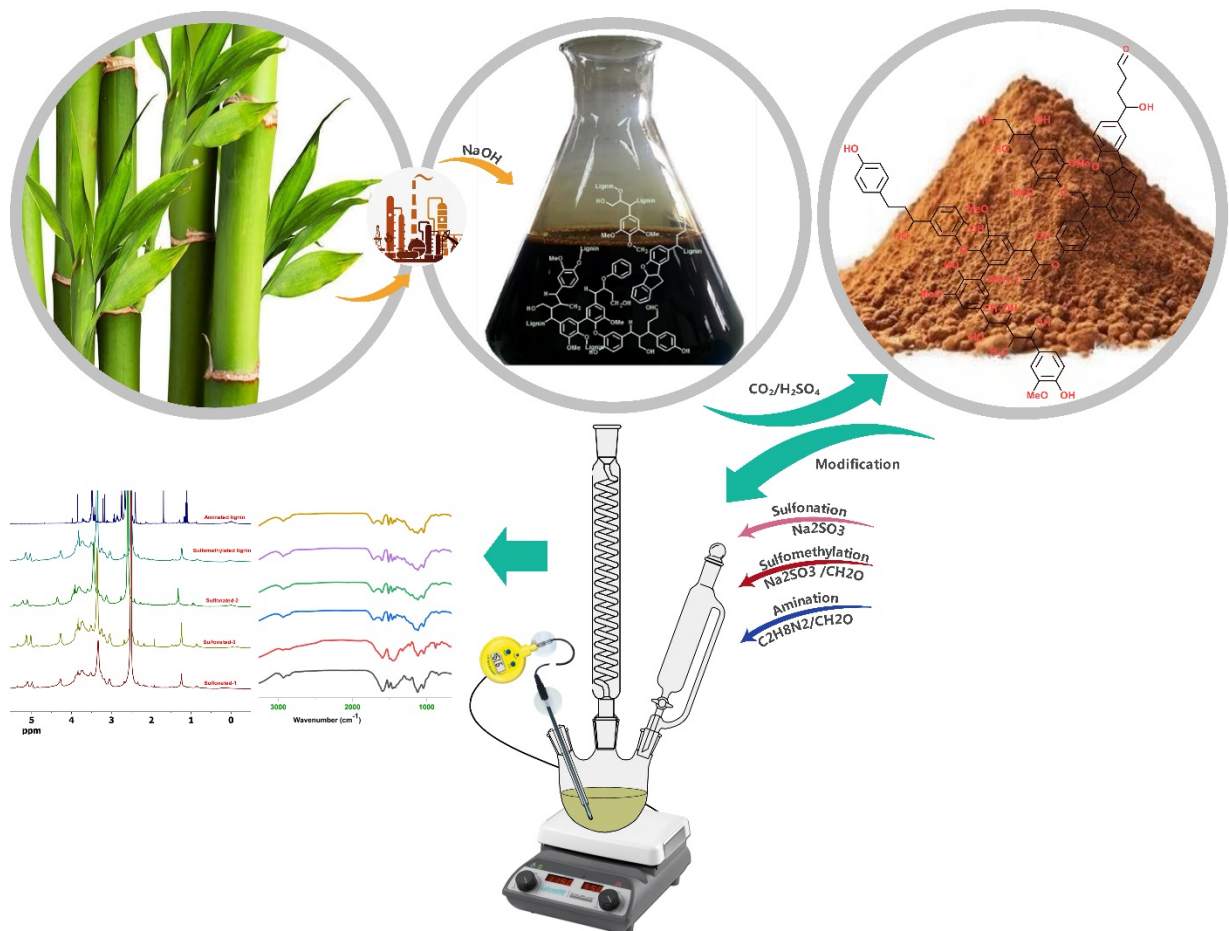


Valorization of bagasse alkali lignin to water-soluble derivatives through chemical modification

Graphical abstract



Valorization of bagasse alkali lignin to water-soluble derivatives through chemical modification

Ali.Abdolkhani *^a, Zeinab Khorasani ^a, Yahya Hamzeh ^a, Fariborz Momenbeik ^b, Zahra Echresh zadeh^c, Fubao Sun ^d, Meysam Madadi^d, XueMing Zhang^e

^a Department of Wood and Paper Science and Technology, Faculty of Natural Resources, University of Tehran, Karaj 31585-4314, Iran

^b Department of Analytical chemistry. University of Isfahan, Isfahan 81746-73441, Iran

^c Department of Chemical Engineering, University College London, Torrington Place, WC1E 7JE, London, UK

^d Key Laboratory of Industrial Biotechnology, Ministry of Education, School of Biotechnology, Jiangnan University, Wuxi 214122, China.

^e Beijing Key Laboratory of Lignocellulosic Chemistry, College of Materials Science and Technology, Beijing Forestry University, Beijing 100083, China

* Corresponding author: Abdolkhani@ut.ac.ir

ABSTRACT

Black liquor is the by-product of the pulping process where the lignin, hemicellulose, and extractive materials are separated from wood to produce paper pulp. As one of the primary lignin sources, black liquor is considered an important energy source from biomass to produce biofuels and value-added chemicals. However, soda alkaline lignin has limited industrial applications due to its insolubility in water and lack of reactivity. Therefore, chemical modification is essential to enhance its industrial applications. In this study, alkali lignin from bagasse was modified through sulfonation, sulfomethylation, and amination processes using different reaction conditions. The structural analysis of obtained products was investigated by FTIR and ¹H-NMR. The molecular weight distribution and thermal stability of the water-soluble products were analyzed using gel permeation chromatography (GPC) and thermogravimetric analysis (TGA), respectively. The elemental analysis was used to measure the elements (CHNSO) of the obtained water-soluble derivatives. The chemical structure analysis of the samples with FTIR and ¹H-NMR confirmed the modification processes. The results indicate that modification led to increased water solubility and a decrease in the precipitation pH of lignin samples, due to the introduction of sulfonate and amin functional groups on lignin. In addition, the molecular weight and thermal stability of modified lignins were increased due to the presence of sulfonate and amine groups compared to unmodified lignin.

Keywords: Alkali lignin, Amination, Sulfomethylation, Sulfonation, Solubility

1. INTRODUCTION

The environmental issues of the insane use of fossil-based resources during the last decade lead to innovative strategies for producing materials, chemicals, and energy from renewable bioresources to slow down climate changes [1]. Unfortunately, the industrial production of bio-based materials is far from dealing with our needs for commodity materials. For example, despite the incredible potential to convert to a wide range of bioproducts, only 3% of lignocellulosics is used by our industries [2].

Lignin, the most abundant aromatic biopolymer, is produced mainly as a by-product of the pulp and paper industry [3, 4]. Black liquor is a complex mixture of depolymerized lignin, polysaccharides, extractives, and pulping chemicals [5, 6]. Lignin is the main component of the black liquor and makes up 30-45% of the total solids present in the black liquor [7]. The most common method to process the black liquor is to concentrate it and burn it in the recovery boilers of pulp mills to generate heat and recover non-organic chemicals. Alkali lignin within the black liquor of pulping plants has a unique capability to be converted to bio-based materials. It is estimated that more than 80 million tons of lignin could be separated from pulping black liquor and valorized to many of today's products manufactured from fossil-based raw materials [8]. The proposed schematic valorization process of lignin to high value-added bio-products in a pulping mill is depicted in Fig. 1.

The low reactivity of alkali lignin restricts its valorization due to its carbon-carbon based backbone, low functionality and vast structural degradation during pulping [9]. The valorization of lignin through chemical modification is interesting due to the considerable economic and environmental advantages.

The chemical modification of lignin enhances its reactivity by increasing the number of active groups. Extensive studies have been performed on the Physico-chemical modification of alkali lignin structure to increase its water solubility [10–12]. The chemical modification of lignin can be achieved by different approaches include reaction with epichlorohydrin, formaldehyde, phenol, propylene carbonate, polyethylene glycol [13–15]. Moreover, The modified lignin can be obtained by introducing cationic or anionic moieties to increase its solubility [16]. The modified lignin was used as cement dispersants, solvents (in vinegar and oil), binder, vanillin, dimethyl sulfoxide production, leather, activated carbon, lubricant and printing pigment [17–19].

An improved dispersion and agglomeration on properties were reported upon sulfonation and sulfomethylation of alkali lignin [9, 15, 20–22]. Water-soluble sulfonated lignin was used in a wide variety of applications such as plasticizers [23], deflocculant [24], oil drilling aid [25], cement additive [26], battery additive [27] and dust suppression agent [28, 29].

This study was aimed to valorize alkali lignin from bagasse soda liquor through modification by sulfonation, sulfomethylation and amination processes to obtain water-soluble moieties. **In the literature, the valorization of bagasse alkali lignin through amination was not reported nor**

compared with sulfonation and sulfomethylated processes. The characteristics of modified lignins were analyzed by FTIR, ¹H-NMR, TGA, GPC, and elemental analysis techniques.



Fig.1. proposed lignin valorization to bio-based materials and chemicals

2. Materials and Methods

2.2.1 Materials

Bagasse soda black liquor was provided from the local pulping plant in the southwest of Iran. All the chemicals were purchased from Merck as laboratory grade and were used as received.

2.2.2 Isolation of lignin

The isolation of lignin was performed *via* the LignoBoost process by using carbon dioxide (CO₂) and sulfuric acid (H₂SO₄). In this process, the CO₂ gas was injected into black liquor to reach the pH 10, and the pH was then reduced to 2 by acidification process using sulfuric acid

(98%), and the precipitated lignin was washed with distilled water and filtered. Finally, the lignin was Lyophilized by freeze-drying to obtain raw lignin (RL) [30].

2.2.3 Modification of lignin

RL (2g) was sulfonated by mixing with sodium sulfite (0.1 M) under three different reaction conditions. RL was sulfonated at different temperatures (75 and 90 °C) for 6 h to obtain SL-1 and SL-2 fractions, respectively. The SL-3 sample was obtained by sulfonation of RL at 90 °C for 4 h. All the reactions were conducted in a stirred (500 rpm) 500 ml three-neck flask, assembled with a thermometer and a Graham condenser. At the end of the reaction, the product was filtered by anionic and cationic exchange columns, followed by freeze-drying. The sulfomethylated lignin (SML) was obtained by mixing formaldehyde (0.1 M) and sodium sulfite (0.1 M) with the RL at 75 °C for one hour [31]. After the reaction, the product was filtered by ionic and cationic exchange columns in sequence. Amination of RL was conducted by Mannich reaction. RL (10 g) was mixed with ethylenediamine (0.6 M) and formaldehyde (0.6 M), and the mixture was added to 100 ml of NaOH (0.5 M) in a 500 ml three-neck flask under vigorous stirring at 75 °C for 3 hours. Isopropanol was added to precipitate the aminated lignin (AML). AML filtered and washed with isopropanol and vacuum dried for 48 hours [32].

2.2.4 Solubility and precipitation pH

Lignin samples (0.2 g) were suspended in 20 ml of deionized water by stirring at 100 rpm for 2 h at 30 °C. The samples were centrifuged at 1000 rpm for 5 min. The insoluble samples were vacuum dried overnight at 60 °C [15]. The lignin solubility was determined using equation 1.

$$\text{Water solubility (\%)} = (\text{Mass of dissolved lignin}) / (\text{Initial mass of lignin}) \times 100 \quad (1)$$

To determine the solubility of lignin samples at different pHs, raw and modified lignins samples (0.2 g) were suspended in deionized water (20 mL) at different pHs using diluted hydrochloric acid (0.1 M). Samples were incubated for 2 h at 30 °C and 100 rpm. The pH at which the solution began to precipitate was recorded using a pH meter [33].

2.2.5 Molecular Weight

The molecular weight analysis of acetylated raw lignin was determined by Gel Permeation Chromatography (GPC) (KNAUER Smart line 2300). RL (100 mg) was dissolved in 2 mL of acetic anhydride/pyridine 1:1 (v:v) solution at 25 °C and stirred overnight. The solution was

added to an excess of diethyl ether (50 mL) to precipitate the acetylated lignin. The unreacted pyridine was further removed from the sample by sequential washing with ethanol followed by washing with deionized water. Lignin samples were dissolved in a mixture of tetrahydrofuran (THF) and NaNO₃ (0.1 mol/L), and the same solution was used as the eluent (flow rate 1 mL/min) for molecular weight analysis using UV detector.

2.2.6 FTIR Analysis

The FT-IR spectra were measured using the KBr pellet technique. The oven-dried samples (0.05 g) were used for functional group analysis using FTIR spectrometer (Mattson Galaxy 6020). The spectra were recorded in the range of 400 cm⁻¹ to 4000 cm⁻¹ with a 4 cm⁻¹ resolution, and 20 scans per min were conducted.

2.2.7 TGA Analysis

The thermal stability of the modified and raw lignin samples was conducted using a thermogravimetric analyzer, TGA, 601 series, Leco model. The analysis was done under a nitrogen environment at a steady flow rate of 30 mL/min. Mass loss of the samples was recorded in the temperature range 40- 550 °C at the rate of 10 °C/min.

2.2.8 NMR Analysis

The ¹H-NMR analysis of lignin samples was conducted to determine the lignin structure before and after modification using a Bruker Avance III 400 MHz spectrometer (Bruker, Germany) equipped with a 5 mm BBO probe using an inverse gated proton decoupling sequence. DMSO-d₆ and D₂O were used as the solvents for ¹H-NMR analysis of raw and modified lignins, respectively.

2.2.9 Elemental Analysis

Elemental analysis of lignin was done using an Elementar Vario Micro Cube CHNOS elemental analyzer (Elementar Analysensysteme GmbH, Germany) to determine carbon, hydrogen, nitrogen, sulfur and oxygen content.

3. Results and Discussion

3.1 Water solubility

The solubility test results of lignin samples alongside precipitation pH are presented in Fig.2. the solubility trend of lignin samples at different pHs is depicted in Fig. 3. According to the obtained results, All the lignin samples was soluble in pH>10 values. The precipitation of RL

was started at pH 9, while the onset precipitation of SL-1, SL-2, SL-3 and SML was commenced at pH 2. The AML was completely soluble even at the pH<2 values. In general, the solubility of lignin in water depends on the number of hydrophilic groups present in lignin. Therefore, the chemical modification of lignin by sulfonation or sulfomethylation lignin increases its hydrophilicity due to the introduction of sulfonate groups in the lignin structure. Sulfomethylation of kraft lignin was reported to increase lignin's solubility [34]. The acid separation logarithmic index (PK_a) for the sulfonate group is reported to be 2.8 [35]. Therefore, the protonated sulfonate groups at pH>2 reduce the solubility of SL and SML samples. At higher pH, the sulfonate groups are deprotonated, which leads to hydrophilicity and high solubility of the SL and SML[35]. The increased water solubility of SL-3 regarding the SL-1 and SL-2 is probably due to the introduction of higher sulfonate groups resulting from reaction intensity. Moreover, the amination process increases the solubility due to the cationic property of amine groups. Amination of alkali lignin was previously reported to increase the solubility of lignin [32]. Furthermore, temperature and time have a positive effect, which means that with increasing temperature and reaction time, the solubility due to increasing of sulfonate and amine groups has improved [15, 36]. It can be the main reason that the solubility increases from 40% to 91%.

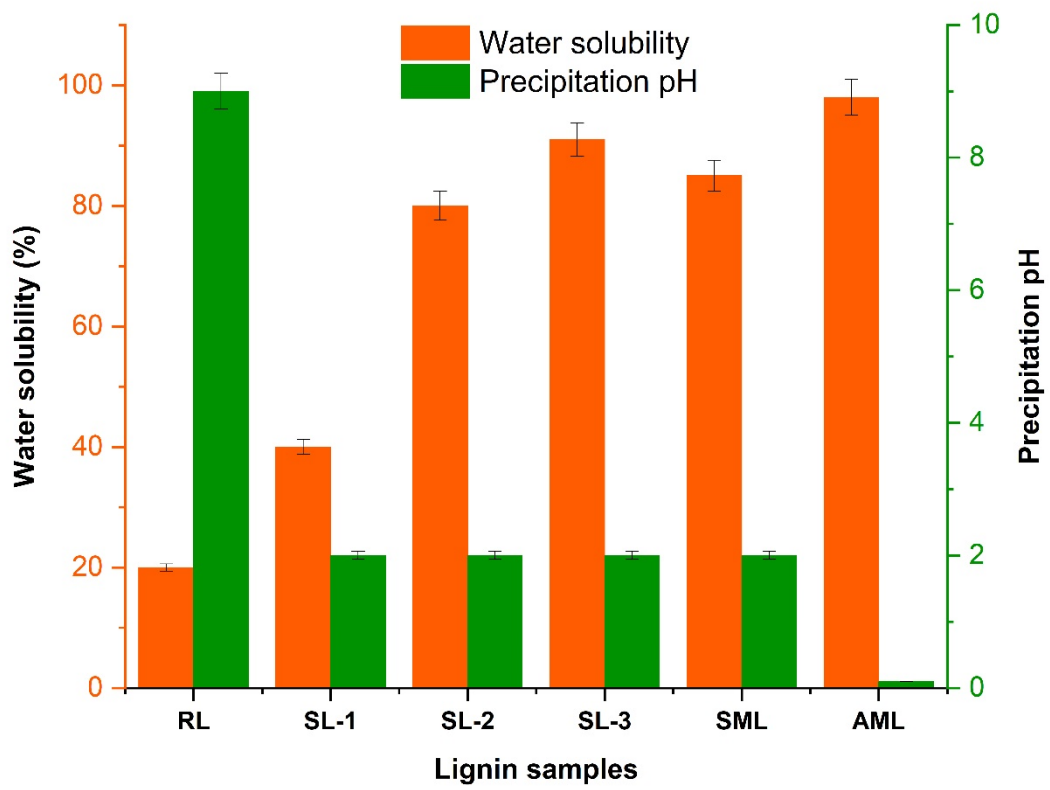


Fig. 2. Solubility vs precipitation pH of RL, AML, AML, SL-1, SL-2 and SL-3

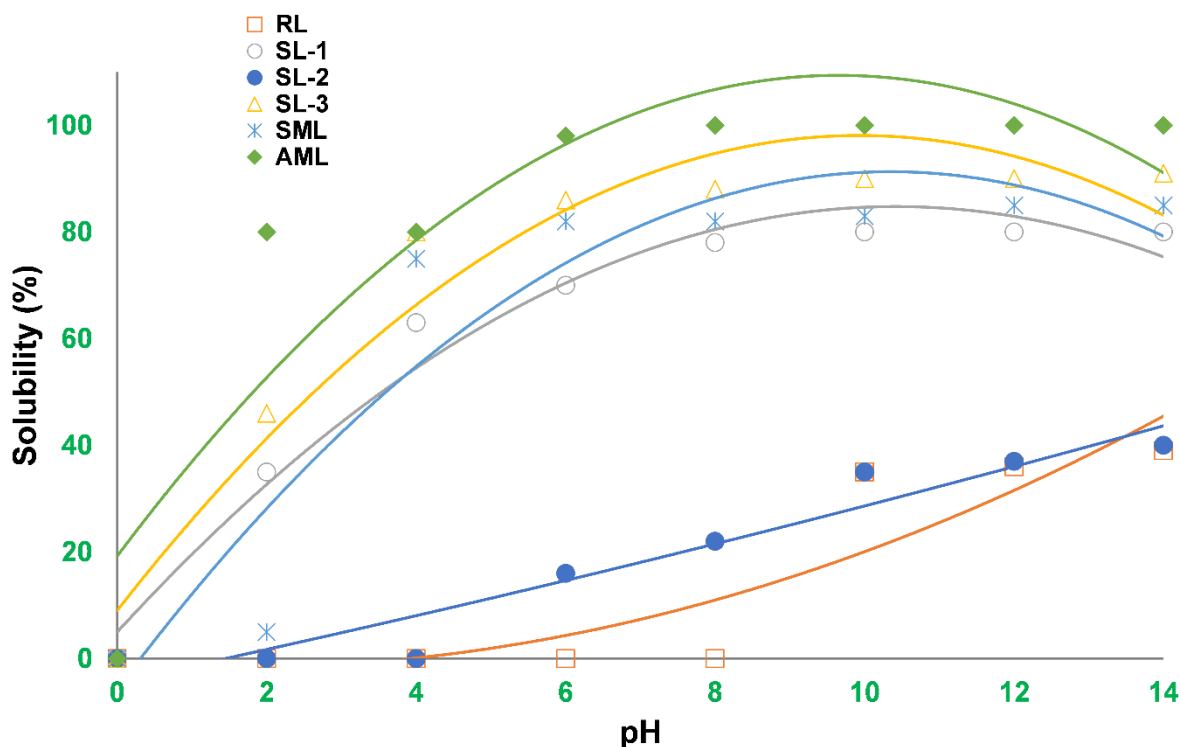


Fig. 3. Solubility trend of the RL, AML, AML, SL-1, SL-2 and SL-3 lignin samples at different pHs.

3.2. Molecular Weight

The weight averaged molecular weight (M_w), numerical average molecular weight (M_n), and Polydispersity (M_w/M_n) of RL and modified lignins are shown in Table 1. Corresponding GPC chromatograms of the prepared lignin samples were represented in Fig. 4. Generally, the molecular weight of sulfonated, sulfomethylated and aminated lignins was increased upon the modification. The introduction of sulfonate and methylene sulfonate to the RL increased the molecular weight due to the expansion of chain size and condensation of the lignin moieties. The sulfonation, sulfomethylation and amination chemical reaction are presented in Fig. 5. Formaldehyde was used as a crosslinker of phenolic moieties of lignin in acidic or basic environments [37, 38]. Despite using optimum conditions to discourage unwanted side reactions, the polymerization occurred through the formaldehyde reaction[39]. The polymerization of formaldehyde with lignin sub-structures occurs mainly through the para and ortho positions of the C₆-C₃ units [40]. The sulfonation by sodium sulfite occurs mainly on

aliphatic hydroxyl groups of the lignin side chain (e.g., α -position) and the phenolic β -O-4 structure under alkaline conditions[10, 41]. The sulfonate group is not supposed to react at the ortho position of the aromatic ring since stronger conditions are needed for ring substitution [42]. The M_n and M_w of commercial lignosulfonate were reported to be 3060 and 12180 g/mol, respectively, comparable to the SL-3 sample [43]. The formaldehyde and sodium sulfite combination led to hydroxymethylsulfonate formation; the reactive species is responsible for introducing a sulfonic group onto the C₅ position in the aromatic ring, resulting in lignosulfonate [43]. Moreover, the polydispersity index was increased upon lignin modifications due to increasing the inhomogeneity of the reactions that led to the formation of moieties with different molecular weights.

Table 1. Molecular weight analysis results of RL, AML, AML, SL-1, SL-2 and SL-3 lignin samples

Sample	M_w (g/mol)	M_n (g/mol)	PDI
RL	1633	980	1.66
SL-1	6384	1456	4.38
SL-2	14571	5001	2.91
SL-3	15265	3696	4.13
SML	13119	6934	1.89
AML	4815	1762	2.73

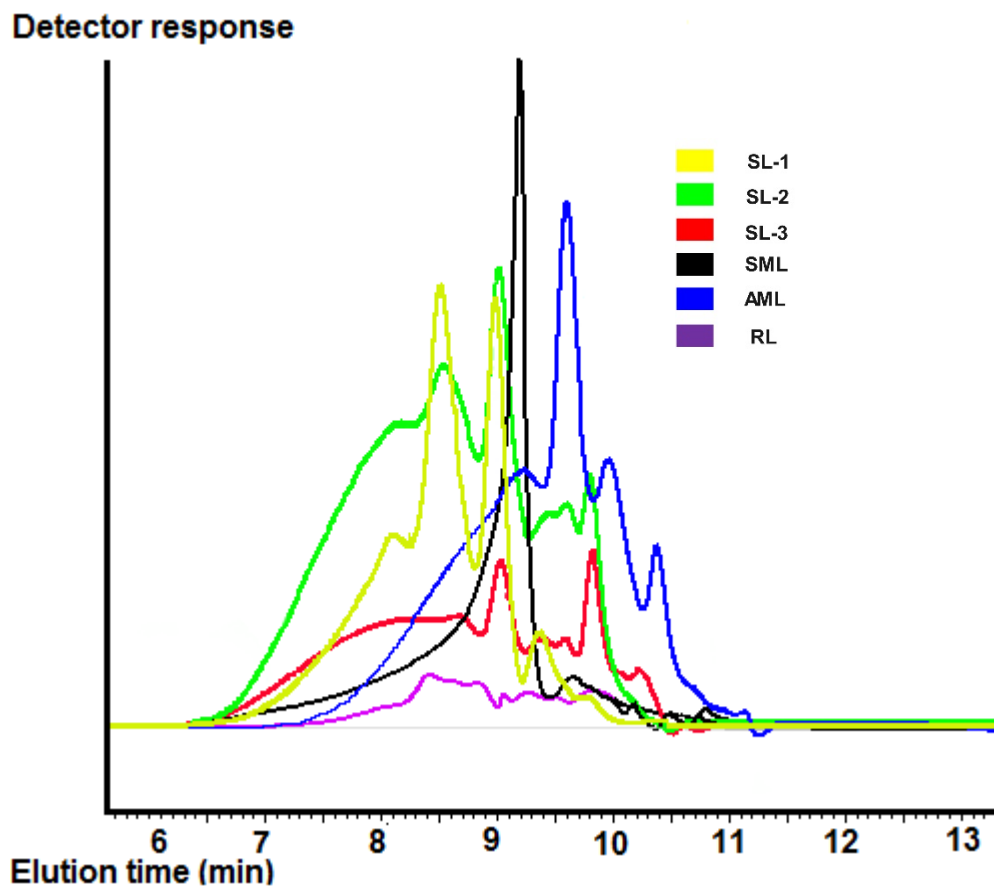


Fig. 4. GPC chromatograms of molecular weight distribution (M_w) of RL, AML, AML, SL-1, SL-2 and SL-3 lignin samples

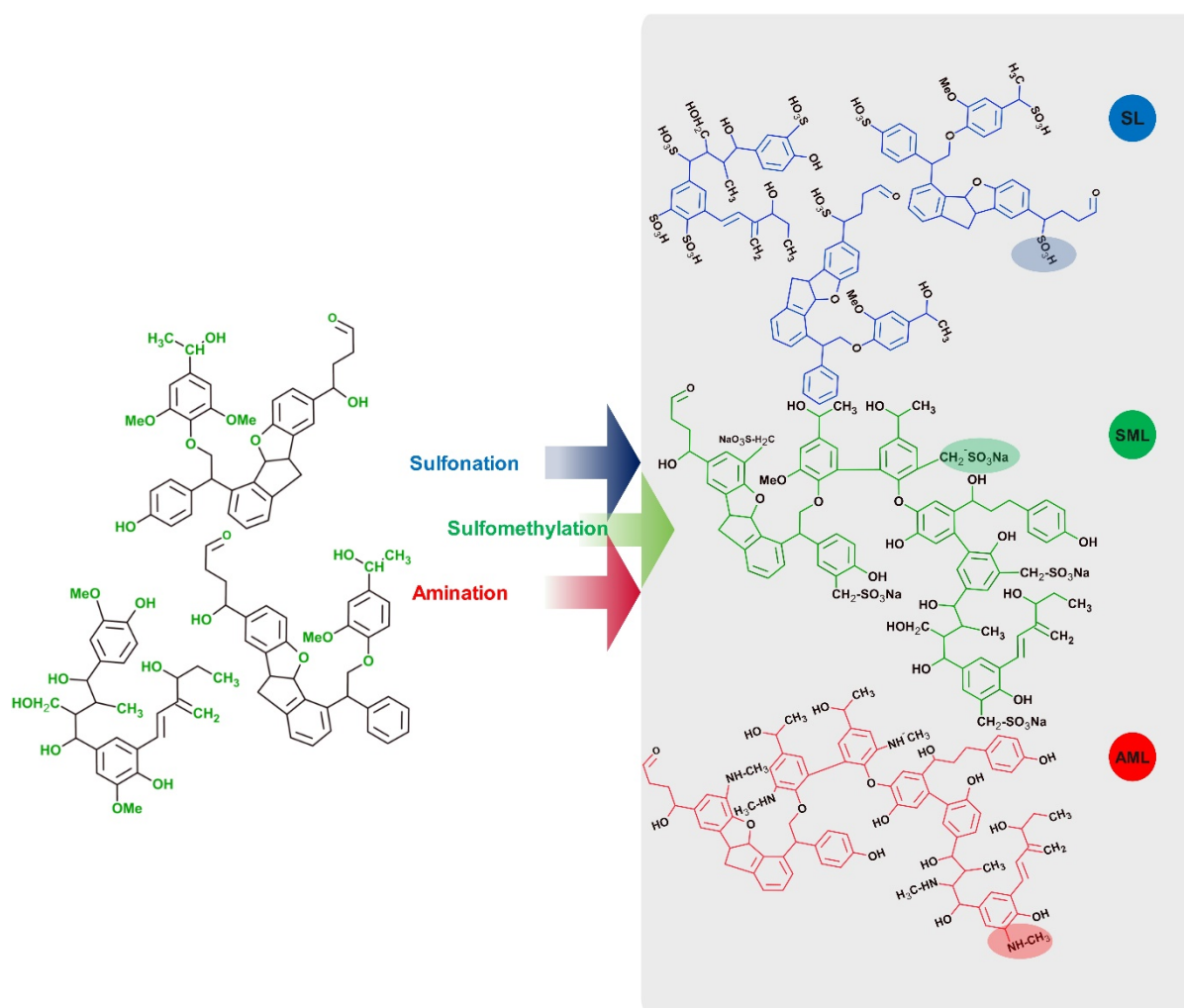


Fig. 5. Proposed reaction scheme for sulfonation, sulfomethylation and amination of alkali lignin

3.3 FTIR Analysis

The results for functional group analysis of lignin samples with FTIR are presented in Fig. 6. The overall assignments of the FTIR spectra are represented in supplementary data (S1-S4). The general pattern of RL and modified lignins indicates that structural deformation of lignins has not occurred upon the modification processes. The sulfonated lignin absorption at 2940 cm^{-1} , which indicates the vibration of the C-H bond in CH_2 , has increased compared to the RL. The most characteristic infrared bands of lignin are found at about 1500 and 1600 cm^{-1} representing the C=C aromatic skeletal vibrations, and the sulfonic acid groups in sulfonated lignins appeared at about 1200 cm^{-1} .

An absorption band at around 620-640 cm^{-1} is assigned to the sulfonic groups (S-O stretching vibration) formed from the reaction of sodium sulfite with the secondary OH of the aliphatic side chain of lignins. There are also two bands at 1170 and 1149 cm^{-1} representing asymmetric and symmetric SO_2 vibrations [44]. This suggests that these samples have the same main structure. In other words, this means that the sulfonation did not change the main structure of lignin and the change to be only occurred in lignin chains. Moreover, the peak at 1710 cm^{-1} , which is related to the vibration of the C = O bonds, is more intense in the sulfonated lignins compared to RL [45].

Moreover, emerging peaks in the 1200-1400 region are assigned to C-O and C=O vibrations in aromatic rings in the guaiacyl structures. The presence of sulfonate groups in sulfonated lignins led to an increase in peak intensity in 1200-1150 and 1040-1110 regions, indicating that the binding of sulfonate groups to the RL has been achieved[46]. Absorption at 1040 cm^{-1} in the SML is due to sulfonate groups interaction with lignin in the sulfomethylation process [31]. The enhanced band intensity at 1085 cm^{-1} is related to the C-O bonds. The peak intensity around 1510 cm^{-1} , which corresponds to aromatic C-H vibrations, is significantly reduced in the AML, indicating the amination of the aromatic ring. Moreover, a strong peak at 1360 cm^{-1} , assigned to C-N bonding, and a significant peak intensity around 1460 cm^{-1} , is related to the vibration of amine groups in AML. The intensity of aromatic C-H vibrations at 1603 cm^{-1} , 1506 cm^{-1} , 1453 cm^{-1} and 832 cm^{-1} were decreased in AML spectrum because of the versatile amination of the aromatic region by Mannich reaction [47].

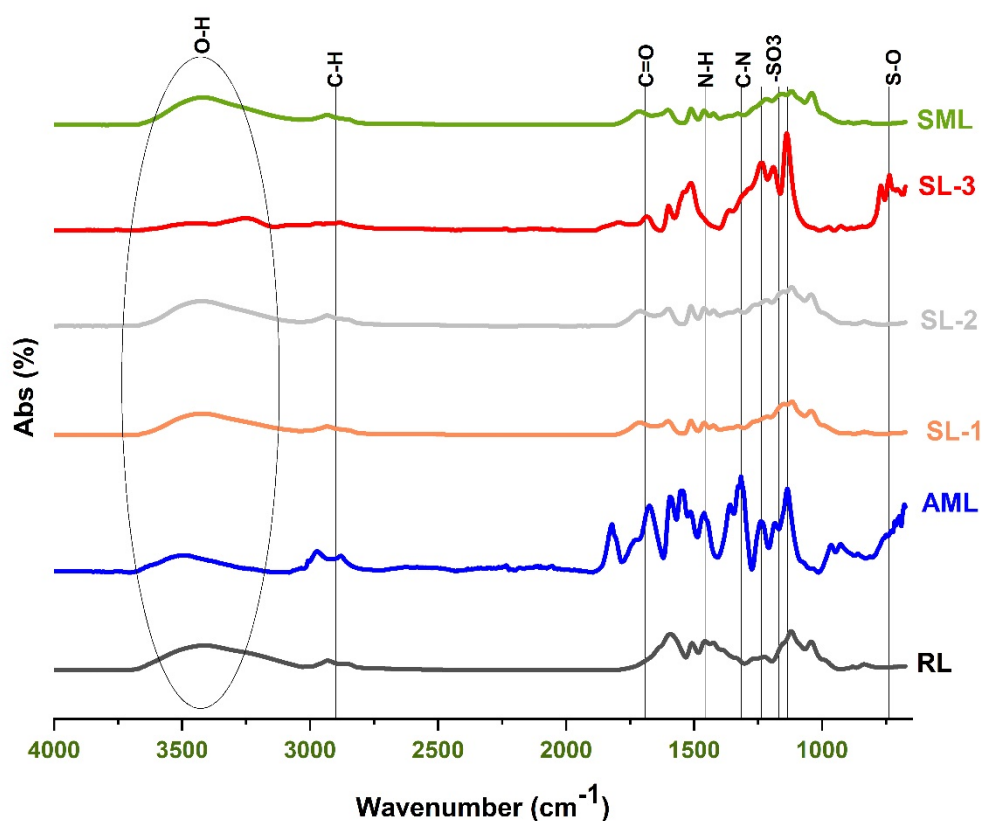


Fig. 6. FTIR spectra of RL, AML, AML, SL-1, SL-2 and SL-3

3.4 TGA Analysis

The thermal analysis of the lignin samples is presented in Fig. 7 for modified and unmodified lignin. As shown in Fig. 6, RL's degradation and weight loss starts at the initial temperatures beyond the moisture loss and then increases, and eventually, about 80% of the RL mass was lost at 520 °C. Conversely, the onset degradation of sulfonated lignins starts at higher temperatures (~200 °C), where about 80% of their weight was lost at 500 °C. It has been reported that sulfonation of kraft lignin led to an increase in thermal stability due to the introduced sulfonate groups in lignin moieties [31]. Moreover, increasing the temperature and reaction time in the sulfonation process (SL-3) led to an increase in the number of sulfonate groups and intermolecular bonds, which increased the thermal stability of lignin. This increase can also be related to the higher molecular weight of sulfonated products [48–50].

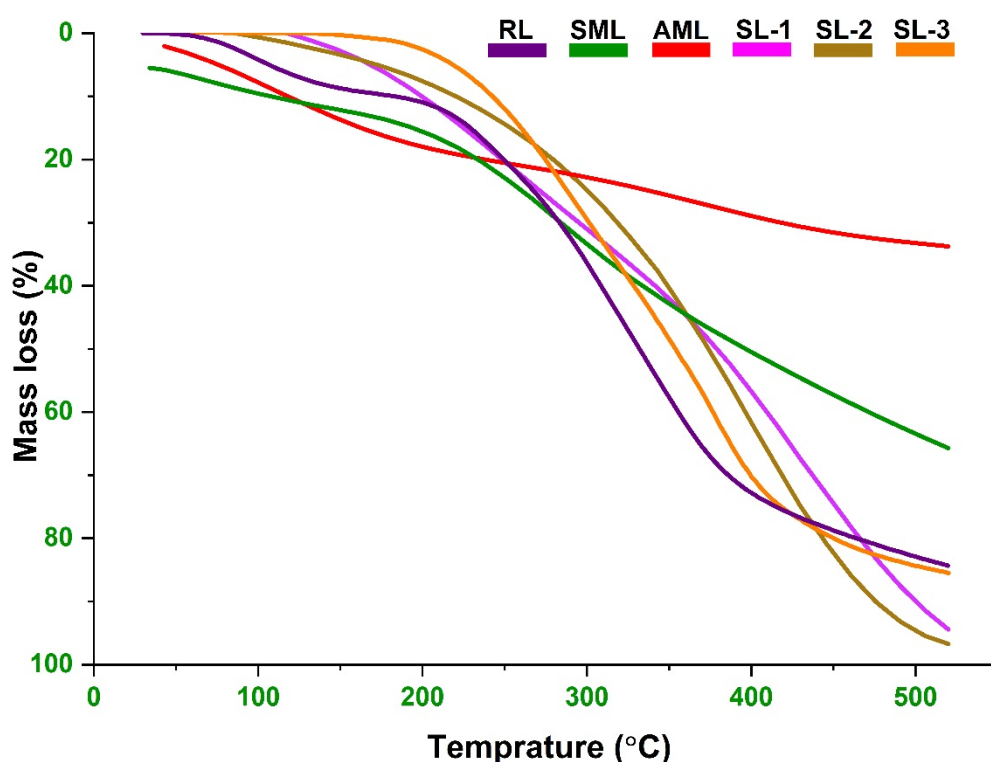


Fig. 7. TGA Analysis of RL, AML, AML, SL-1, SL-2 and SL-3 lignin samples

Sulfomethylation was also led to an improvement in the thermal stability of lignin compared to the RL. The onset degradation temperature starts at 200 °C, and 60% of the sample weight was lost at 500 °C. This increase in thermal stability is due to methyl and sulfonate groups' binding to the sulfomethylated lignin [14].

The thermal stability of lignin was increased by the amination of lignin [32]. The mass of the AML was continuously decreased with a low rate upon the thermal degradation. However, at the endset degradation temperature (500 °C), mass loss of the AML was only 30%, indicating the thermal stability of aminated lignin during thermal treatment. The improvement of thermal stability is considered an advantage that enhances lignin applications.

3.5 ¹H-NMR Analysis

The ¹H-NMR spectra of RL, SL-1, SL-2, SL-3, SML and AML are shown in Fig. 8. The detailed assignments of the ¹H-NMR spectra of all the samples were presented in supplementary data (S5-S8). The assignments of peaks were done using the prediction of the proposed structures. **Assigned** regions for ¹H-NMR analysis of isolated lignins are presented in supplementary data (S9). The peak at 4-5 ppm is related to protons of β-O-4 bonds in RL.

According to the $^1\text{H-NMR}$ spectrum results, the peaks 7-8 ppm in the SL-1, SL-2 and SL-3 belong to aromatic ring protons and represent the chemical reaction in this area. The peak at 5.49 ppm in RL is associated with H-alpha in the lignin side chain, which almost disappeared in sulfonated lignins, indicating the substitution of the lignin side chain at alpha-position[42, 51].

Moreover, a single peak at 1-2 ppm is related to the methyl group protons that is emerged from hydroxysulfomethyl groups [52]. $^1\text{H NMR}$ analysis provided more evidence about the successful amination of RL sample. The peak of hydroxyl group protons of RL in 8.5 ppm was disappeared in the AML spectrum, indicating the occurrence of a chemical reaction in this area. Moreover, As shown in Fig. 8, a pronounced signal intensity from protons of the aromatic region (6–8 ppm) is observed in the spectra of RL. Subsequently, this signal was definitely reduced after the Mannich reaction, suggesting the successful amination of the aromatic ring in RL. Moreover, emerging signals at 2–3 ppm of the AML spectrum were assigned to the amine groups.

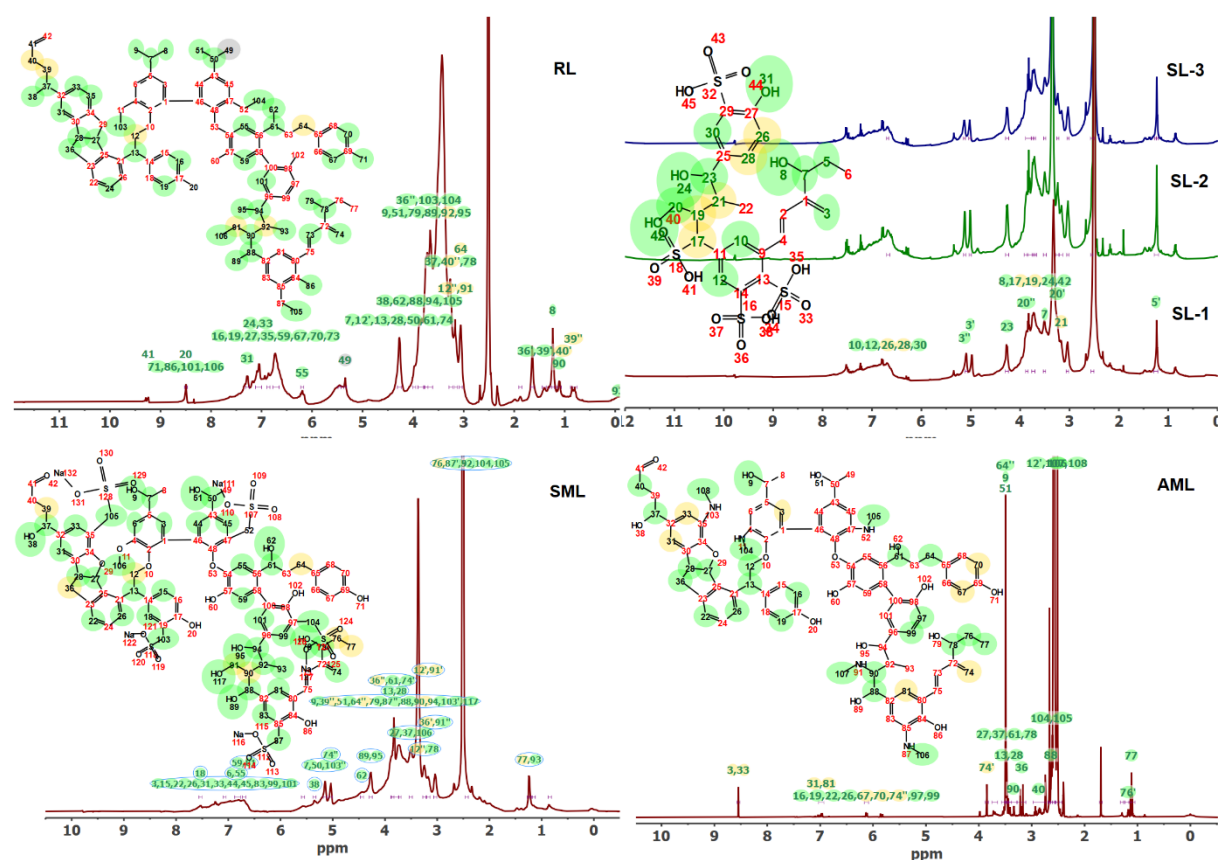


Fig. 8. $^1\text{H-NMR}$ of RL, SML, AML, SL-1, SL-2 and SL-3 lignin samples

3.6 Elemental Analysis

The elemental analysis results for the weight percentage of carbon, hydrogen, oxygen, nitrogen and sulphur in lignin and its derivatives are shown in Table 2. The percentage of oxygen is obtained by subtracting the total carbon, hydrogen, nitrogen, and sulphur. The RL and sulfonated/sulfomethylated lignins represent a different sulfur content that mainly emerged from sulfonic groups. The results also show that the number of sulfonate groups increased while the H decreased. Fatehi et al. (2015) also examined the process of lignin sulfomethylation and reported that with lignin sulfonation, the amount of sulphur increased and hydrogen decreased [14]. Table 3, shows that amount of sulphur element in lignin was increased from 1.767% on unmodified lignin to approximately 3.40% on modified lignins.

Furthermore, the results indicate that the number of sulfonate groups increased with increasing the reaction time. Wu et al. (2014) reported an increase in sulfur content and a decrease in hydrogen content due to the sulfomethylation of corn stalks lignin [50]. In the sulfomethylated lignin, the amount of sulphur element (3.81 %) was higher than sulfonated lignin, which could be due to the use of formaldehyde in the sulfomethylated process as a crosslinker of the sulfonate group. It was found that the amount of H element of the sulfomethylated lignin decreased compared to unmodified lignin. There was a considerable difference between the amount of nitrogen element in unmodified and aminated lignin, where the amount of this element in the aminated lignin is approximately 4.5 times **higher than** its amount in unmodified lignin. The results show that the amount of H element also was increased *via* the amination process. Yu et al. (2011) examined the amination of soda lignin and found that nitrogen and hydrogen in lignin increased after the amination process. The higher heating values (HHV), which present the energy content of each lignin, were obtained. It was found that there were almost similar values for HHV for all types of modified lignin compared to unmodified lignin apart from aminated lignin[53]. The HHV for aminated lignin was 9.643 MJ/kg, which is considerably decreased compared to RL. It could be due to the reduced number of carbon atoms in this type of modified lignin.

Table 2. Elemental Analysis of lignin samples

Sample	C (%)	H (%)	O (%)	N (%)	S (%)	HHV (MJ.kg ⁻¹)
RL	49.31	5.703	42.862	0.538	1.767	19.884
SL-1	49.37	4.458	42.15	0.743	3.279	18.637
SL-2	49.09	5.510	42.008	0.544	2.848	19.576
SL-3	49.17	4.481	42.259	0.588	3.502	18.609
SML	47.33	4.131	44.145	0.563	3.831	17.397
AML	24.06	6.458	64.77	3.259	1.447	9.643

4. Conclusions

This study has investigated the isolation and conversion of alkali lignin to water-soluble derivatives. The obtained results from the analytical and structural characterization of RL and modified lignins confirm that lignin's chemical modification, including sulfonation, sulfomethylation and amination processes, has been achieved for the production of water-soluble derivatives. The results indicate that the amount of sulfonate and amine groups has been increased by lignin's chemical modification compared to RL. The structural analysis has been performed by FTIR and NMR analyses on RL modified lignins to confirm the structural change due to chemical modification. The solubility of the modified lignins was investigated, and the results show that the solubility has been increased by performing the sulfonation, sulfomethylation, and amination processes. Moreover, the molecular weight of lignin increased significantly after the medication processes, which improved the thermal stability of the obtained lignins as it was determined TGA analysis. Chemically modified lignin is suggested to have a great potential to be used as a dispersant, adhesive, chemical additive and lubricant.

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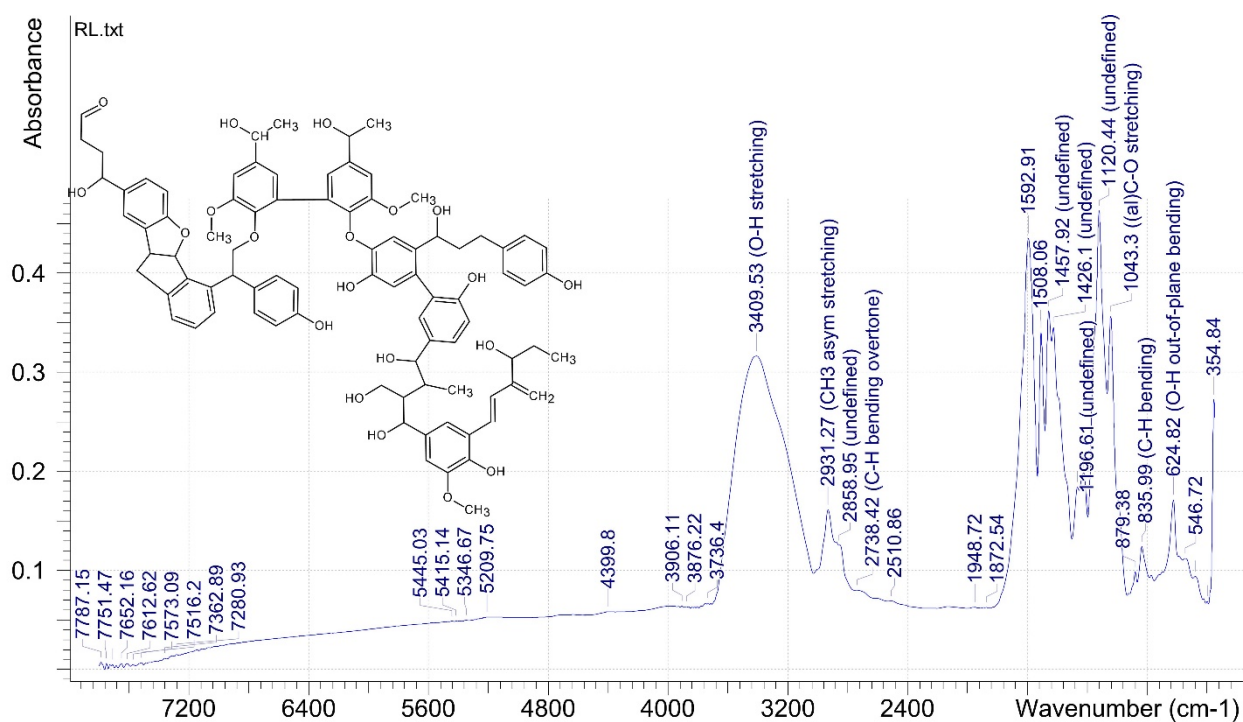
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Supplementary data

S1. Assignments of the FTIR spectra of the RL

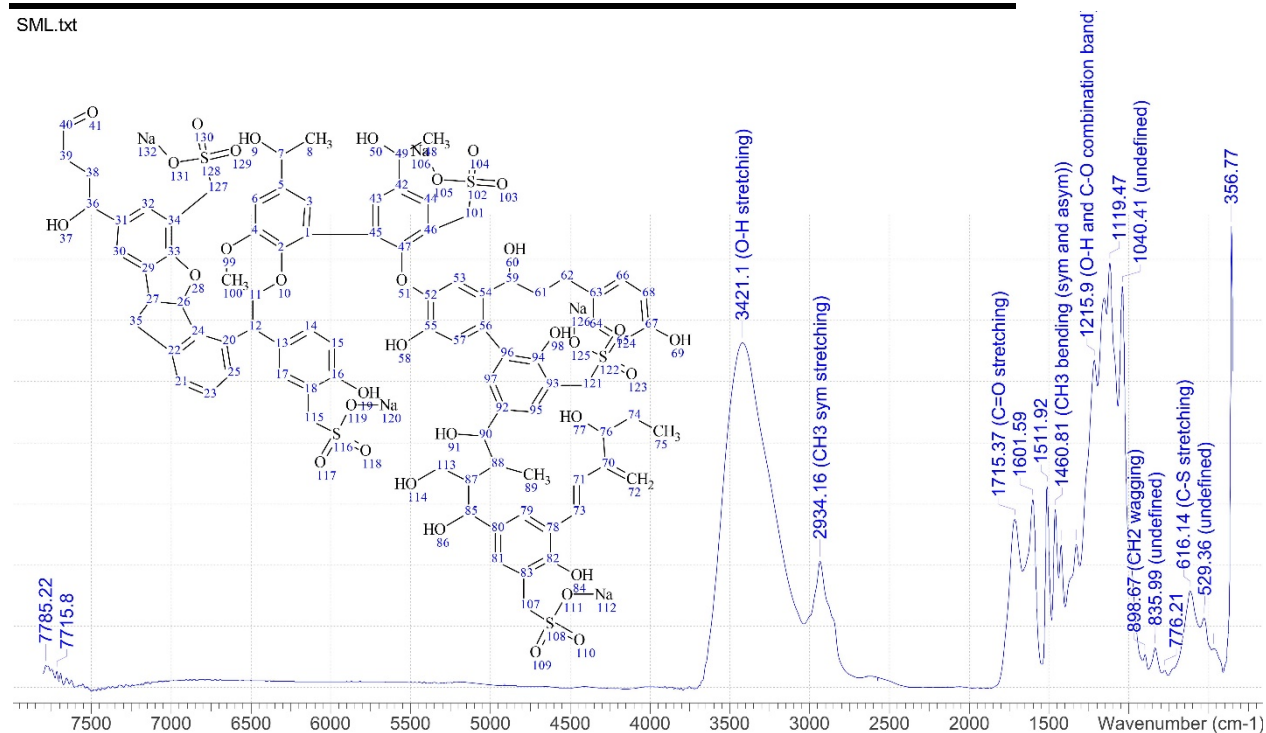
No	Band (cm-1)	Abs	Formula	Vibr/Trans
1	624.82	0.171	OH	O-H out-of-plane bending
2	835.99	0.124	CH	C-H bending
3	1043.3	0.357	C ₂ H ₃ O	(al)C-O stretching
4	1120.44	0.463	CH ₂ O	undefined
5	1196.61	0.154	CH ₃	undefined
6	1224.58	0.199	OH	O-H and C-O combination band
7	1266.04	0.184	C ₂ O	C-O-C stretching
8	1426.1	0.345	OH	undefined
9	1457.92	0.362	CH ₃	undefined
10	2738.42	0.08	CH	C-H bending overtone
11	2858.95	0.125	CH ₃	undefined
12	2931.27	0.161	CH ₃	CH ₃ asym stretching
13	3409.53	0.316	OH	O-H stretching



S2. Assignments of the FTIR spectra of the SML

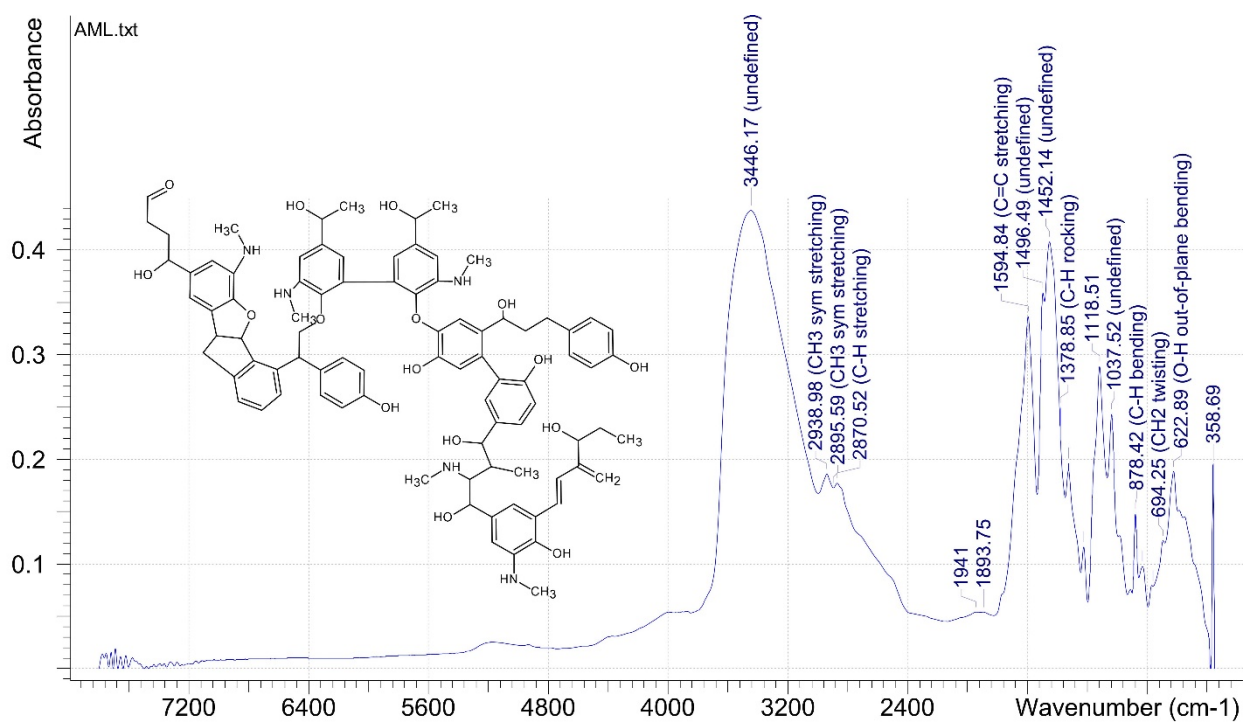
No	Band (cm ⁻¹)	Abs	Formula	Vibr/Trans
1	468.62	0.032	CH ₂ O ₂ S	undefined
2	529.36	0.057	CH ₂ O ₂ S	undefined
3	616.14	0.079	CH ₂ S	C-S stretching
4	835.99	0.032	CHO	undefined
5	898.67	0.027	CH ₂	CH ₂ wagging
6	1040.41	0.328	CH ₂	undefined
7	1196.61	0.247	CH ₃	undefined
8	1215.9	0.267	OH	O-H and C-O combination band
9	1329.68	0.117	CH ₂ OS	undefined
10	1399.1	0.066	CH	undefined
11	1424.17	0.116	OH	undefined
12	1460.81	0.145	CH ₃	CH ₃ bending (sym and asym)
13	1715.37	0.137	CHO	C=O stretching
14	2934.16	0.103	CH ₃	CH ₃ sym stretching
15	3421.1	0.282	OH	O-H stretching

SML.txt



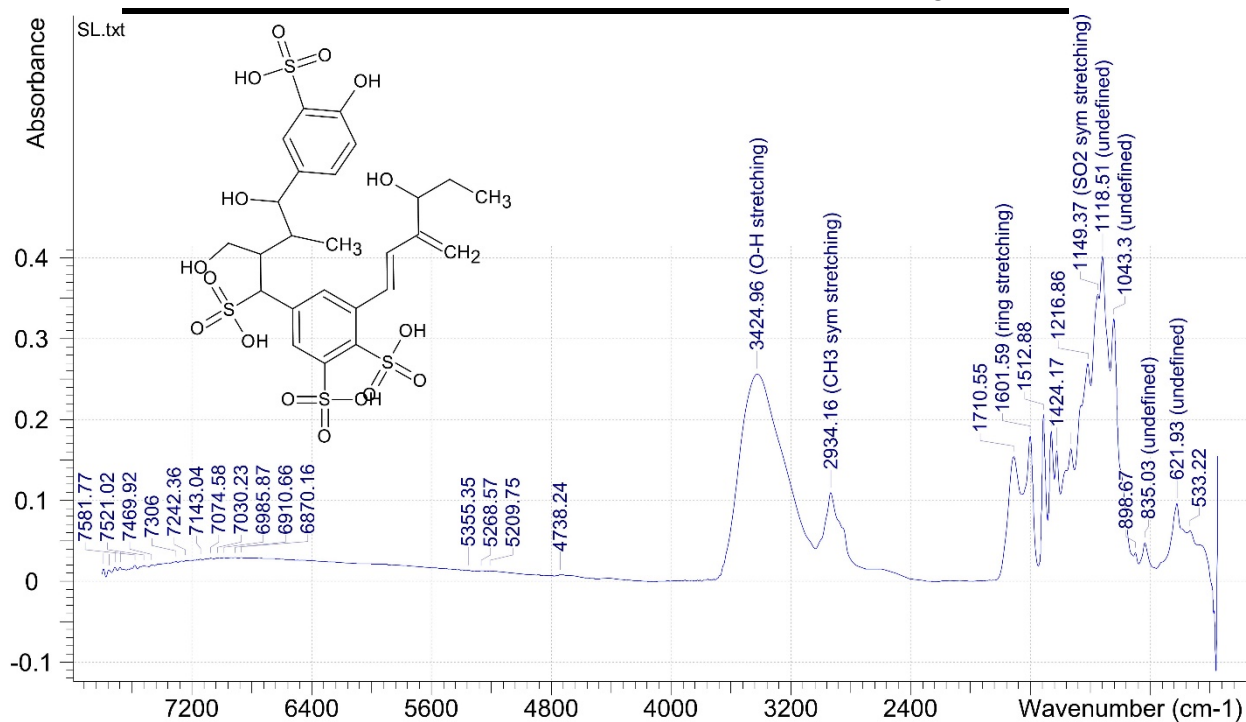
S3. Assignments of the FTIR spectra of the AML

No	Band (cm ⁻¹)	Abs	Formula	Vibr/Trans
1	622.89	0.188	OH	O-H out-of-plane bending
2	694.25	0.122	CH ₂	CH ₂ twisting
3	759.82	0.079	HN	N-H wagging
4	830.2	0.097	HN	undefined
5	878.42	0.148	C ₃ H ₅ O	C-H bending
6	1037.52	0.243	CH ₄ N	undefined
7	1223.61	0.116	C ₂ H ₄ N	(al)C-N stretching
8	1378.85	0.249	C ₂ H ₃ O	C-H rocking
9	1379.82	0.226	CH ₃	CH ₃ umbrella mode
10	1452.14	0.408	CH ₄ N	undefined
11	1496.49	0.359	CH ₃	undefined
12	1594.84	0.336	C ₂ H ₂	C=C stretching
13	2870.52	0.177	CH	C-H stretching
14	2895.59	0.173	CH ₃	CH ₃ sym stretching
15	2938.98	0.186	CH ₃	CH ₃ sym stretching
16	3446.17	0.438	OH	undefined

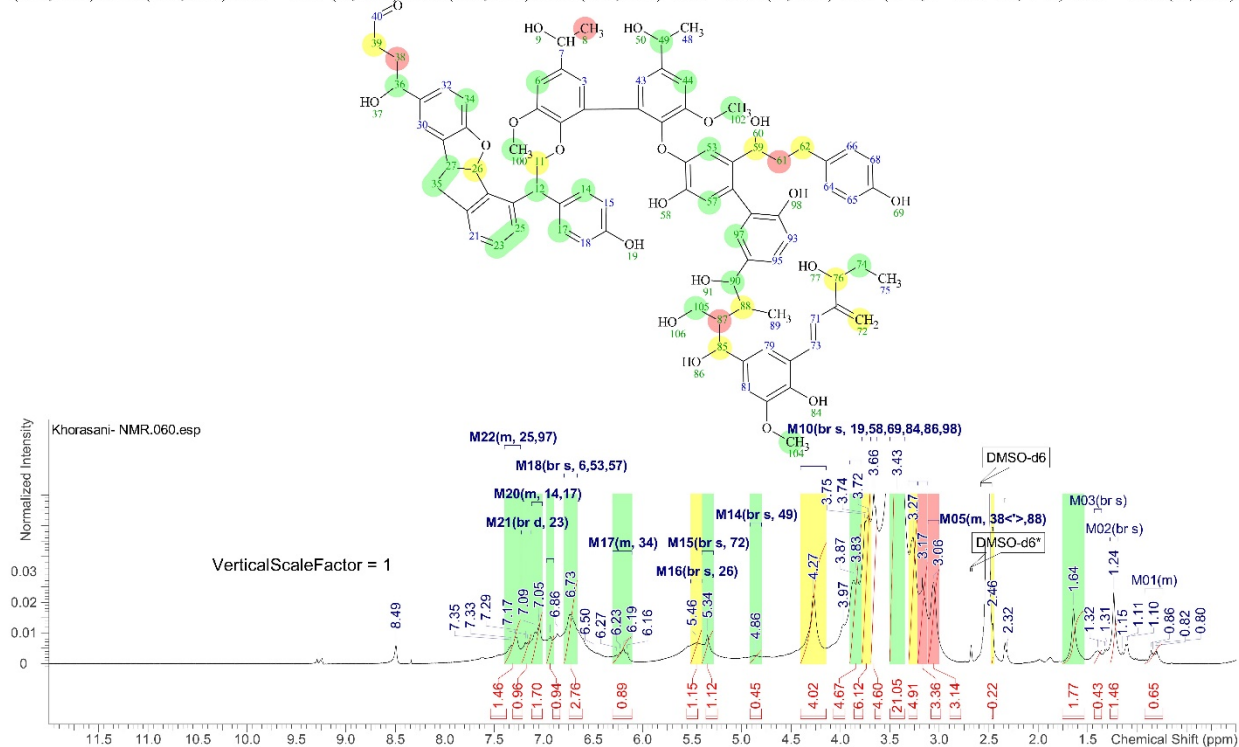


S4. Assignments of the FTIR spectra of the SL

No	Band (cm ⁻¹)	Abs	Formula	Vibr/Trans
1	621.93	0.096	CHOS	undefined
2	835.03	0.048	CH ₂	undefined
3	1043.3	0.324	C ₂ H ₂	undefined
4	1118.51	0.402	CH ₂ O	undefined
5	1149.37	0.355	O ₂ S	SO ₂ sym stretching
6	1329.68	0.164	CH ₂	CH ₂ wagging
7	1460.81	0.185	CH ₃	CH ₃ asym bending
8	1601.59	0.179	C ₆ H ₂	ring stretching
9	2934.16	0.11	CH ₃	CH ₃ sym stretching
10	3424.96	0.256	OH	O-H stretching

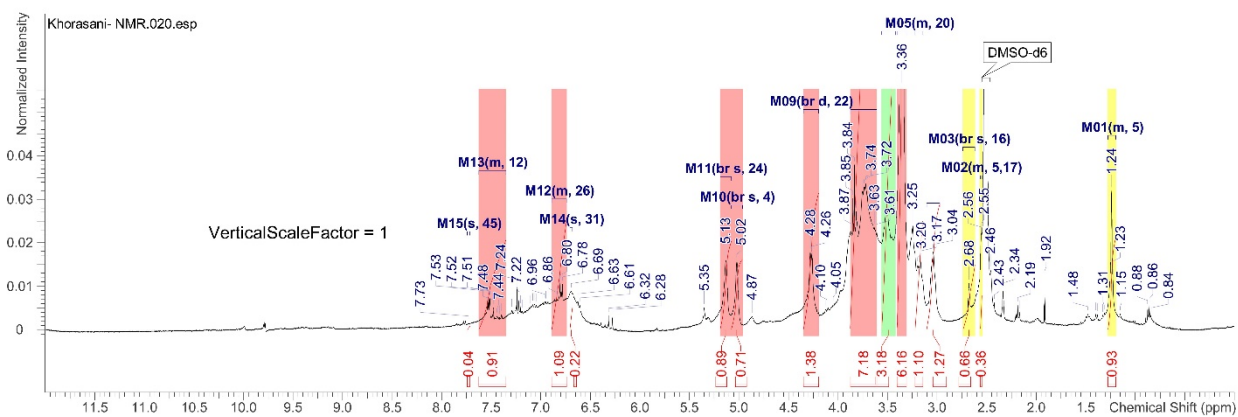
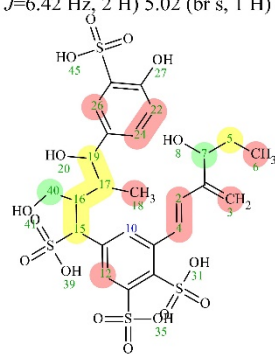


¹H NMR (400 MHz, DMSO-*d*₆) δ ppm 0.74 - 0.92 (m, 1 H) 1.24 (br s, 1 H) 1.40 (br s, 1 H) 1.64 (br s, 2 H) 2.46 - 2.47 (m, 1 H) 3.06 (br s, 4 H) 3.17 (br s, 3 H) 3.27 (br s, 6 H) 3.43 (br s, 25 H) 3.66 (br s, 11 H) 3.69 - 3.78 (m, 6 H) 3.85 (br d, *J*=16.44 Hz, 5 H) 4.27 (br s, 4 H) 4.86 (br s, 1 H) 5.34 (br s, 2 H) 5.46 (br s, 2 H) 6.11 - 6.30 (m, 1 H) 6.73 (br s, 3 H) 6.93 (br s, 1 H) 7.02 - 7.12 (m, 2 H) 7.18 (br d, *J*=8.22 Hz, 1 H) 7.24 - 7.40 (m, 2 H)



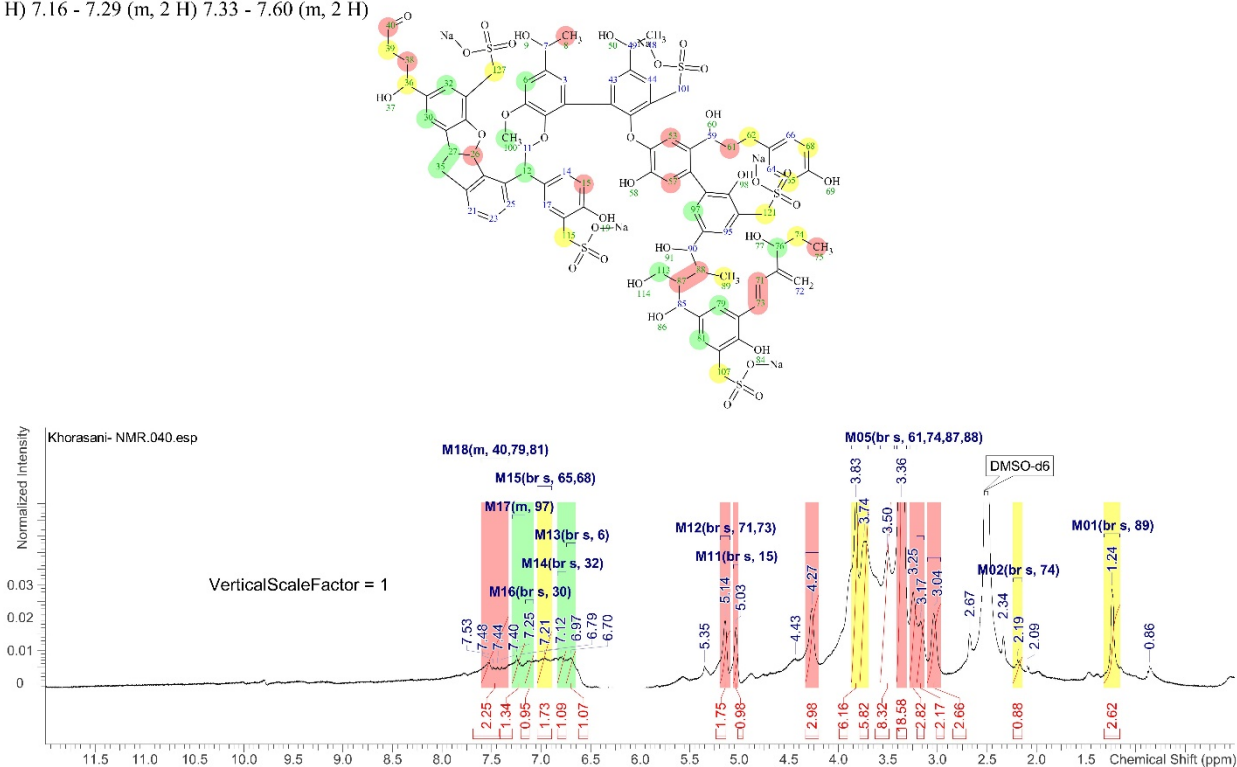
S5. ¹H-NMR of RL sample

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ ppm 1.20 - 1.28 (m, 1 H) 2.55 - 2.56 (m, 1 H) 2.68 (br s, 1 H) 3.04 (br s, 2 H) 3.15 - 3.22 (m, 1 H) 3.36 (br s, 6 H) 3.42 - 3.56 (m, 4 H) 3.61 - 3.88 (m, 7 H) 4.27 (br d, $J=6.42$ Hz, 2 H) 5.02 (br s, 1 H) 5.13 (br s, 1 H) 6.69 (s, 1 H) 6.74 - 6.89 (m, 1 H) 7.35 - 7.63 (m, 1 H) 7.73 (s, 1 H)



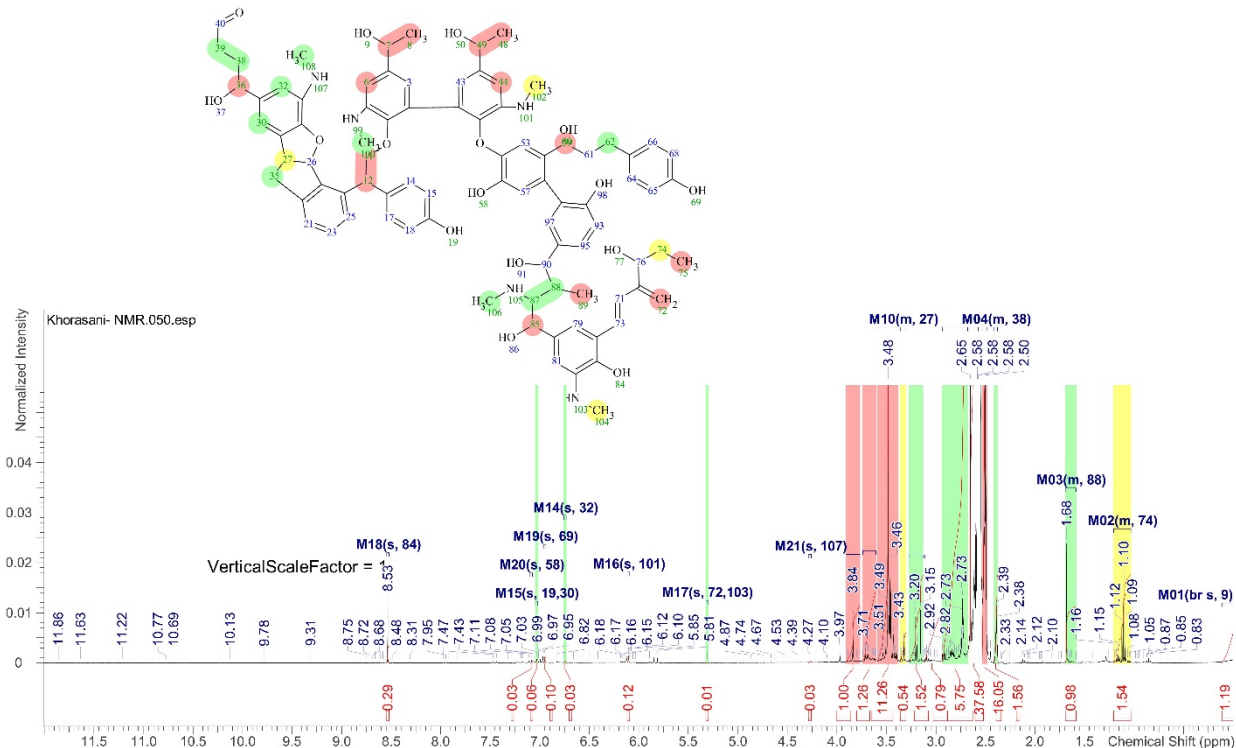
S6. ^1H -NMR of SL-1, SL-2 and SL-3 samples

¹H NMR (400 MHz, DMSO-*d*₆) δ ppm 1.24 (br s, 3 H) 2.19 (br s, 1 H) 3.04 (br s, 3 H) 3.17 (br s, 3 H) 3.25 (br s, 4 H) 3.36 (br s, 20 H) 3.50 (br s, 11 H) 3.74 (br s, 10 H) 3.83 (br s, 12 H) 4.27 (br s, 3 H) 5.03 (br s, 1 H) 5.14 (br s, 2 H) 6.70 (br s, 1 H) 6.79 (br s, 2 H) 6.97 (br s, 2 H) 7.12 (br s, 1 H) 7.16 - 7.29 (m, 2 H) 7.33 - 7.60 (m, 2 H)



S7. ¹H-NMR of SML sample

¹H NMR (400 MHz, DMSO-*d*₆) δ ppm -0.01 (br s, 1 H) 1.03 - 1.20 (m, 2 H) 1.59 - 1.69 (m, 1 H) 2.38 - 2.41 (m, 2 H) 2.48 - 2.53 (m, 17 H) 2.57 - 2.66 (m, 38 H) 2.68 - 2.94 (m, 6 H) 2.97 - 3.11 (m, 1 H) 3.13 - 3.27 (m, 2 H) 3.30 - 3.36 (m, 1 H) 3.38 - 3.59 (m, 11 H) 3.61 - 3.74 (m, 1 H) 3.77 - 3.91 (m, 1 H) 4.27 (s, 1 H) 5.31 (s, 1 H) 6.10 (s, 1 H) 6.75 (s, 1 H) 6.95 (s, 1 H) 7.03 (s, 1 H) 7.08 (s, 1 H) 8.53 (s, 1 H)



S8. ¹H-NMR of AML sample

S9. Assigned regions for ^1H -NMR analysis of isolated lignins

Structure	δ ^1H-NMR (ppm)
Carboxylic acid	14.0 – 11.0
Aldehyde	11.0 – 9.4
Unsubstituted phenolic	9.4 – 8.5
Substituted phenolic	8.5 – 7.9
Aromatic and vinylic	8 – 6
Aliphatic ($\text{H}\alpha$ and $\text{H}\beta$)	6.3 – 4.0
Methoxy and $\text{H}\gamma$	4.0 – 3.5
$\text{H}\beta$ in β-1	2.9 – 2.8