



Original Article

Lignin isolation from black liquor from oil palm empty fruit bunch using acid



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ABSTRACT

This study aimed to obtain the characteristics of lignin isolated from oil palm empty fruit bunch by using HCl. Treatments were conducted using HCl at concentrations of 10%, 20%, 30% and 40% (v/v). Increasing HCl concentrations reduced yields but increased equivalent lignin weights and methoxyl contents. Results of functional group testing via Fourier transform infrared spectroscopy showed no change in the structure of functional groups at all HCl concentrations employed. Amongst the acid concentrations employed in this work, 20% HCl produced the maximum yield (15.61%). Increases in HCl concentration could increase methoxyl contents. In this study, average methoxyl contents were in the range of 12.4–44.95%. The equivalent weight produced in this study ranged from 200% to 250%. Scanning electron microscopy–energy-dispersive X-ray results further showed that the dominant elements were carbon, oxygen, aluminium and iron. In addition, Chromatograms and identification of lignin compounds isolated using 40% HCl were presented.

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1. Introduction

Processing of pulp from biomass raw materials produces a black liquid known as black liquor. Black liquor mainly consists of water, organic and inorganic substances [1,2] and is composed of approximately 65–85% solids [3] and 10–50% heavy lignin [4]. Black lye contains lignin amounting to approximately 25–35% of the total solid content [5,6]. Moreover, black lye contains 30–35% carboxylic aliphatic acids,

5–10% organic compounds (extractive and hemicellulose) and 30–40% inorganic materials ([7,8]). Lignin, an abundant biopolymer with high carbon content and aromaticity, is often used as a raw material for fuels, chemicals and lignocellulosic biopolymers [9,10]. Lignin can be isolated from black liquor via proper chemical treatment and screening processes [11]. Different isolation methods, isolate types, insulation temperatures and raw material sources can affect the structure and physicochemical properties of the obtained lignin [12–18]. Lignin can be used as an adhesive, dispersant formulation, surfactant and antioxidant in plastics and rubbers, dyes, synthetic floors, thermosets, paints, UV-light absorbents, phenolic resins and fuels for highway maintenance [19–28]. Lignin isolation can be performed in several ways, including physical

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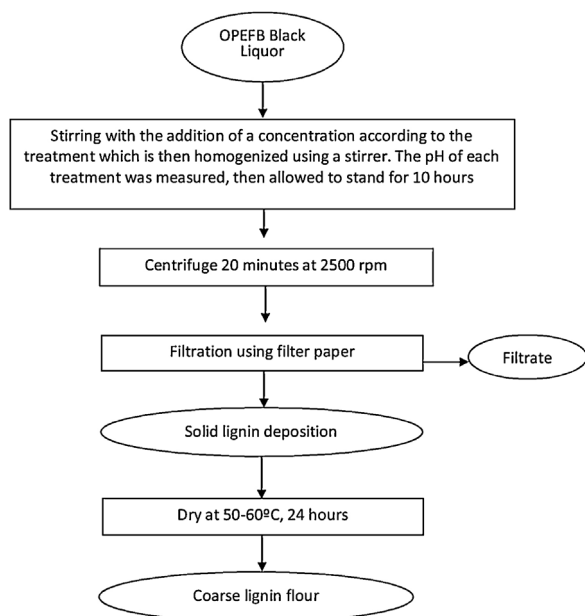


Fig. 1 – Flowchart of the modified lignin isolation process.

[14,15], chemical (alkali, acid) [12,17], biological and combined [29] methods. Acid solutions, such as HCl and H₂SO₄, can also be used for hydrolysis [30,31].

The purpose of this study is to determine the effect of HCl concentration on the yield, chemical properties and functional groups of lignin obtained from black liquor using the formacell method with raw materials from palm oil.

2. Materials and methods

The materials used in the study were oil palm empty fruit bunch (OPEFB) obtained from PT Rejosari, glacial acetic acid, KMNO₄, KI, Na₂S₂O₃, HCl, H₂SO₄ (72%) and starch indicator (0.2%). The tools used included a reactor, Soxhlet apparatus, 1000 ml extraction flask, upright cooler, heating mantle, digester, thermometer, burette, vacuum filter, rotary evaporator, Fourier transform infrared (FTIR) spectrophotometer (Cary 630 FTIR Agilent), gas chromatograph-mass spectrometer (Varian CP-3800 GC and Saturn 2200 MS) and scanning electron microscope (SEM; JEOL JSM 6510 LA).

Pulp cooking was achieved using the formacell process. A total of 1000 g of OPEFB was poured into a rotary digester, and the cooking process was carried out using the method of Hidayati et al. [32]. Cooking was performed using an acetic acid ratio of 1:14. The maximum cooking temperature was 150 °C, and the time required to reach the maximum temperature was 90 min. The pulp was filtered through a hydraulic screener, and the fibres obtained were passed through another hydraulic screener of 80 mesh. Black filtrate or leachate was precipitated with 10%, 20%, 30% or 40% HCl (v/v), doped for 24 h at room temperature and filtered (Fig. 1). Thereafter, pH, total solid content of black OPEFB leachate, yield of lignin [33], content of methoxyl groups [34] and equivalent weight of lignin [35] were determined. Lignin analysis via FTIR spectroscopy [36], GC-MS and SEM were

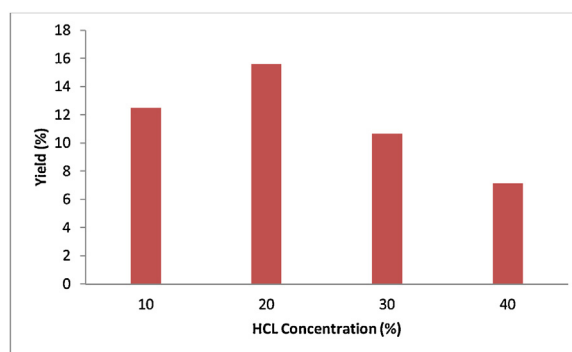


Fig. 2 – Effect of HCl concentration on lignin yield.

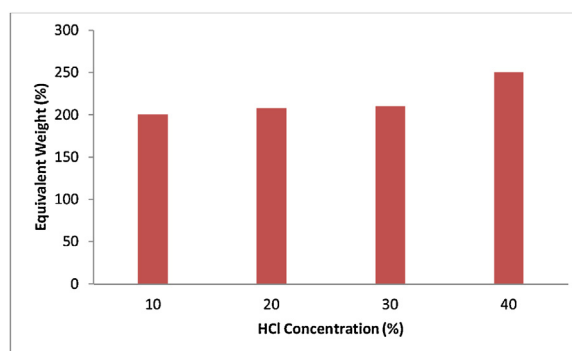


Fig. 3 – Effect of HCl concentration on the weight of equivalent lignin.

also conducted. GC-MS was carried out on a VF-5ms column (30 mm × 0.25 mm) via the manual injection method at 240 °C for 40 min.

3. Results and discussion

3.1. Extraction yield

Increasing the HCl concentration could reduce the lignin yield (Fig. 2). The yield produced ranged from 7.14% to 15.61%, which is higher than that of Surina et al. [37], who isolated lignin from black liquor using H₂SO₄ and obtained 9.3–10.5% yield. Yields depended on the concentration of hydrogen ions in the solution and the strength of the ions. One of the factors influencing the results of lignin deposition is the concentration of H⁺. Protonation of phenolic groups in lignin causes a decrease in electrostatic repulsion amongst lignin molecules [38,39]. Consequently, lignin molecules become less hydrophilic, and the solubility of lignin is reduced. Rudatin et al. [40] claimed that hydrogen bonds caused by the phenolic-phenolic or phenolic-ether relationship can play a role in the lignin kraft relationship with decreasing pH. Amongst the acid concentrations employed in this work, 20% HCl produced the maximum yield (15.61%). Surina et al. [37] used 25% H₂SO₄ to achieve a maximum lignin yield of 9.4%; however, as the H₂SO₄ concentration exceeded 25%, lignin yields decreased. The extraction yield of pure lignin ranged from 7.9 g/mL to 9.4 g/mL; higher yields were achieved by precipitation with 25% (w/w) H₂SO₄. These results agree with the findings of

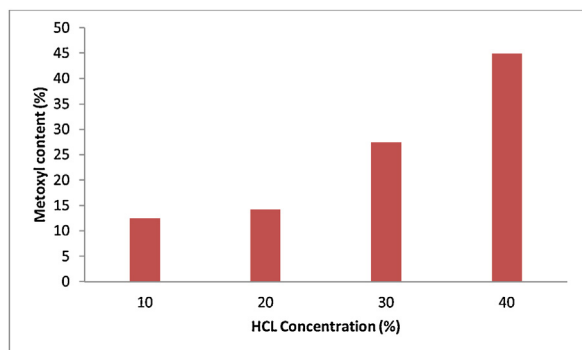


Fig. 4 – Effect of HCl concentration on methoxyl contents.

Ibrahim et al. [18], who assessed maximum lignin yields obtained from H_2SO_4 , HCl, and H_3PO_4 . Increasing the HCl concentration from 20% to 100% reduced the yield from 1.4% to 1.37%. The yield of precipitated lignin soda from HCl and HNO_3 was in the range of 1.20–1.33 g for every 100 ml of black liquor used. This result is lower compared with the yields obtained from H_2SO_4 and H_3PO_4 (1.42–1.50 g/100 ml of black liquor), thereby indicating that lignin yields depend on the number of hydrogen ions in the acid. Ibrahim et al. [18] attributed their findings to localised acidification or non-uniform precipitation effects when high acid concentrations are used.

Precipitation of lignin in the residual cooking solution occurs as a result of the condensation of the constituent units of lignin (e.g., *p*-coumaryl, coniferil and synapyl alcohol), which are initially soluble, and subsequent polymerisation to form larger molecules ([41,42]). Stated that cooking OPEFB black liquor in highly acidic conditions would decrease the yield of lignin because increasing the reaction temperature forces lignin to undergo structural changes into other compounds, such as formic acid, methane, acetic acid and vanillin.

3.2. Equivalent weight

Increases in HCl concentration could increase the equivalent weight of lignin (Fig. 3). The equivalent weight produced in this study ranged from 200% to 250%. HCl treatment condenses lignin constituent units into larger molecules and, therefore, increases the equivalent weight of lignin. Achmadi [43] reported that lignin tends to condense in acidic atmospheres. Surina et al. [37], however, found that lignin isolation from black liquor using H_2SO_4 at concentrations of 5%, 25%, 50% and 75% does not affect the equivalent lignin weight.

3.3. Methoxyl content

Increases in HCl concentration could increase methoxyl contents. In this study, average methoxyl contents were in the range of 12.4–44.95% (Fig. 4).

The methoxyl content of Indulin AT is between 14.00% and 14.30% [44]. Lignin contains functional groups, such as aliphatic hydroxyl, phenolic hydroxyl, methoxyl and carbonyl groups. The use of HCl at pH 2 produces greater methoxyl numbers (15.5) than those produced by HCl at pH 4 (15.6) and 3 (15.8) [45]. Damat [46] suggested that lignin with low methoxyl contents is more beneficial than that with high methoxyl contents when used as an adhesive because the former is better able to form a gel. Low contents of methoxyl groups may be attributed to the partial degradation of methoxyl groups by strong acids or bases, which, in turn, yields other compounds.

Lignin contains hydroxylphenolic groups that are mostly bound to adjacent phenyl propane units, thereby allowing the material to bond with formaldehyde via a reaction similar to that between phenol and formaldehyde [47]. Lignin with high methoxyl contents is favourable when used as a raw material for lignosulphonate (surfactant) because greater contents of $-CH_2CH_3$ groups enhance the solubility of lignin in water. This property is necessary for raw materials for lignosulphonates.

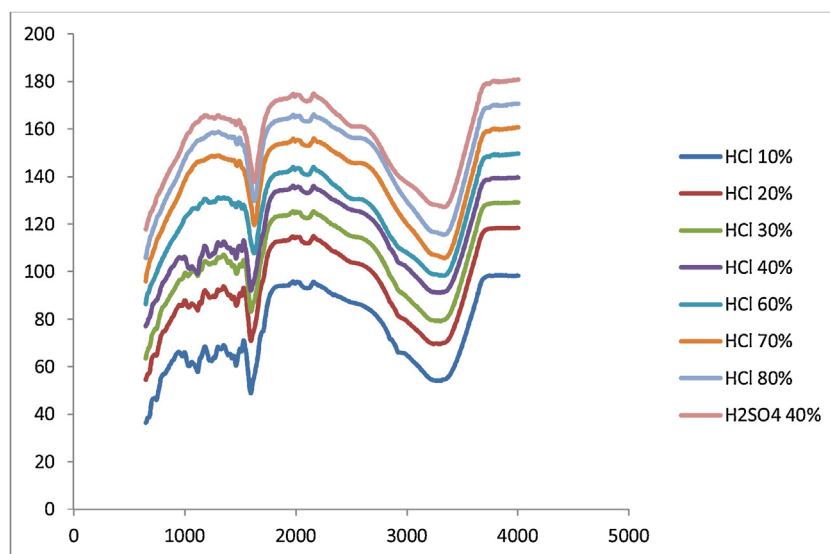


Fig. 5 – FTIR spectrum at various HCl concentration.

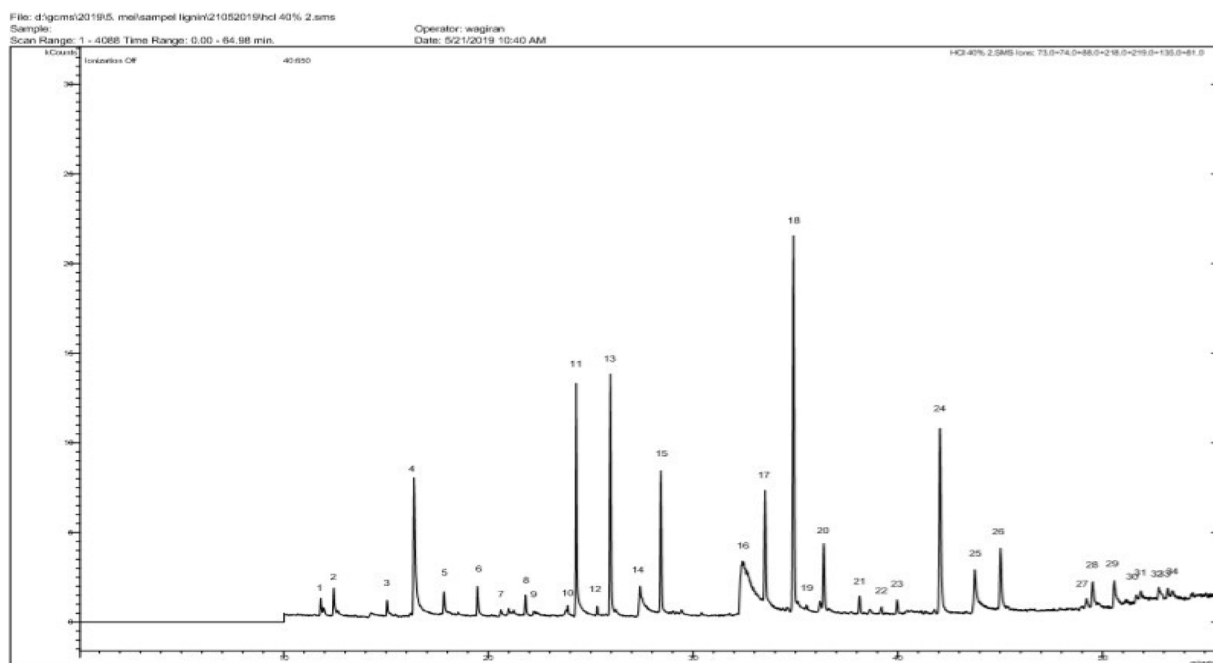
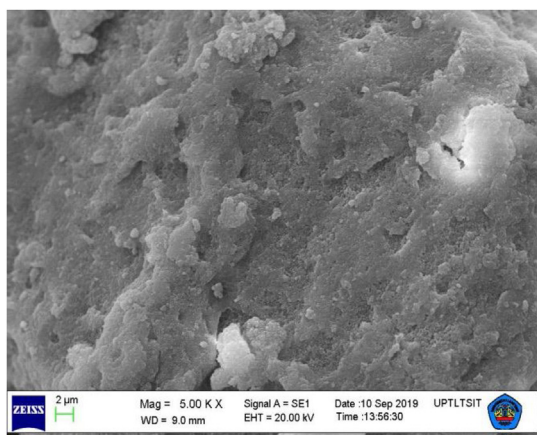
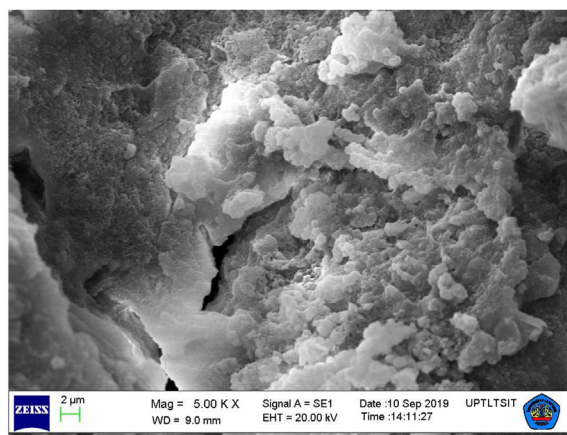


Fig. 6 – Chromatograms of lignin compounds isolated using 40% HCl.



(a)



(b)

Fig. 7 – SEM images of lignin compounds isolated; (a) using 10% HCl, (b) using 40% HCl.

3.4. Fourier transform infrared spectroscopy

FTIR was used to analyse differences in the functional groups of the lignin samples. No significant changes in peaks were observed at wavenumbers of 4000–1500 cm^{-1} . At wavenumbers of 1400–700 cm^{-1} , however, decreases in intensity and the disappearance of some peaks, such as those at 1155, 1051, 1021, 946, 920 and 708 cm^{-1} , could be observed in the spectra of lignin isolated using HCl at concentrations above 40% (Fig. 5). Peaks at 1595 cm^{-1} and 1513 cm^{-1} could be attributed to aromatic lignin skeletal vibrations ([48,49]. Strong peaks at 1460–1420 cm^{-1} may be associated with the stretching vibrations of CH (methyl and methylene) [48,50]. Peaks observed in the range of 1155–1150 cm^{-1} in all spectra may refer to C–H deformation vibrations of guaiacyl groups and C–H vibrations in syringyl groups. The peak at 830–840 cm^{-1} indicates C–H

deformation and ring vibrations. Strong and sharp bands at 620 cm^{-1} , which are only found in the spectra of lignin precipitated from H_2SO_4 . The bands at 1330, 1220 and 1120 cm^{-1} corresponded to syringyl units, whilst weak bands at 1275, 1153 and 1037 cm^{-1} correspond to guaiacyl units. In general, the IR spectra of lignin isolated by acid of various concentrations are similar, thereby indicating that the general composition of lignin is not affected by the concentration and type of acid used.

3.5. Gas chromatography

GC–MS was employed to identify lignin compounds isolated using 40% HCl (Fig. 6). Table 1 shows that the most formed compounds were 2,6-di-tert-butyl-4-dimethyl aminomethylphenol, undecanoic acid, 10-methyl-, methyl

Table 1 – Identification of lignin compounds isolated using 40% HCl.

No	RT	MW	m/z	Compound name	R.Match	% Prob	Area	% Area
1	11.802	142	41	Nonanal	795	31.45	4392	0.72
	11.802	142	57	2-Nonen-1-ol, (E)-	771	17.18		
	11.802	142	45	1-Methoxy-3-(2-hydroxyethyl)nonane	761	14.68		
2	12.449	158	74	Octanoic acid, methyl ester	843	76.43	6512	1.06
	12.449	158	74	Methyl 6-methyl heptanoate	752	20.76		
	12.449	158	74	2-Methylheptanoic	730	14.34		
	15.054	172	88	Octanoic acid, ethyl ester	809	83.64		
4	16.379	135	135	Benzothiazole	940	83.07	49747	8.11
	16.379	135	135	1,2-Benzisothiazole	916	30.71		
	16.379	135	135	Thieno[3,2-c]pyridine	850	13.33		
5	17.830	135	88	Carbonimidodithioic acid, methyl-, dimethyl ester	753	91.58	5319	0.87
6	19.463	186	74	Decanoic acid, methyl ester	829	64.24	7718	1.26
	19.463	200	74	Undecanoic acid, 2-methyl-	837	24.49		
	19.463	242	74	Methyl tetradecanoate	790	13.25		
7	20.994	370	355	Cyclopentasiloxane, decamethyl-	805	29.06	1320	0.22
	20.994	370	355	Benzoic acid, 2,5-bis(trimethylsiloxy)-,trimethylsilyl ester	838	26.84		
	20.994	428	355	3,4-Dihydroxymandelic acid, ethyl ester, tri-TMS	844	22.23		
	21.822	284	88	Hexadecanoic acid, ethyl ester	716	27.63		
8	21.823	200	88	Decanoic acid, ethyl ester	759	26.99	5256	0.86
	22.226	370	355	Benzoic acid, 2,5-bis(trimethylsiloxy)-,trimethylsilyl ester	849	34.33		
9	22.226	370	355	Benzoic acid, 2,4-bis(trimethylsiloxy)-,trimethylsilyl ester	889	29.12	1115	0.18
	22.226	428	355	3,4-Dihydroxymandelic acid, ethyl ester, tri-TMS	803	24.65		
	23.782	518	73	Cycloheptasiloxane, tetradecamethyl-	845	97.67		
10	23.782	518	73	Cycloheptasiloxane, tetradecamethyl-	845	97.67	1139	0.19
11	24.302	218	161	1s,4R,7R,11R-1,3,4,7-Tetramethyltricyclo[5.3.1.0(4,11)undec-2-en 8-one	781	34.21	47322	7.71
	24.302	218	161	1s,4R,7R,11R-1,3,4,7-Tetramethyltricyclo[5.3.1.0(4,11)undec-2-en 8-one	781	34.21		

- Table 1 (Continued)

No	RT	MW	m/z	Compound name	R.Match	% Prob	Area	% Area
	24.302	218	218	2(3H)-Naphthalenone,4,4a,5,6,7,8-hexahydro-4a,5-dimethyl-3-(1-methylethylidene)-, (4ar-cis)-	784	30.45		
	24.302	218	218	5(1H)-Azulenone,2,4,6,7,8,8a-hexahydro-3,8-dimethyl-4-(1methylethylidene)-(8S-cis)-	766	26.48		
12	25.318	276	205	2,4,6-Tris(1,1-dimethylethyl)-4-methylcyclohexa-2,5-dien-1-one	913	35.24	1604	0.26
	25.318	220	205	Phenol, 4,6-di(1,1-dimethylethyl)-2-methyl-	888	31.32		
	25.318	220	205	Butylated Hydroxytoluene	886	29.66		
13	25.974	214	74	Undecanoic acid, 10-methyl-, methyl ester	830	50.24	53176	8.67
	25.974	214	74	Dodecanoic acid, methyl ester	822	40.82		
	25.974	228	74	Dodecanoic acid, 2-methyl-	816	16.21		
14	27.409	200	60	Dodecanoic acid	858	83.06	13601	2.22
	27.409	186	60	Undecanoic acid	837	16.18		
	27.409	214	73	Tridecanoic acid	785	14.85		
15	28.420	228	88	Dodecanoic acid, ethyl ester	792	67.91	32835	5.35
	28.420	242	88	Ethyl tridecanoate	761	19.14		
	28.420	228	88	Undecanoic acid, 2,8-dimethyl-, methyl ester	774	18.79		
16	32.413	263	219	2,6-di-tert-Butyl-4-(dimethylaminomethyl)phenol	835	94.81	70446	11.48
17	33.513	242	74	Tridecanoic acid, 12-methyl-, methyl ester	884	86.67	31223	5.09
	33.513	242	74	Methyl tetradecanoate	840	24.11		
	33.513	298	74	Octadecanoic acid, methyl ester	761	11.27		
18	34.901	234	219	3,5-di-tert-Butyl-4-hydroxybenzaldehyde	905	90.7	98215	16.01
	34.901	234	219	2,3,5,6-Detetrahydrocyclohexanone,2,6-di-t-butyl-4-hydroxymethylene-	839	22.77		
	34.901	234	219	Phenol, 2,6-bis(1,1-dimethylethyl)-4-ethyl	811	13.68		
19	35.549	666	73	Cyclononasiloxane, octadecamethyl-	792	89.85	1018	0.17
20	36.382	256	88	Tetradecanoic acid, ethyl ester	773	61.51	19191	3.13
	36.382	256	88	Tetradecanoic acid, 2-methyl-, methyl ester	791	24.59		
	36.382	256	88	Hexadecanoic acid, ethyl ester	721	21.47		
21	38.137	296	81	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	874	41.53	4673	0.76
	38.137	278	81	9-Eicosyne	834	16.35		
	38.137	264	81	7-Octadecyne, 2-methyl-	836	14.36		
22	39.195	474	149	Phthalic acid, isobutyl octadecyl ester	758	20.32	2062	0.34
	39.195	374	149	Phthalic acid, isobutyl undec-2-en-1-yl ester	739	18.72		
	39.195	318	149	Phthalic acid, isobutyl cyclohexylmethyl ester	761	17.36		
23	39.965	296	81	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	888	59.48	3702	0.60

– Table 1 (Continued)

No	RT	MW	m/z	Compound name	R.Match	% Prob	Area	% Area
24	39.965	278	68	1,4-Eicosadiene	796	17.81	63482	10.35
	39.965	278	81	9-Eicosyne	825	12.61		
	42.068	270	74	Pentadecanoic acid, 14-methyl-, methyl ester	884	69.05		
	42.068	270	74	Hexadecanoic acid, methyl ester	876	27.69		
	42.068	270	74	Pentadecanoic acid, 13-methyl-, methyl ester	858	27.69		
25	43.775	256	43	n-Hexadecanoic acid	771	63.06	18488	3.01
	43.775	652	57	I-(+)-Ascorbic acid 2,6-dihexadecanoate	747	27.78		
	43.775	494	98	Palmitic anhydride	716	14.75		
26	45.014	284	88	Hexadecanoic acid, ethyl ester	796	69.81	21295	3.47
	45.014	372	43	Octadecanoic acid, 2-(2-hydroxyethoxy)ethyl ester	752	27.27		
	45.014	284	88	Hexadecanoic acid, 2-methyl-, methyl ester	766	22.19		
27	49.225	294	67	7, 10-Octadecadienoic acid, methyl ester	811	18.23	5712	0.93
	49.225	294	67	12, 15-Octadecadienoic acid, methyl ester	808	16.95		
	49.225	294	67	8,11-Octadecanoic acid, methyl ester	807	16.41		
28	49.521	296	55	9-Octadecenoic acid, methyl ester, (E)	858	16.3	13139	2.14
	49.521	478	43	9-Octadecenoic acid (Z)-, tetradecyl ester	865	16.05		
	49.521	422	43	Decyl oleate	864	15.83		
29	50.582	298	74	Heptadecanoic acid, 15-methyl-, methyl ester	853	42.28	11545	1.88
	50.582	298	74	Octadecanoic acid, methyl ester	851	29.56		
	50.582	298	74	Heptadecanoic acid, 14-methyl-, methyl ester	835	28.04		
30	51.664	308	67	9,12-Octadecadienoic acid, ethyl ester	790	35.8	1705	0.28
	51.664	308	67	Linoleic acid ethyl ester	784	32.8		
	51.664	354	67	9,12-Octadecadienoic acid (Z,Z)-, 2,3-dihydroxypropyl ester	761	21.75		
31	51.890	310	55	Ethyl Oleate	738	22.43	2897	0.47
	51.890	310	55	(E)-9-Octadecenoic acid ethyl ester	716	19.27		
32	52.755	312	88	Heptadecanoic acid, 15-methyl-, ethyl ester	794	84.09	2784	0.45
	52.755	312	88	Octadecanoic acid, ethyl ester	743	28.31		
33	53.193	298	43	1-Eicosanol	889	18.81	3546	0.58
	53.193	254	43	13-Tetradecen-1-ol acetate	859	17.44		
	53.193	312	43	Acetic acid, octadecyl ester	873	15.4		
34	53.446	436	43	9,12,15-Octadecatrienoic acid, 2,3-bis(acetyloxy)propyl ester, (Z,Z,Z)-	741	17.36	4151	0.68
	53.446	268	43	10-Methyl-8tetradecen-1-ol acetate	709	15.05		
	53.446	250	43	Formic acid,	708	14.85		
				3,7,11-trimethyl-1,6,10-dodecatrien-3-yl ester				
			Total	613631	100.00			

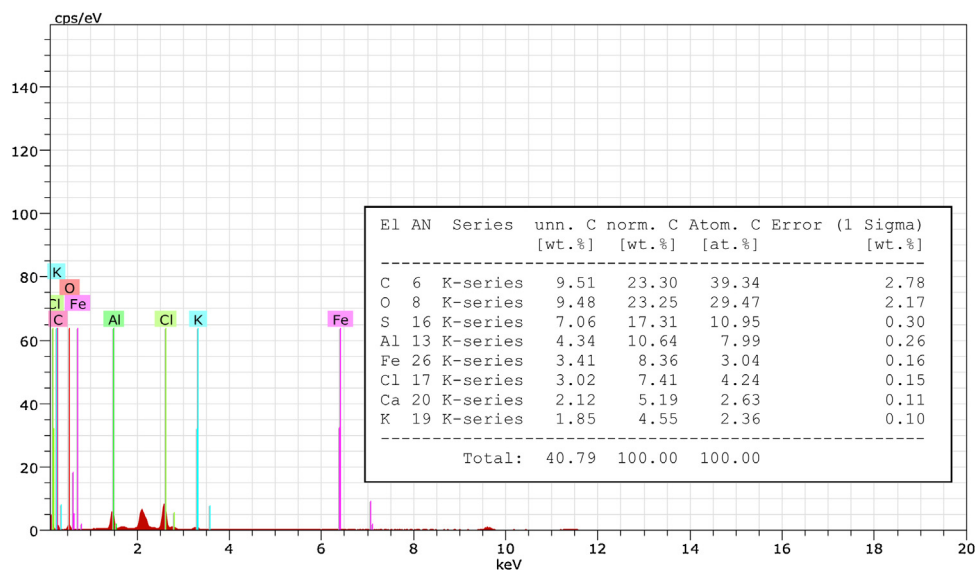


Fig. 8 – EDX spectrum of lignin compounds isolated using 40% HCl.

ester, 1s,4R,7R,11R-1,3,4,7-tetramethyltricyclo[5.3.1.0(4,11) undec-2-en, dodecanoic acid, ethyl ester, 3,5-di-tert-Butyl-4-hydroxybenzaldehyde, pentadecanoic acid, 14-methyl-, methyl ester, n-hexadecanoic acid, 9-octadecenoic acid, methyl ester, (E), benzothiazole, tridecanoic acid, 12-methyl-, methyl ester, tetradecanoic acid and ethyl ester.

The lignin structure obtained from EFB fibres is more complex than the lignin structures extracted from wood because of the complex arrangement of syringyl and guaiacyl-propane units with *p*-hydroxy-propane units in the former. EFB fibres contain approximately 17.2% lignin, which is relatively low compared with the lignin contents of hardwood and softwood materials [51]. Radoykova et al. [52] showed that extraction of black liquor using toluene and ethyl acetate results in 2-methoxy phenol, 4-ethyl-2-methoxy phenol, 2,6-dimethoxy phenol, 4-hydroxy-3-methoxy benzaldehyde, 4-hydroxy-3,5-dimethoxy-benzaldehyde, 1-(4-hydroxy-3-methoxyphenyl) ethanone and 1-(4-hydroxy-3,5-dimethoxy phenol) ethanone after treatment with lignin alkaline sulphate.

3.6. Scanning electron microscopy–energy dispersive X-ray spectroscopy

SEM-EDX was used to evaluate the size and morphology of lignin compounds at 5× magnification. Increasing the concentration of HCl from 10% to 40% caused differences in lignin morphology. Specifically, increases in HCl concentration resulted in a decrease in the compactness of the lignin morphology (Figs. 7 and 8). The presence of cavities in the morphology of the material indicate degradation. Moreover, the dominant elements were carbon, oxygen, sulphur, aluminium and iron.

4. Conclusion

The results showed that increasing HCl concentrations up to 40% can reduce yield but increase the weight of equiva-

lent lignin and methoxyl lignin levels. There was no change in the structure of the lignin functional group until the addition of 40% lignin concentration but changes mainly in wave numbers 1000–2000 cm^{-1} . GC-MS test results show that the most formed compounds are from phenol groups, namely: 2,6-di-tert-Butyl-4-dimethylaminomethyl) phenol, methyl esters such as Undecanoic acid, 10-methyl-, methyl esters, 1s, 4R, 7R, 11R-1,3,4,7-Tetramethyltricyclo [5.3.1.0 (4.11) undec-2-en, Dodecanoic acid, ethyl ester, Pentadecanoic acid, 14-methyl-, methyl ester, n-Hexadecanoic acid, 9-Octadecenoic acid, methyl esters, and benzene groups such as (E), Benzothiazole and 3,5-di-tert-Butyl-4-hydroxybenzaldehyde.

Conflicts of interest

None.

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