

Antioxidant and anticorrosive properties of oil palm frond lignins extracted with different techniques

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Abstract

• **Context** Oil palm (*Elaeis guineensis* Jacq.) fronds are produced as waste during the harvest of oil palm fruits. It mainly consists of cellulose, lignin, and hemicelluloses. Lignins like other polyphenols are potent free radical scavengers and are considered to be a valuable source of antioxidant phenolic compounds.

• **Aims** The aim was to quantify the antioxidant properties of lignins extracted from oil palm biomass using Kraft, soda, and organosolv pulping. The potential of the extracted lignins as inhibitors of mild steel corrosion was also assessed.

• **Methods** Ground and dried 1–3-mm-mesh-size oil palm fronds were submitted to Kraft, soda, and organosolv pulping in rotary digesters. The extracted lignin was characterized and oxygen uptake was measured. Anticorrosion properties of extracted lignins were monitored via electrochemical measurements and surface analysis.

• **Results** Soda-extracted lignins displayed the highest antioxidant activities as compared to Kraft and ethanol organosolv lignins. The highest inhibition of corrosion of mild steel was reached in the presence of soda-extracted lignins.

• **Conclusion** Oil palm fronds are potential sources of lignins usable as green antioxidant for corrosion inhibition of mild steel.

Keywords Oil palm fronds · Lignin · Mild steel · Antioxidant · Corrosion inhibitor

1 Introduction

Lignin is an aromatic amorphous biopolymer, a binder that holds together the lignocellulosic fibers to ensure rigidity of all vascular plants. It is built up by oxidative coupling of three phenylpropanoid units (*trans-p*-coumaryl alcohol, *trans*-coniferyl alcohol, and *trans*-sinapyl alcohol) which form a randomized structure in a 3D network inside the cell wall (Ammalahti et al. 1998; Garcia et al. 2009; She et al. 2010). Unlike most natural polymers that consist of a single intermonomeric linkage, lignin is a branched polymer made up of many carbon-to-carbon and ether linkages. The most abundant inter-ether unit linkage in all lignins is the β -aryl ether bond (β -O-4). Furthermore, a small proportion of lignin units remains as phenolic, being linked only by C–C bonds, such as β -5, β -1, β -5, β - β , and α - β linkages. Although this phenolic moiety represents a low and variable fraction of the total lignin, it can strongly affect the reactivity of the polymer (Garcia et al. 2009).

Lignins as well as other polyphenols are potent free radical scavengers and considered to be a valuable source of antioxidant phenolic compounds. One of the analytical methods used to measure the antioxidant capacity is based on the inhibition of the oxidation of organic substrates (Burton et al. 1985; Wanasundara and Shahidi 1994). The oxygen uptake measurement is the most direct method used to measure the reaction extent (Poaty et al. 2010; Saha et al. 2013). Moreover, the induced oxidation of methyl linoleate and its radical long chain reaction is well known to be inhibited by various antioxidants (Uri 1961). The applicability of lignins from different sources as antioxidants has been also successfully tested (Urgatondo et al. 2009). Recent studies by Garcia

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et al. (2010) have revealed that the extraction processes of lignin may give major effect on its antioxidant capacity. The antioxidant properties exhibited from lignin can give broader applications such as antimicrobiology, antiaging, and corrosion inhibitor.

Corrosion affects most of industrial sectors and may cost billions of dollars each year for corrosion prevention and replacement of parts of materials. The use of inhibitors is one of the most effective ways to prevent corrosion. Corrosion inhibitors will reduce the rate of either anodic oxidation or cathodic reduction or both. This will give us anodic, cathodic, or mixed type of inhibition. In an attempt to find corrosion inhibitors which are environmentally safe and readily available, there has been a growing trend in the use of natural products such as leaf or plant extract as corrosion inhibitors for metals in acid cleaning processes. Most of the potential corrosion inhibitors possess an active functional group such as nitro ($-\text{NO}_2$) and hydroxyl ($-\text{OH}$), heterocyclic compound, and π electron (Sastri et al. 2007).

The oil palm fronds (OPF) have been identified as the major contributor of biomass waste in Malaysia. OPF is a lignocellulosic material available at a very low cost which would represent a valuable renewable source of various products and chemicals. Recently, we have demonstrated the potential of lignin obtained from OPF for green material applications (Hussin et al. 2013). In this paper, three different processes were chosen for lignin extraction: Kraft, soda, and aqueous ethanol organosolv processes. The influence of lignin structure by its syringyl (S), guaiacyl (G), and *p*-hydroxyphenyl (H) basic units, phenolic/aliphatic hydroxyl content, and molecular size are also identified via ^{31}P nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC). The antioxidant activities of different types of lignin were also studied using the oxygen uptake index method in the presence of methyl linoleate. The possibility of lignin samples to be applied as corrosion inhibitor was studied. The assessment of the corrosion behavior was studied using potentiodynamic polarization measurement, electrochemical impedance spectroscopy (EIS), and X-ray diffraction (XRD), and the morphology of inhibited mild steel surface was analyzed via scanning electron microscopy (SEM). Next, the inhibition efficiency of lignin samples was correlated with its antioxidant activities.

2 Materials and method

The OPF (*Elaeis guineensis* Jacq.) were obtained from Valdor Palm Oil Mill near Sungai Bakap plantation (Seberang Prai, Malaysia) in mid-2012. The OPF strands were chipped into small pieces. After sun dried for 3 days, the chips were then ground to a 1–3-mm size using Wiley mill, and the fiber was further dried in an oven at 50 °C for 24 h. The OPF biomass

was first subjected to Soxhlet extraction with ethanol/toluene (2:1, v/v) for 6 h before use. All chemical reagents used in this study were purchased from Sigma-Aldrich (USA) and VWR (France) and used as received. Dried matter contents were determined using a moisture balance, KERN MRS 120-3 Infra-red moisture analyzer (drying at 105 °C to constant weight). The effective dry matter content of raw OPF biomass was ~89 %. All experiments were run in triplicates, and its average values were represented in the results.

2.1 Lignin extraction

Both Kraft and soda pulping processes were carried out in a 10-L rotary digester. All pulping conditions followed the method outlined by Wanrosli et al. (2007) with slight modifications. For Kraft pulping, a 20 % of active alkali and 30 % of sulfidity with water to fiber ratio of 8 was used. The time of maximum cooking temperature (170 °C) was set for 3 h. For soda pulping, 30 % of active alkali alone was applied at the same conditions as described above. The pressure of both Kraft and soda pulping was around 12–15 bar. The pulp was washed and separated by screening through a sieve and the black liquor was collected. Soda (SL) and Kraft (KL) lignins were precipitated from the concentrated black liquor by acidifying it with 20 % (v/v) sulfuric acid until pH 2 (Mohamad Ibrahim et al. 2011). The precipitated lignins were filtered and washed with water (pH 2). Both lignins were then dried in an oven at 50 °C for 48 h. The purification of lignin was conducted by extracting it in the Soxhlet apparatus for 6 h with *n*-pentane to remove lipophilic non-lignin matters such as wax and lipids. The precipitate was filtered and washed twice with pH 2 water to remove the excess *n*-pentane and non-lignin phenolic compounds which may remain after the pulping process. The purified KL and SL were then dried in an oven for another 48 h.

For organosolv pulping process, the OPF were treated with aqueous ethanol (35/65, v/v) with 0.5 % (w/w) sulfuric acid as a catalyst at 190 °C for 60 min (El Hage et al. 2009). The material-to-liquid ratio used was 1:8. After the reactor was loaded with OPF and cooking liquor, it was heated to the operating temperature which was then maintained throughout the experiment (pressure around 25 bar). After the treatment, the pre-treated OPF was filtered and washed with warm aqueous ethanol (8:1, 3 × 50 mL). The liquor was diluted with three volumes of water to precipitate the ethanol organosolv lignin (EOL), and the precipitate was then collected by centrifugation at 3,500 rpm for 10 min. The resulting EOL was dried in an oven at 50 °C for 48 h.

2.2 Characterization of lignin

All NMR spectroscopy experiments were performed on a Bruker Avance 300 spectrometer operating at a frequency of

100.59 MHz. ^{31}P NMR spectra were acquired after derivatizing 25-mg lignin with 2-chloro-4,4,5,5-tetramethyl-1,1,3,2-dioxaphospholane (TMDP) as previously described by Granata and Argyropoulos (1995).

Lignin samples were subjected to acetylation in order to enhance their solubility in organic solvents used in GPC. The number average molecular weights (M_n) and weight (M_w) of lignin and cellulose were determined after derivatization by GPC with a Dionex Ultimate 3000 HPLC system consisting of an autosampler and a UV detector and using tetrahydrofuran as eluent. Standard polystyrene samples were used to construct a calibration curve. Data were collected and analyzed with Chromeleon software version 6.8 (Dionex Corp., USA).

2.3 Measurement of lignin antioxidant activity by oxygen uptake method

Antioxidant properties of lignins were investigated by evaluating oxygen uptake inhibition during oxidation of methyl linoleate. The induced oxidation by molecular oxygen was performed in a gas-tight borosilicate glass apparatus (El Oualja et al. 1995). Butanol was used as solvent; it is a reference solvent of different studies on natural antioxidant in our apparatus; the solvent should not be oxidized and its vapor pressure must be low enough. Temperature was set to 60 °C, and initial conditions inside the vessel were as follows: methyl linoleate (Fluka, 99 %) concentration 0.32 mol L⁻¹; 2,2'-azobisisobutyronitrile (AIBN) (Fluka, 98 %) concentration 7.2 × 10⁻³ mol L⁻¹; lignin concentration 0.2 g L⁻¹; and oxygen pressure 150 Torr. As the intensity of oxygen bubbling in the reaction media has no influence on the oxidation, dissolution of oxygen is not a limiting step. Through lignins are soluble in butanol at 60 °C, they are fairly soluble at room temperature so that we have used methanol lignin solution. Methanol was evaporated before reaction.

Oxygen uptake was monitored continuously by a pressure transducer (Viatron model 104). Without any additive, oxygen uptake is roughly linear and constitutes the control. In the presence of an antioxidant, oxygen consumption is slower, and the oxygen uptake inhibition (OUI) of extract was estimated by comparing oxygen uptake at a chosen time (3 h), in the presence of this compound (pressure variation ΔP_{sample}) and in the absence of the compound ($\Delta P_{\text{control}}$) according to:

$$\text{OUI (\%)} = (\Delta P_{\text{control}} - \Delta P_{\text{sample}}) / \Delta P_{\text{control}} \times 100 \quad (1)$$

This ratio defines antioxidative capacity as an OUI; it should spread from 0 to 100 %, for poor and strong antioxidants, respectively, and may be negative for prooxidants.

2.4 Preparation of specimens and electrolytes

Mild steel coupons having chemical composition (wt%) of 0.08 C, 0.01 Si, 1.26 Mn, 0.02 P, and remaining Fe were used. The specimens were polished successively using 400, 600, and 800 gritted emery papers. Next, they were degreased with methanol and washed with distilled water before and after each experiment.

The solutions were prepared using AR grade hydrochloric acid. Appropriate concentrations of acids were prepared by using distilled water. The lignin samples were first dissolved in a small volume of methanol and sonicated to increase solubility. The dissolved lignin samples were next diluted with 0.5 M HCl. The concentration of inhibitor at 500 ppm was prepared by diluting the stock lignin solution.

2.5 Electrochemical measurements

A three-electrode cell assembly consists of a mild steel coupon (9 cm × 3 cm × 0.1 cm dimension with an exposure surface of 3.124 cm²) as a working electrode (WE), platinum rod as a counter electrode (CE), and saturated calomel electrode (SCE) as a reference electrode (RE) containing 100 mL of electrolyte. The temperature of the electrolyte was maintained at room temperature (28 ± 2 °C).

The EIS, was carried out using Gamry Reference 600 after the open circuit potential, E_{ocp} , has stabilized (30 min) over a frequency range of 100 kHz to 0.1 Hz with a signal amplitude perturbation of 5 mV and scan rate of 1 mV s⁻¹. Next, it was fitted with several sets of circuits using ZSim Demo software to obtain the charge transfer resistance, R_{ct} values. The inhibition efficiency (IE%) was calculated by the following equations:

$$\text{IE\%} = \left(1 - \frac{R_{\text{ct}}}{R'_{\text{ct}}}\right) \times 100 \quad (2)$$

where R_{ct} and R'_{ct} are referred to charge transfer resistance without and with addition of inhibitor (lignin), respectively.

Potentiodynamic polarization studies were carried out without and with addition of lignin solution (500 ppm) in 0.5 M HCl solutions at a scan rate of 1 mV s⁻¹. The E_{ocp} was measured for 30 min to allow stabilization of the steady-state potential. The potential range was calculated from the E_{ocp} values obtained (±250 mV). The percentage of IE% was calculated by using the following equation:

$$\text{IE\%} = \frac{I_{\text{corr}} - I_{\text{corr}(i)}}{I_{\text{corr}}} \times 100 \quad (3)$$

where I_{corr} and $I_{\text{corr}(i)}$ are referred to corrosion current density without and with addition of inhibitor (lignin), respectively. Potentiodynamic polarization curves were produced using Echem Analyst software.

2.6 Surface and rust transformation analyses

The nature of the film formed on the surface of the metal specimens was evaluated by SEM analysis (Leo Supra 50VP). Corrosion-inhibited and blank (without inhibitor) specimens from the electrochemical measurement were examined. Pre-rusted samples were prepared by subjecting the mild steel plates to the salt spray chamber according to the American Society for Testing and Materials ASTM B 117 (6 h exposure in 5 % (w/v) NaCl at 98 % humidity, 1.0 mL h⁻¹ spray rate, 1.0 kg cm⁻³ of pressure and followed by drying in an oven at 40 °C) (ASTM 1973). The pre-rusted plates were immersed in 1 g L⁻¹ lignin in methanol solution for 24 h. The changes in the rust structures were observed from XRD patterns (PANalytical X'Pert PRO MRD PW3040).

3 Results

3.1 Characterization of lignin

Higher yield of Kraft (KL 18.29 %) and soda (SL 15.86 %) and lower yield of EOL (9.26 %) lignins were observed after delignification process which indicates that alkaline process accelerates the removal of lignin from OPF biomass. Data from the quantitative ³¹P NMR of the three lignin samples (Fig. 1), obtained following their derivatization with TMDP, are presented in Table 1. The concentration of each hydroxyl functional group (in mmol g⁻¹) was calculated on the basis of the hydroxyl content of the internal standard cyclohexanol and its integrated peak area (Granata and Argyropoulos 1995). According to this data, it can be observed that alkaline lignins (KL and SL) gave lower concentration of aliphatic -OH groups and higher concentrations of phenolic -OH groups compared to EOL. The weight average (M_w) and number average (M_n) molecular weight of all lignins were computed from their chromatograms. From the results, it can be seen that the weight average (M_w) of SL (1,660 g mol⁻¹) and EOL (1,215 g mol⁻¹) lignin was lower than KL (2,063 g mol⁻¹) lignin.

3.2 Antioxidant activity by oxygen uptake

In this study, we have determined the antioxidant activity of lignin by employing oxygen uptake inhibition method. Unlike antiradical tests broadly used in the literature (e.g., di(phenyl)-(2,4,6-trinitrophenyl)iminoazanium (DPPH), ABTS), the oxygen uptake inhibition is a realistic model of autoxidation reactions taking place in food and living systems, even though substrates more complex than methyl linoleate are more representative of specific situations. In addition, previous studies done by Poaty et al. (2010) and Saha et al.

(2013) have revealed that the inhibition obtained by oxygen uptake test shows similar trend to that of DPPH assay. The oxygen uptake profile during autoxidation of methyl linoleate is shown in Fig. 2. By comparing the linear curve of methyl linoleate alone (control), it appears that all lignin samples exhibited antioxidant activity by slowing down the oxidation of methyl linoleate. In order to correlate our observation with the previous finding by El Hage et al. (with regards to structure, molecular weight, and phenolic -OH content), butanol has been chosen as the corresponding solvent to dissolve lignin samples. SL gives highest inhibition (OUI=74 %) followed by EOL (OUI=60 %) and KL (OUI=55 %).

3.3 Electrochemical impedance spectroscopy measurement

The corrosion of mild steel in 0.5 M HCl solution in the presence of lignin samples was investigated by EIS at room temperature after an exposure period of 30 min. Nyquist plots for mild steel obtained at the interface in the absence and presence of lignins at constant concentration (500 ppm) are given in Fig. 3. The impedance diagram obtained with 0.5 M HCl shows only one depressed capacitive loop at the higher frequency range. The same trend was also noticed for mild steel immersed in 0.5 M HCl containing KL, SL, and EOL. Table 2 lists the impedance parameters of the Nyquist plots of the lignin extractives at the concentration of 500 ppm. The EIS measurement reveals that at the concentration of 500 ppm, the percentage of inhibition efficiency of lignin is highest for SL ($IE_{\text{soda}}=85.81\%$) and followed by EOL ($IE_{\text{organosolv}}=81.84\%$) and KL ($IE_{\text{Kraft}}=67.85\%$) lignin.

3.4 Potentiodynamic polarization measurement

Figure 4 represents the anodic and cathodic Tafel polarization curves of mild steel at 500 ppm of lignins in 0.5 M HCl. The inhibition efficiency of lignin at the concentration of 500 ppm is given in the following order: $IE_{\text{soda}}=98.67\% > IE_{\text{organosolv}}=97.21 > IE_{\text{Kraft}}=85.89\%$. Lower current density values ($I_{\text{corr Kraft}}=0.1580\text{ mA cm}^{-2}$; $I_{\text{corr soda}}=0.0146\text{ mA cm}^{-2}$; $I_{\text{corr organosolv}}=0.0312\text{ mA cm}^{-2}$) of lignin samples than blank solution ($I_{\text{corr blank}}=1.12\text{ mA cm}^{-2}$) were observed.

3.5 Surface and rust transformation analysis

Surface analysis using SEM proved a significant improvement on the surface morphology of mild steel plates in the presence of SL. From Fig. 5a, a rough surface was noticed for mild steel immersed in 0.5 M HCl solution. On the other hand, a smooth surface was observed on the inhibited mild steel surface (Fig. 5b). XRD pattern (Fig. 6) of the pre-rusted plate shows that lepidocrocite (L: $\gamma\text{-FeOOH}$) and magnetite (M: Fe_3O_4) were the main components present, with traces of goethite (G: $\alpha\text{-FeOOH}$). Upon immersion in the SL solutions, several

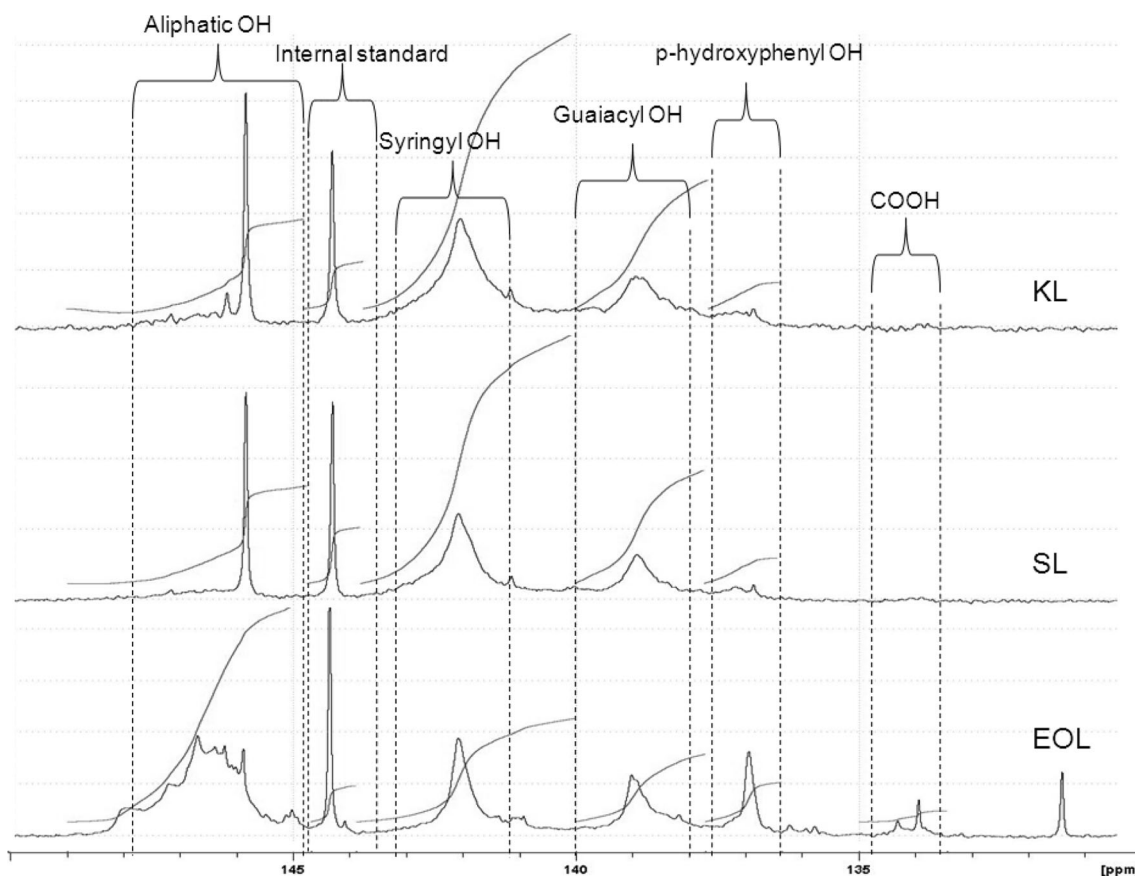


Fig. 1 ^{31}P NMR spectrum of Kraft (KL), soda (SL), and ethanol organosolv lignin (EOL)

lepidocrocite peaks diminished as well as reduced in favor of formation ferric-lignates, thus impeding further corrosion process.

4 Discussion

4.1 Characteristic of lignin

The lower yield of lignin after ethanol organosolv process was perhaps due to (i) low severity reaction conditions used and

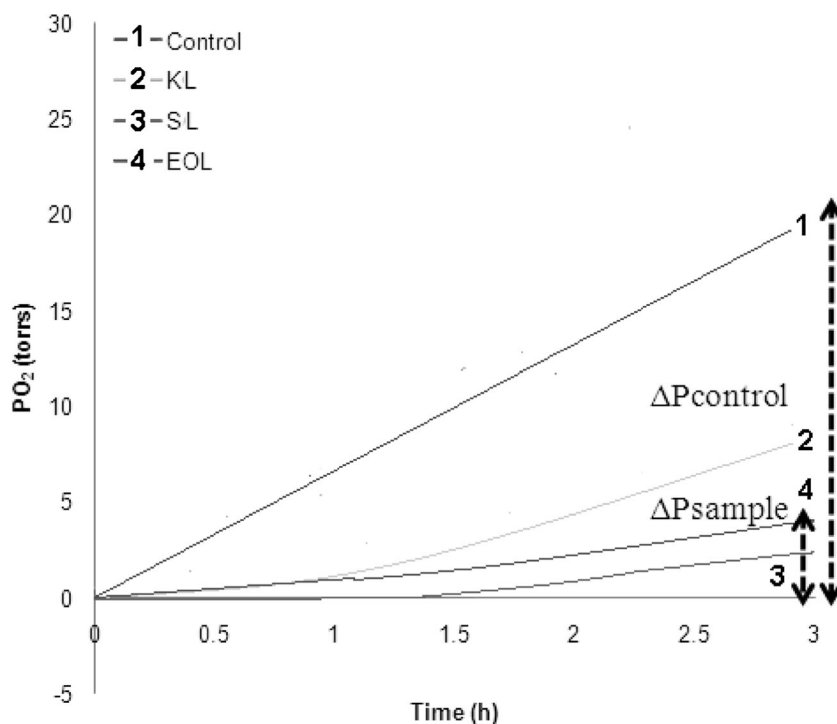
(ii) the effect of aqueous ethanol solvent which dissolves small molecular weight of lignin (El Hage et al. 2010; Hussin et al. 2013). The degree of delignification of OPF lignin can be possibly increased by using alkaline pulping method as reported previously by Hussin et al. (2013). In addition, EOL yield can be improved by changing the severity factor of organosolv pulping (changing of temperature, extraction time, percentage of acid, and solvent ratios). The extraction of lignin via different pulping process will produce different composition and structures. This can be evidenced through the S and G content, hydroxyl content, and molecular weight values obtained from ^{31}P NMR and GPC analysis.

In the ^{31}P NMR studies, the amount of hydroxyl groups based on the integration was calculated in the phosphorylated lignin samples. It was observed that the amount of aliphatic –OH from EOL is slightly higher compared to KL and SL which justify the presence of more aliphatic –OH functional groups in EOL structure. This phenomenon is mainly due to the extensive depolymerization of lignin during alkaline pulping through the scission of β -O-4 bonds leading to the production of phenolic –OH groups (Hussin et al. 2013). In addition, the reduction of aliphatic –OH is probably due to the dehydration reactions through acid-catalyzed elimination reaction (El Hage et al. 2009; Obama et al. 2012). Higher content of phenolic –OH is indeed beneficial for later

Table 1 Lignins characterized by ^{31}P NMR

ppm	Assignments (^{31}P NMR)	mmol g $^{-1}$		
		KL	SL	EOL
150–145	Aliphatic –OH	0.45	0.42	1.49
144.8	Cyclohexanol (internal standard)			
144–140	Syringyl –OH	1.42	1.07	0.69
140–138	Guaiacyl –OH	0.65	0.48	0.45
138–136	<i>p</i> -Hydroxyphenyl –OH	0.13	0.11	0.26
135–133	Carboxylic acid	–	–	0.07

Fig. 2 Oxygen uptake profile (oxygen pressure variation, PO_2 in Torr vs time in hours) of Kraft (*KL*), soda (*SL*), and ethanol organosolv lignin (*EOL*)



applications especially antioxidant activity and corrosion inhibition. In addition, all lignin samples show a small value for G unit and higher S unit. Higher signals for S unit in all OPF lignin may suggest that both alkaline and organosolv processes will produce lignins that contain more syringal basic unit than guaiacyl unit.

GPC analyses have shown that weight average (M_w) of SL ($1,660 \text{ g mol}^{-1}$) and EOL ($1,215 \text{ g mol}^{-1}$) lignin was lower than KL ($2,063 \text{ g mol}^{-1}$) lignin. This phenomenon can be explained according to the different lignin composition. Even though β -O-4 is the most common linkage in all lignin types, there are also some quantities of C-C bonds between the phenylpropanoic

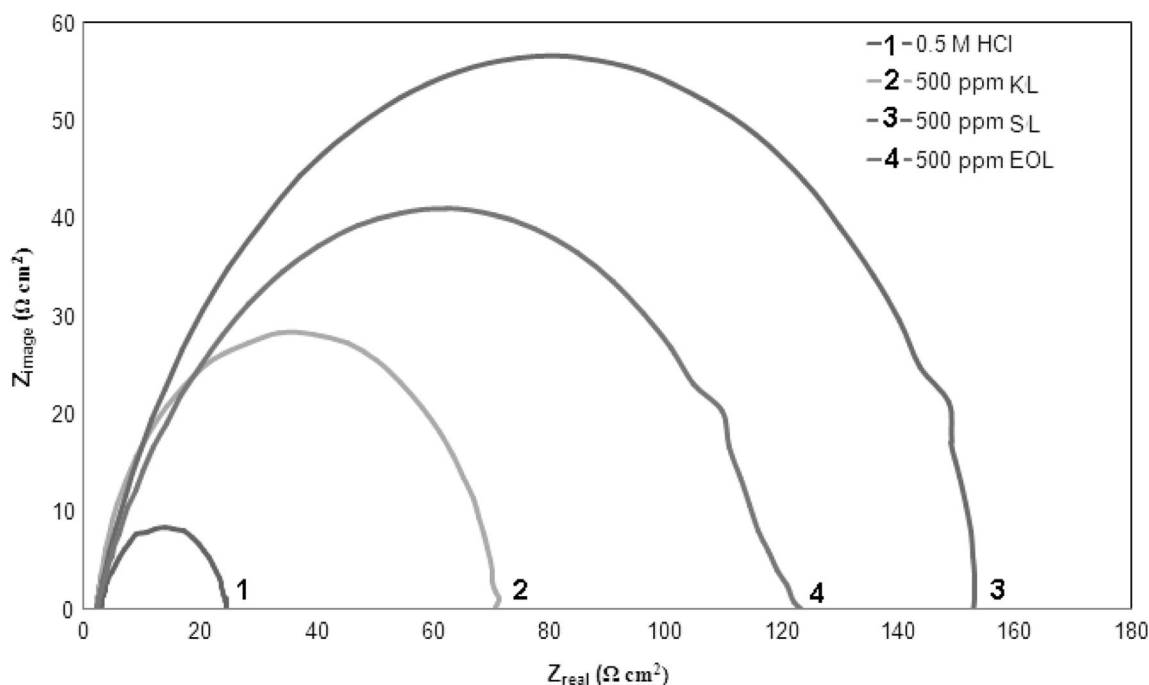


Fig. 3 Nyquist plot (imaginary impedance, Z_{image} in $\Omega \text{ cm}^2$ vs real impedance, Z_{real} in $\Omega \text{ cm}^2$) of mild steel in 0.5 M HCl solution in the absence and presence of Kraft (*KL*), soda (*SL*), and ethanol organosolv lignin (*EOL*)

Table 2 Impedance parameters and inhibition efficiency of mild steel in 0.5 M HCl solutions containing 500-ppm lignin solutions

Samples	R_{ct} (Ω cm ²)	R_s (Ω cm ²)	Number	IE%
0.5 M HCl	68.41	8.89	0.84	–
500 ppm KL	212.8	6.93	0.91	67.85
500 ppm SL	482.0	7.38	0.80	85.81
500 ppm EOL	376.8	6.98	0.76	81.84

units (which involve C5 of aromatic ring). According to Van de Klashorst (1989), under alkaline conditions, some α -hydroxyl groups from quinone methide intermediates form the alkali-stable methylene linkages after it reacted with other lignin fragments. Due to the more severe conditions used in Kraft pulping, high value of lignin molecular weight can be observed. On top of that, previous studies have shown that organosolv pulping process can promote the fragmentation of small molecular weight lignin (El Hage et al. 2010). Meanwhile, low M_n value for SL is due to the soda pulping process. In this process, the hydroxide ions react with the lignin causing the fragmentation of polymer in the water/alkali soluble fragment. This corroborates that the cleavage of α and β -O-4 is the predominant process in alkaline medium (Hussin et al. 2013). Low polydispersity of EOL ($M_w/M_n=1.17$, $M_n=1,036$) compared to KL ($M_w/M_n=1.89$, $M_n=1,063$) and SL ($M_w/M_n=2.33$, $M_n=713$) indicated the uniformity of overall packing structures of lignin.

Besides the severe condition, the molecular weight of lignins was also affected by its S and G content. As β -O-4 is the most common linkage in lignin, small quantities of C–C bonds between the phenylpropanoic units which involve C5 of aromatic ring may also be present. Guaiacyl-type units are capable of forming this kind of bond, but this is not possible in syringyl-type units as it has both C3 and C5 positions substituted by methoxy groups. As a result, these C–C bonds are not cleaved during the pulping process due to its high stability. Hence, the lignin that contains slightly high guaiacyl-type units is expected to show high molecular weight (HMW) than those having high contents of syringyl-type units (Tejado et al. 2007; Hussin et al. 2013).

4.2 Antioxidant activity of lignin and its correlation to anticorrosion properties

Lignin has been identified as potent free radical scavenger and considered to be a valuable source of antioxidant phenolic compounds. The antioxidant activity determined by oxygen uptake test has revealed that SL has higher tendency to reduce the evolution of oxygen gas as compared to KL and EOL. It is believed that the small molecular weight and high phenolic –OH content of SL and EOL affect the performance of the antioxidant activity. The antioxidant efficiency of lignin has been described to be related with their structure, purity, and

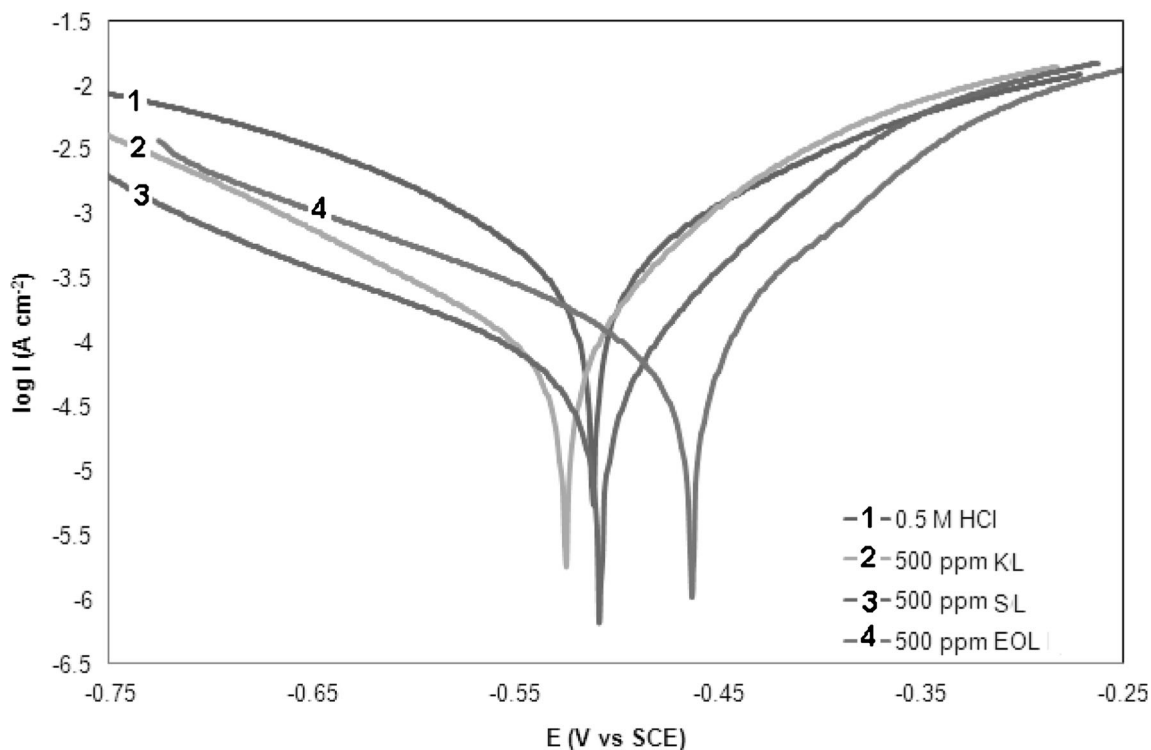
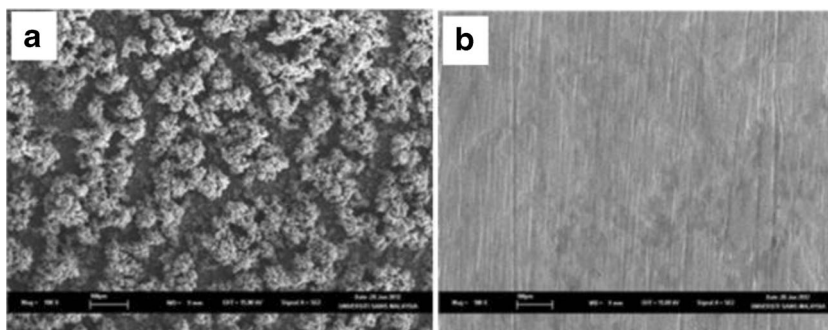


Fig. 4 Tafel curve (corrosion current density, I in $A\ cm^{-2}$ vs corrosion potential, E in V vs SCE) of mild steel in 0.5 M HCl solution in the absence and presence of Kraft (KL), soda (SL), and ethanol organosolv lignin (EOL)

Fig. 5 Scanning electron microscope (SEM) micrographs of **a** mild steel without inhibitor, 0.5 M HCl, and **b** mild steel with soda lignin, 500 ppm, at magnification of $\times 100$



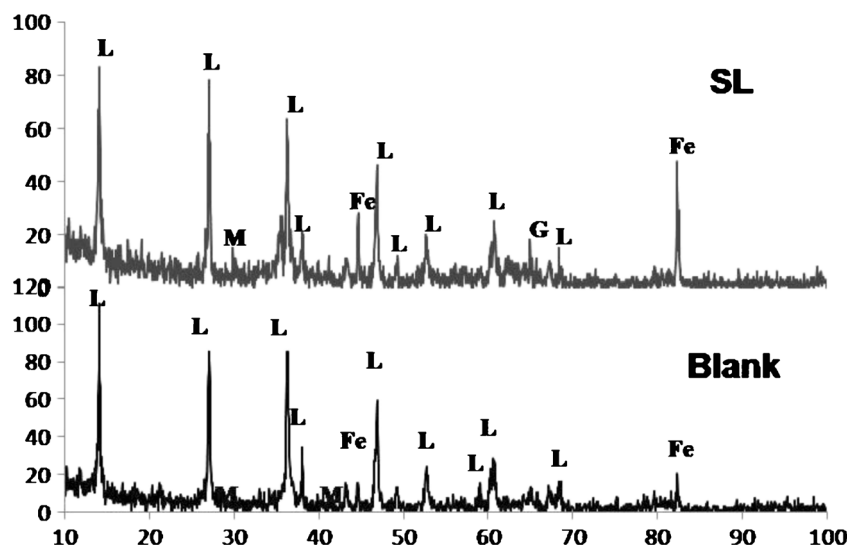
polydispersity (Pouteau et al. 2003; Pan et al. 2006). Lignin with high molecular weight, low phenolic –OH content, and polydispersity value tends to experience poor antioxidant activity (El Hage et al. 2012) as observed in KL. Nevertheless, this result is effective only for antioxidant activity of lignin in butanol, and since alkaline lignins (KL and SL) do not completely dissolve in butanol, the results sometimes could vary.

A positive correlation between the antioxidant and anticorrosion properties has been obtained in this study. In the EIS study, the R_{ct} represents the charge transfer resistance whose value is a measure of electron transfer across the surface and is inversely proportional to corrosion rate (Abdel-Gaber et al. 2006). The constant phase element (CPE) is introduced in the circuit instead of a pure double-layer capacitor to give a more accurate fit (Hussin and Kassim 2011). The diameter of Nyquist plots increased on addition of lignins which suggested that inhibitive film was formed that increased the resistivity of the mild steel surface. The high frequency (HF) loops have depressed semicircular appearance, $0.5 \leq n \leq 1$, which is often referred to as frequency dispersion as a result of the inhomogeneity (Boomersbach et al. 2005) or the roughness (Benedeti et al. 1995) of the solid surface.

Meanwhile, polarization measurements have shown that the decrease of current density values was due to the adsorption of the inhibitor on mild steel/acid solution interface (Ahamad et al. 2010). Here, the decrease of current density of lignins in comparison with 0.5 M HCl (blank) for both anodic and cathodic sites may suggest the mixed type of corrosion inhibition behavior. A study of corrosion prevention and protection has supported that mixed type of inhibitors is generally represented by organic compounds with donor atoms Se, S, N, or O instead of having reactive functional groups which latch on to the metal (Sastri et al. 2007; Hussin and Kassim 2011). Thus, the presence of S and O heteroatoms in KL, SL, and EOL lignin structure may have an important role on the corrosion inhibition of mild steel. Both EIS and polarization studies have revealed that the highest corrosion inhibition was obtained with SL, and this is in a good agreement with the antioxidant studies where SL gave the highest OUI value compared to KL and EOL.

Both EIS and polarization measurements have revealed that SL gave the highest percentage of IE% than to KL and EOL. Hence, this clearly shows that SL will give better antioxidant and corrosion inhibition properties than KL and EOL lignin. It was believed that during soda pulping,

Fig. 6 X-Ray diffraction (XRD) patterns of pre-rusted samples (*blank*) and those treated with soda lignin (*SL*)



extensive depolymerization of lignin has occurred through the scission of β -O-4 bonds leading to the production of phenolic -OH groups. Meanwhile, higher phenolic -OH content and low molecular weight of SL show better antioxidant activity and anticorrosion properties than KL and EOL. It is suggested that the corrosion inhibition of mild steel in the presence of lignin extract occurs through the interaction between the electron-donating atoms of oxygen and sulfur with the metal ion surface. On top of that, the phase transformation of corrosion products upon the immersion in the SL solutions has reduced several lepidocrocite peaks. Perhaps, the formation ferric-lignates will slow down further oxidation process of iron metal into other corrosion products. Better corrosion inhibition properties exhibited by the lignin extracts give new alternative way for the sustainability of green material applications.

5 Conclusion

In this work, the treatment of OPF with alkaline and organic alcohol solution is practically suitable for the isolation of lignins. The differences in the spectral characteristics and analytical results among the lignin samples are related to the delignification process. ^{31}P NMR spectra of the three lignin samples have classified them as *p*-hydroxyphenyl/guaiacyl/syringyl (HGS) lignins since KL and SL lignin samples comprised mainly of phenolic -OH, while EOL comprised mainly of aliphatic -OH functional groups. High molecular weight of KL (as compared to SL and EOL) was influenced by the repolymerization reaction during the alkaline pulping process. The corrosion inhibition studies have revealed that the highest IE% was obtained with SL, and this is in a good agreement with the antioxidant studies where SL also gave the highest OUI value compared to KL and EOL.

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