 1.71 for AGOL, 1.44 for FAWOL 1, 1.34 for FAWOL 2, and 1.52 for FAWOL 3). Due to esterification in the presence of formic acid, the A_{1720}/A_{1511} ratio of FAWOL 1, FAWOL 2, and FAWOL 3 are higher than 1 (1.24, 1.15, 1.06, respectively). The presence of glycerol in the lignin was also observable from the A_{1033}/A_{1511} ratio, where the ratio had its highest value (3.96) for AGOL. The $A_{1368\text{--}1370}/A_{1511}$ ratio,

which shows the ratio of the absorbance of in-plane deformation vibration of O–H in phenolic structure to the absorbance of aromatic skeleton of lignin, showed that the ratio of AAOL was higher as compared with FAWOL 1, FAWOL 2, and FAWOL 3, and the ratio was lower than 1 for each.

3.3 Molecular weight

Weight-average molecular weight (M_w), number-average molecular weight (M_n), and polydispersity index (M_w/M_n) of EOL, AAOL, AGOL, FAWOL 1, FAWOL 2, and FAWOL 3 are shown in Table 1. The difference between the molecular weights of lignin was quite remarkable. This result indicated that organosolv conditions together with the organosolv solvent had a definite influence on M_w and M_n of the lignins.

The lignins isolated with formic acid/acetic acid/water mixture have a higher molecular weight than the others. Sequeiros and Labidi, who found a similar result, attributed this to the severe organosolv conditions [66]. Repolymerization and recondensation due to highly reactive and unstable molecules were reported to cause an increase in the molecular weight of lignin.

There was a remarkable difference in the polydispersity index of the lignins. Polydispersity index, which is an indicator of how homogeneous the molecular weight is, was observed to vary between 2.5 and 7.4. The polydispersity of FAWOL 1 is the highest, which shows that it has the widest molecular weight distribution.

In their study, Xu et al. isolated and characterized lignin from wheat straw by using acetic acid-water, acetic acid-formic acid-water, methanol-water, and ethanol-water mixtures at atmospheric conditions (at $85\text{ }^\circ\text{C}$ for 4 h) [33]. The weight-average molecular weights ranged from 3960 g/mol (acetic acid-water) to 4340 g/mol (methanol-water), and polydispersity index ranged from 1.56 to 1.71. Compared with the present study, only FAWOL 2 and FAWOL 3 lignins had similar M_w . However, the polydispersities of FAWOL 2 and FAWOL 3 were higher. In the study of Maniet et al., organosolv lignin of fall fescue, which was obtained at same conditions as FAWOL 2, had an average molecular weight (1756 g/mol) less than FAWOL 2 and a polydispersity index (8.7) higher than that of FAWOL 2 [67]. When the EOL and AAOL lignins were compared with the lignins isolated in the study of Xu et al. [33], the EOL and AAOL were found to have lower molecular weight and moderate polydispersity.

In the study of Perez-Cantu et al. (rye straw to solution ratio = 1:8; 50% ethanol concentration; H_2SO_4 as catalyst), they found that organosolv treatment temperature had a strong effect on the molecular weight of lignin [68]. As the temperature was changed from 170 to $190\text{ }^\circ\text{C}$, the average molecular weight decreased from 5200 to 2800 g/mol . It was stated in the same study that increasing reaction time is effective in decreasing the molecular weight of lignin in organosolv process

Table 1 M_w , M_n , and M_w/M_n of isolated lignins

	EOL	AAOL	AGOL	FAWOL 1	FAWOL 2	FAWOL 3
M_w (g/mol)	1756	1493	1373	7400	3852	4200
M_n (g/mol)	687	587	454	1007	1353	871
M_w/M_n	2.55	2.54	3.02	7.35	2.85	4.82

M_w weight-average molecular weight

M_n number-average molecular weight

M_w/M_n polydispersity index

performed at high temperature (190 °C). This was also observed in our study. The higher temperatures (170 °C for AGOL) resulted with lower molecular weight lignins, where severe solvent-catalyst mixtures caused to obtain lignins with higher polydispersity.

3.4 Thermal decomposition characteristics

Thermal decomposition characteristics and thermal stability of lignin samples were investigated by using thermogravimetric analysis (TGA). The characteristic curves of thermogravimetric (TG) and differential thermogravimetric (DTG) analysis are shown in Figs. 3 and 4, respectively.

As seen from curves, each isolated lignin sample represented different degradation profile. However, the common feature of all samples was that lignin degradation occurred over a wide temperature range. Similar degradation profiles of lignin, irrespective of purification methods, have been observed in previous studies [58, 69]. In this wide temperature range, lignin samples were degraded in stages [47]. In the first stage, moisture evaporation (or dehydration) was observed between ambient temperature and 110 °C [70]. When the weight loss percentages were compared (see in Table 2), it was found that AGOL sample contained more moisture in its structure, which was also observed in FTIR spectra. In contrast, lignin, which contained the least amount of moisture in its structure, was

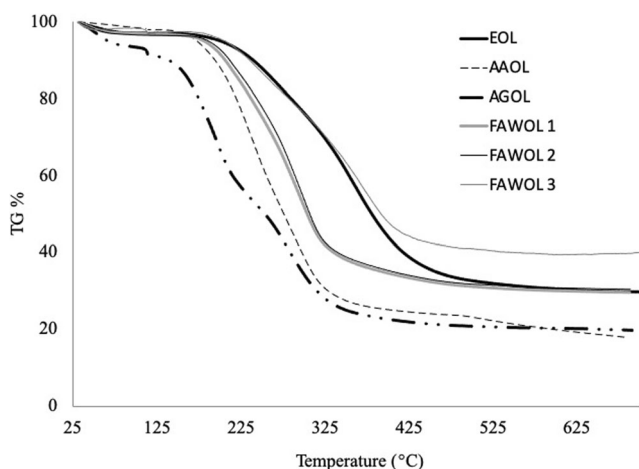


Fig. 3 TG curves of EOL, AAOL, AGOL, FAWOL 1, FAWOL 2, and FAWOL 3

AAOL. Except for AAOL and AGOL, the DTG curve of the other lignins had a shoulder on the left side of the maximum weight loss temperature (< 300 °C). This shoulder was observed due to formation of volatile and low molecular weight compounds, which were formed by the degradation of carbohydrates and hemicellulose [47, 71]. The hemicellulose, which is bound to lignin with ester and ether linkages, can be dissolved in organic solvents including organic acids and alcohols; and the dissolved hemicellulose can be precipitated in water [72]. Xu et al. also detected small amounts of hemicellulose in the precipitate [33]. However, there are also studies concluding that degradation of lignin could start at temperatures as low as 200 °C [73]. As stated by Manara et al., this shoulder could be explained by the combined degradation of lignin and hemicellulose, which was co-precipitated with lignin [74]. Unlike other lignin samples, this shoulder appeared to be a sharp peak (at 243.5 °C) in the DTG curve of AGOL sample. This might be due to high amount of low molecular weight compounds (alcohols) that are produced during the pyrolysis of AGOL. Similar observation was done by Cheng et al., who found the initial decomposition temperature of glycerol lignin as 231.7 °C [23]. In the case of AAOL, the main peak was observed at 325 °C, and the shoulder was above 350 °C.

T_{max} , which is the temperature of maximum weight loss rate, ranged between 243.5 °C (AGOL) and 404.7 °C (FAWOL 2). T_{max} observed in degradation of lignins obtained using formic acid/acetic acid/water mixtures were much

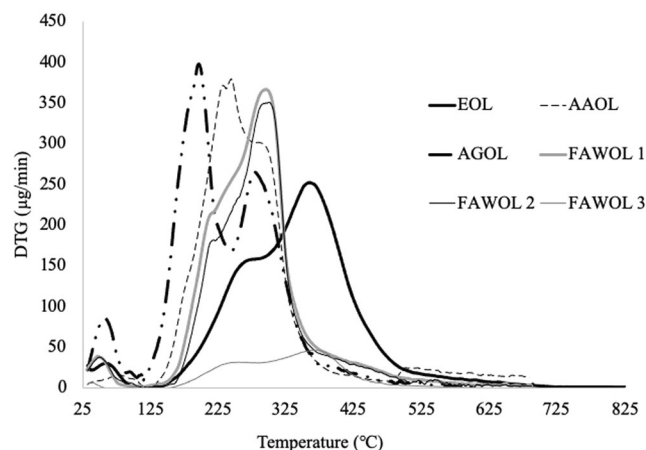


Fig. 4 DTG curves of EOL, AAOL, AGOL, FAWOL 1, FAWOL 2, and FAWOL 3

Table 2 Thermal degradation parameters and ash content of EOL, AAOL, AGOL, FAWOL 1, FAWOL 2, and FAWOL 3

	EOL	AAOL	AGOL	FAWOL 1	FAWOL 2	FAWOL 3
Weight loss percentage (25–110 °C), %	3	2	8.4	2.9	3.4	2.6
Weight loss percentage (110–900 °C), %	67.2	79.7	70.6	66.4	65	57.5
Char yield, %	29.8	18.3	21	30.7	31.6	39.9
Ash, %	1.23	3.8	3.9	1.3	0.5	2.8
T _{max} , °C	358.5	324.9	243.5 (1st peak), 369.5 (2nd peak)	397.7	404.7	393.3

higher than those of lignins obtained with other organic solvents. FAWOL 3 had the highest thermal stability and char yield (39.9%), which was followed by FAWOL 2 (31.6%), FAWOL 1 (30.7%), EOL (29.8%), AGOL (21%), and AAOL (18.3%).

3.5 Fast pyrolysis of organosolv lignins

Pyrolysis products obtained from rapid pyrolysis of lignin were identified using Py-GC/MS [74]. In the pyrolysis of all lignins, the solvents used in the organosolv process were clearly detected in Py-GC/MS. Their peak areas were much higher than the peak areas of other pyrolysis products. Zhang et al. did a similar observation while using 1-butanol as the organosolv solvent [75]. In that study, 1-butanol was excluded, and relative peak areas were corrected. In the study of Custodis et al., dioxane and ethanol, which were used during isolation separately, were observed in the GC/MS analysis of pyrolysis oil [76]. Since the presence of those solvents in the GC/MS analysis was explained with the fact that they were used in high volumes during the treatment, the high peak areas of these

solvents were excluded, and relative peak areas of the compounds were corrected. Therefore, in the present study, in order to make a better qualitative comparison between the components, the relative area of each component was corrected after excluding the peak area of the solvents.

Based on results, 50 pyrolysis products were detected in the fast pyrolysis of AAOL, AGOL, FAWOL 1, FAWOL 2, and FAWOL 3, respectively. The products were classified as phenolics, carboxylic acids, alcohols, ketones, esters, aldehydes and hydrocarbons. The distribution of the products obtained from the fast pyrolysis of lignins is shown in Fig. 5. The most common components in pyrolysis oil were phenolic compounds. As shown in Fig. 5, the pyrolytic oils of all lignins contained the same groups, but the components and amounts in these groups differed. Undoubtedly, the solvents we used to isolate lignin had a great effect on the composition of pyrolysis oil. As seen in Fig. 5, the greatest contribution to the alcohol compounds in the pyrolysis oil was made by AGOL, which was pretreated with glycerol. Similarly, the greatest contribution to acids and esters in pyrolytic oil was made by AAOL, in which acetic acid was used as solvent.

Fig. 5 The distribution of the products based on Py-GC/MS

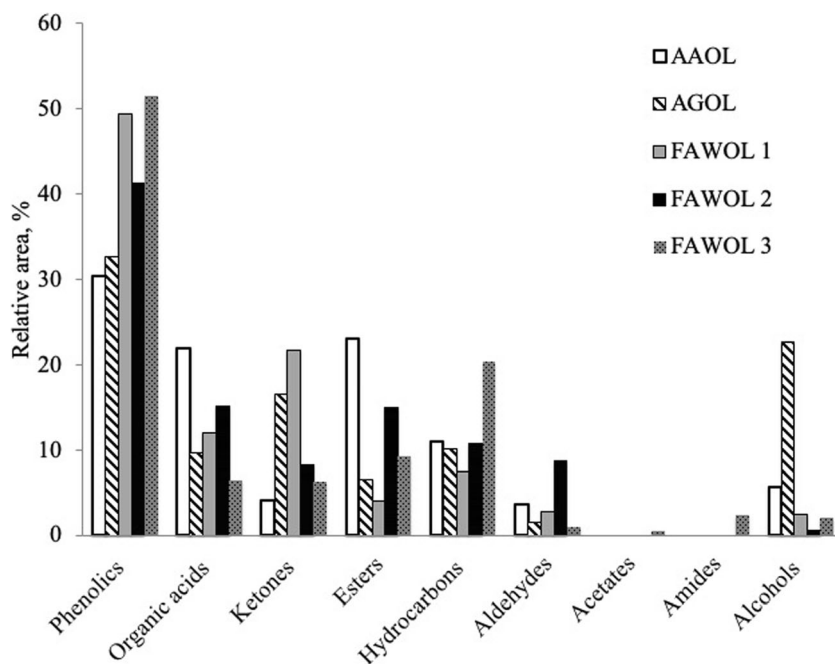
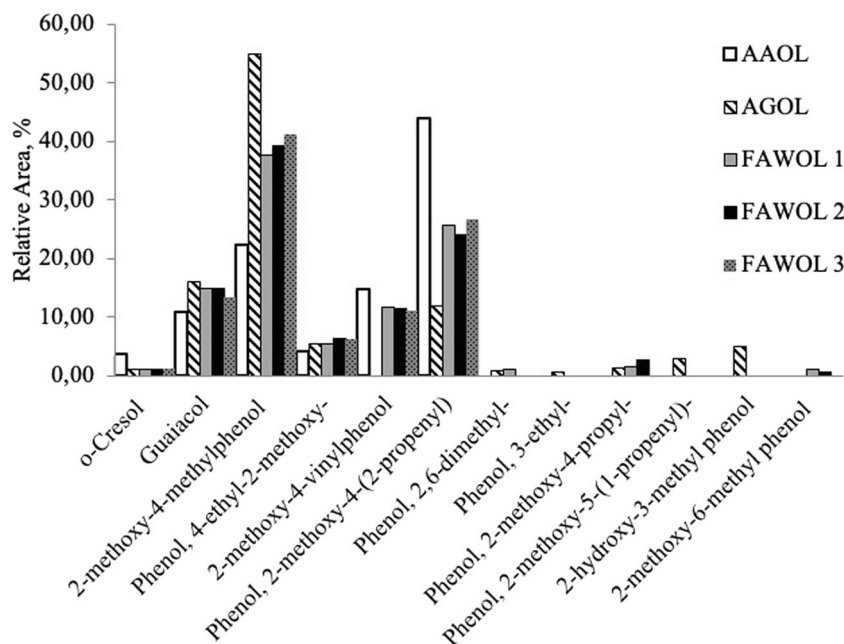


Fig. 6 The distribution of phenolic compounds based on Py-GC/MS



When the pyrolysis products of AAOL and FAWOL were compared (Fig. 5), the effect of formic acid on lignin structure was clearly seen. The pyrolysis of FAWOL 1, FAWOL 2, and FAWOL 3 yielded more phenolic compounds than AAOL. In addition, the pyrolysis products of AAOL contained more organic acid, ester, and alcohol groups as compared to the pyrolysis products of FAWOL 1, FAWOL 2, and FAWOL 3. In contrast, in the pyrolysis products of FAWOL 1, FAWOL 2, and FAWOL 3, there are more ketone compounds than the others. The strong C=O stretch at 1720 cm^{-1} observed in the FTIR spectrum confirms this result.

The comparison of the compounds detected by Py-GC/MS for each lignin AAOL, AGOL, FAWOL 1, FAWOL 2, and FAWOL 3 is shown in Table S1 in the Supplementary Material. The common products are: o-cresol (2-methyl phenol), guaiacol (2-methoxyphenol), 2-methoxy-4-methyl phenol, 4-ethyl-2-methoxy phenol, 2-methoxy-4-(2-propenyl) phenol, acetovanillone, and dehydroabietic acid methyl ester. The presence of phenolic compounds is explained by the cleavage of the phenyl-propane units of lignin [77]. Several studies indicate that acetovanillone, which is a guaiacyl-derived ketone, is a natural product of lignin pyrolysis [77–81]. Its presence is not affected from the lignin isolation method. Abietic acid is a natural resin acid, which is mainly found in pinewood [82]. During the wood sawdust pyrolysis, abietic acid is methylated to form its methyl ester [83]. Its presence is also not affected from the isolation method.

Phenolic compounds in pyrolytic oils obtained from isolated lignins are given in Fig. 6. Although extracted by different methods, all lignins contained the same

phenolic compounds. The most abundant phenolic compound in pyrolytic oil was 2-methoxy-4-methylphenol (4-methylguaiacol). It was followed by 2-methoxy-4-(2-propenyl) phenol (eugenol) and guaiacol, respectively. The presence of guaiacol type compounds in all lignins could be explained by the wood sawdust, which was probably originated from softwoods [52].

4 Conclusions

In the present study, wood sawdust was exposed to organosolv treatment with different solvents (ethanol, acetic acid, glycerol, formic acid/acetic acid/water) under atmospheric pressure. The lignin was precipitated from each solution and characterized. It was found that the amount and structural properties of the lignins obtained were highly affected by the conditions of the organosolv treatment. When evaluating which method worked best, the possible end-uses of lignins, which were obtained, need to be considered. Because each method gives lignin with different character, each lignin will be more suitable for different end-use. If lignin is to be used as an additive or as a filler in other polymers, to have a high miscibility in polymer, its molecular weight and polydispersity should be low. From this point of view, AAOL, EOL, AGOL, and FAWOL 2 are more advantageous than other lignins. If the specialty chemicals will be produced by using the phenolic platform molecules (which is produced by the fast pyrolysis of lignin), the percentage of phenolic components in bio-oil and the pyrolysis conversion yield should be high. When evaluated in this respect, it can be said that FAWOL 1, FAWOL 2, and FAWOL 3 are more advantageous. With high char yield and

low ash content, FAWOL 1, FAWOL 2, and FAWOL 3 can be good candidates for activated carbon production. Since the lignins obtained do not contain sulfur, they can be modified as catalysts after activation. Among all lignins obtained, EOL is the most disadvantageous both in terms of precipitation efficiency and the structure of the lignin obtained. Based on the results, the ethanol organosolv method that takes place under atmospheric conditions definitely needs to be improved.

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