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Research article

Catalytic degradation of kraft lignin to determine its antioxidant potential for industrial purposes

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ABSTRACT

The lignin fraction of the lignocellulosic biomass corresponds to 15–30 % wt. This is largely obtained as a by-product of wood pulping to produce cellulose and paper, with the kraft process being the most used by industry. The chemical composition of lignin makes an excellent raw material for obtaining various chemical compounds with industrial applications, such as phenolic resins, biofuels and fine chemical products. Furthermore, lignin has high potential as a raw material for sustainable additives for liquid fuels, due to its aromatic nature, since its alkylphenols can be used as antioxidants. The present work describes a process of catalytic conversion of kraft lignin into phenolic compounds with potential application as industrial antioxidant agents. The hydrogenolysis reactions were performed using methanol, ethanol, isopropanol or isopropanol: formic acid (1: 1 v/v) as organic solvents. For each solvent, four transition metal catalysts were tested ($Pd/CaCO_3$, Pd/C, Ru/C and In). Through analyzing UHPLC-ESI-MS (ultra-high performance liquid chromatography-electrospray ionization-mass spectrometry), 19 substances were identified in the isolated fractions, with a predominantly phenolic composition. Based on the efficiency of phenolic substances as antioxidants, an ability to eliminate the DPPH (2,2-diphenyl-1-picrylhydrazyl) radical was evaluated, verifying that 43.75 % of the inherited ones exhibited a high antioxidant potential, superior to kraft lignin and commercial antioxidant BHT (butylated hydroxytoluene).

1. Introduction

The high heterogeneity and consequent great chemical complexity of plant biomass make it raw material for various final products, such as energy, food, chemical products and materials, of which we can highlight four types of plant biomass of great economic interest: oilseeds, saccharides (or sugary), starchy and lignocellulosic [1].

Lignocellulosic biomass is the most abundant compared to the others, as it is formed by cellulose, hemicellulose and lignin, which are the three components of the cell wall and the morphological structure of plants - cellulose and hemicellulose are polysaccharide polymers and lignin is a phenolic macromolecule [1]. The lignin fraction corresponds to 15–30 % wt [2,3]. This lignin is largely obtained as a by-product of wood pulping to produce cellulose and paper, with the kraft process being the most used by the industry

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[4]. And its main use is in the generation of electrical energy for the production plant [5], followed by the chemical recovery for industrial applications [36].

Lignin is a complex and heterogeneous polymer, with a polyphenolic structure that has potential natural antioxidant properties [6]. The three precursors of the three monomeric units - the monolignols - are *p*-coumaryl, coniferyl and sinapyl alcohols, which give rise to the phenylpropane subunits *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S), interconnected by C-C and C-O [6,7].

The chemical composition of lignin makes it an excellent raw material for obtaining various chemical compounds with industrial application, such as phenolic resins, biofuels and fine chemical products [8–10]. Lignin has high potential as a raw material for sustainable additives for liquid fuels, due to its aromatic nature, since its alkylphenols can be used as antioxidants [3]. A substantial amount of lignin is produced as a byproduct in the ethanol and pulp and paper industries; however, this lignin must undergo conversion processes before transforming into compounds of greater industrial interest and, consequently, greater added value [11].

Several studies were conducted seeking to increase the market value of lignin, and their conversion methodologies involve approaches such as pyrolysis [12,13], hydrodeoxygenation [7,9], oxidation [14,15], and hydrogenolysis [16,17].

The hydrogenolysis reaction has proven to be an effective way to improve the industrial applicability of lignin, which can be achieved using hydrogen donor compounds or hydrogen gas combined with suitable catalysts, such as metal oxides and salts, such as transition metals, which act as heterogeneous catalysts [3,18,19].

Solvolytic depolymerization involves the conversion of lignin by solvolysis and thermal action [10]. Alcohols such as methanol and ethanol are commonly used as solvents for cracking, or disrupting, the lignin structure due to their high solubility in the reaction medium and their ability to donate hydrogen [7,9].

Zakzeski et al. [20] demonstrated that the reduction of lignin solubilized in the ethanol/water mixture, using supported transition metal catalysts such as Ru/C, Pd/C, Pt/Al_2O_3 and Ni/SiO_2, at 225 °C and 30 bar with hydrogen gas, produced up to 6 % wt. of aromatic hydrocarbons using Pt/Al_2O_3. Wu et al. [10] used different binary solutions as solvent, such as water-methanol (WM), water-ethanol (WE), water-dioxane (WD), methanol-dioxane (MD), ethanol-dioxane (ED), ethanol-dioxane- formic acid and observed that the combination of ethanol, dioxane and formic acid (10:10:2, v/v) produced phenolic monomers with yields of up to 22.4 % wt., under temperatures below 300 °C and reaction time of 2 h.

Antioxidants are a strategic class of industrial chemicals to converse several products and to maintain their properties. For instance, food antioxidants are one of the most important conservation technologies; and although different, all groups of food antioxidants have a same common objective, to conserve food for the longest possible time without altering it, conferring taste or color [21]. In terms of radical sequestration, antioxidants mainly act on $\cdot OH$ and $O_2^- \cdot$. They either give an electron or a hydrogen atom from their hydroxyl group, thus stabilizing the radical. Some compounds with this ability are ascorbic acid, tocopherols and polyphenols [21]. The major phenolic antioxidants used to increase the stability of biodiesel are butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), tertiary-butylhydroquinone (TBHQ), propyl gallate (PG), octyl gallate (OG), dodecyl gallate (DG), pyrogallol (PY) and ethoxyquin (EQ) [22].

The search of natural antioxidants – as an alternative to petrochemicals ones -, as polyphenols, is a great opportunity to apply products derived from residual lignin. This use can meet the circular economy model [23], allied to green chemistry principle 7 for renewable feedstock [24] and to United Nations sustainable development goals, especially the goal 12 for responsible consumption and production [38].

Therefore, the present work evaluated the use of lignin as a renewable raw material, through the conversion of kraft lignin into phenolic chemicals through catalytic processes. Through lignin hydrogenolysis, the influence of the main reaction parameters - type of catalyst and type of solvent - were investigated in order to obtain phenolic compounds with potential antioxidant activity capable of capturing free radicals, which can be used for industrial purposes, such as in biodiesel and food stabilization and conservation, respectively.

2. Experimental

2.1. Materials

The kraft lignin used as raw material in this work was obtained from hybrids of the species *Eucalyptus grandis* x *Eucalyptus urophylla*, provided by the Paper and Cellulose Laboratory at the Federal University of Viçosa (Brazil). The commercial catalysts 10 % Pd/$CaCO_3$, 10 % Pd/C, 5 % Ru/C and In (99.9 %) were obtained from Sigma-Aldrich. Methanol, ethanol and isopropanol were supplied by Vetec (Brazil). Formic acid, sulfuric paranisaldehyde, acetonitrile, *n*-hexane, ethyl acetate, potassium bromide, 2,2-diphenyl-1-picrylhydrazyl, and chloroform were also supplied by Sigma-Aldrich. Sulfuric paranisaldehyde from Merck. All reagents in this study were of analytical grade and were used without prior purification. Acetonitrile, formic acid and methanol used for chromatographic analyzes were of LC-MS (liquid chromatography-mass spectrometry) grade and were supplied by Merck. HPLC (high-performance liquid chromatography) grade water (18MΩ.cm) was obtained using a Milli-Q Purification System (Millipore Co., Bedford, MA, USA).

2.2. Methods

2.2.1. Processing

The hydrogenolysis reactions were carried out in a 5000 multi-reactor (Parr), under constant stirring at 1200 rpm, using a cooling bath (model RE620S, Lauda) and organic solvents with different hydrogen donation capacities (methanol, ethanol, isopropanol or isopropanol: formic acid, 1:1). In each experiment, 3 g of lignin (10 % wt.) and 0.21 g of catalyst (7 % wt.) were added to 30 mL of the solvent - this mass ratio was determined in previous experiments by our research group. The reactor was purged with hydrogen ((high-purity (5.0, 99.999 %), White Martins)) and pressurized to 15 bar at room temperature. The reactor was then heated to 175 °C. The experiments were carried out with lignin as a catalytic substrate. In these tests, the lignin sample reacted alone (blank) and with the addition of catalyst for a reaction time of 6 h. For each solvent, four catalysts were tested ($Pd/CaCO_3$, Pd/C, Ru/C and In), according to Table 1. The reactions were also tested under the same conditions, without the addition of catalyst, for methanol, ethanol, isopropanol and isopropanol: formic acid as solvents.

After the reaction, the reactor vessel was cooled to room temperature with ice in water. Subsequently, the mixture was extracted and dried in a vacuum concentrator (CentriVap®, Labconco) at 1725 rpm, 60 °C and 120 min to remove the extract.

2.2.2. *Analytics*

The kraft lignin, after cracking, was analyzed by Fourier transform infrared absorption spectroscopy (FTIR), using an Affinity-1 spectrometer (Shimadzu), in the range of 400–4000 cm^{-1}, with a resolution of 4 cm^{-1}, at 64 scans, using KBr pellets (Vetec) containing 1 % wt. of the finely ground sample.

The detailed composition of the products was determined using ultra-high-performance liquid chromatography – UHPLC equipment (Shimadzu) – coupled to a Q-TOF mass spectrometer model maXis 4G (Bruker Daltonics), with an electrospray ionization source – ESI; Shim Pack VP-ODS C18 column (5 μm particle size x 200 nm pore size x, Shimadzu). The samples were dissolved and diluted, with a concentration of 2 mg mL^{-1}; injection volume: 0.3 μL; mobile phase flow 0.4 mL min^{-1}. The mobile phase gradient curve was conducted with deionized water and 0.05 % formic acid (phase A) and 75 % acetonitrile, 25 % methanol and 0.1 % formic acid (phase B). The established program was: 0 min: 25 % phase B; 10 min: 50 % phase B; 25 min: 60 % phase B; 27 min: 100 % phase B; 30 min: 100 % phase B; 32 min: 55 % phase B; 36 min: 25 % phase B.

In the mass spectrometer, positive (ESI(+)-MS) and negative (ESI(−)-MS) ionization modes were applied using sodium formate at 1 mmol L^{-1} for calibration. The data obtained were processed using Data Analysis 4.2 software (Bruker Daltonics). The molecular formulas of the compounds with mass/charge (m/z) of interest were obtained using the SmartFormula software and the identification of the ions was carried out with the aid of the KEGG and CheBI databases.

Free radical scavenging activity was conducted using the method described by Brand-Williams et al. [25], using the radical 2, 2-diphenyl-1-picrylhydrazyl (DPPH) with modifications. Methanolic solutions of all samples were prepared at a concentration of 1 mg mL^{-1} for subsequent dilutions. Each aliquot of the methanolic solutions of the samples or standards (0.1 mL) was added to a methanolic solution of DPPH (3.9 mL). The control solution consisted of methanol (0.1 mL) added to the DPPH solution (3.9 mL). Samples were shaken and incubated in the dark for 30 min at room temperature, and then absorbance was measured at 517 nm on a Lambda 35 spectrophotometer (PerkinElmer).

DPPH concentration was evaluated by plotting the DPPH calibration curve ($r^2 = 0.995$) varying the concentration from 10 μmol L^{-1} to 50 μmol L^{-1}. Antioxidant activity was expressed as the percentage of radical scavenging activity and was calculated from the following equation:

$$AA\% = [(Abs_0\text{-}Abs_1) / Abs_0] \times 100 \tag{1}$$

where Abs_0 is the absorbance of the blank (control) and Abs_1 is the absorbance of the substance analyzed.

3. Results and discussion

To investigate the structure of lignin fractions, FTIR spectra were recorded. Representatively, we only present the samples in methanol (Fig. 1). FTIR spectra of the obtained extracts showed the lignin fingerprint bands, with typical absorptions. The variations found correspond to the functional groups that make up the samples with different catalysts. The results showed distinction in the intensities of the bands of different lignin byproducts. This suggests that some of the functional groups were affected by the type of catalyst used, which had already been previously observed by Aadil et al. [26].

For all samples, the bands at 2945 cm^{-1} and 2851 cm^{-1} were attributed to CH stretching in the $–CH_3$ and $–CH_2$ groups [6,27]. The characteristic stretching vibration of the carbonyl was observed at 1702 cm^{-1}, which is more pronounced for by-products of reactions with the In catalyst in isopropanol.

Bands corresponding to vibrations of the aromatic ring of the phenyl-propane skeleton appeared at 1605 cm^{-1}, 1509 cm^{-1} and 1425 cm^{-1} as observed in literature [27–29]. These bands, combined with the aromatic ring vibration at 1460 cm^{-1}, were attributed to the C–H deformation vibration of $–CH_3$, $–CH_2$ groups in the aromatic ring and were observed in all spectra, although the intensity of the

Table 1
Experimental design of catalytic cracking with heterogeneous catalysts for each of the 16 experiments, at 175 °C, 15 bar, 6 h.

Catalyst	Solvent			
	Methanol	Ethanol	Isopropanol	Isopropanol: formic acid (1:1)
$Pd/CaCO_3$	Exp. 1	Exp. 5	Exp. 9	Exp. 13
Pd/C	Exp. 2	Exp. 6	Exp. 10	Exp. 14
Ru/C	Exp. 3	Exp. 7	Exp. 11	Exp. 15
In	Exp. 4	Exp. 8	Exp. 12	Exp. 16

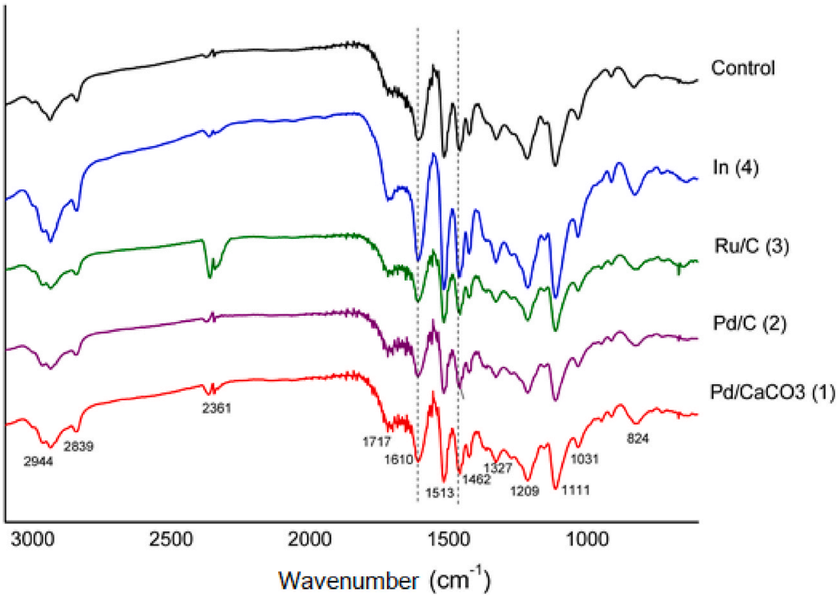

Fig. 1. FTIR spectra of uncracked lignin (control) and sample extracts from Experiments 1, 2, 3 and 4 obtained from lignin cracked with different catalysts.

bands was different. Sample originated from the Experiment 4 presents these more intense bands, suggesting a greater degree of substitution in the aromatic rings, while it is possible to observe a reduction in the intensities of the aromatic bands for the reactions with the Ru/C (Experiment 3) and In (Experiment 4) catalysts in ethanol, according to previous observations in the scientific literature

Table 2
Compounds identified by UHPLC-ESI(+)-MS in the cracked fractions.

Real mass	Theorical mass	Formula	Retention time (min)	M_{δ}	Score	Sample	Probable structure
181.0873	181.0859	$C_{10}H_{13}O_3$	5.823	3.4	40.84	4, 7, 14	coniferyl alcohol; 3,4 hydroxyphenyl lactate; 3,4 dihydroxyphenyl propanoate
197.0810	197.0822	$C_{10}H_{13}O_4$	3.081	20.7	100	1, 18	2,3-dihydroxy-p-cumaric acid; 5-hydroxy coniferyl alcohol
211.0968	211.0965	$C_{11}H_{15}O_4$	2.910	10.3	100	14, 15	synaphyl alcohol, 3,4 dimethoxyphenyl-propanoic acid; 3,4,5 trimethoxyacetophenone
231.1010	231.1016	$C_{14}H_{15}O_3$	6.838	12.7	100	14, 15	2,6-dimethoxy-4-phenylphenol
237.1118	237.1121	$C_{13}H_{17}O_4$	3.858	10.4	100	11, 14	3 -dimetilallyl-4-hidroxymandelic acid
271.0961	271.0965	$C_{16}H_{15}O_4$	5.767	52.71	100	11	4-[(3-methylbut-2-en-1-yl)oxy]-7H-furo[3,2-g]chromen-7-one
281.0842	281.0808	$C_{17}H_{13}O_4$	3.708	86.7	100	5, 11	1-acetoxieugenol acetate; 3-methylflavone-8-carboxylic acid
299.0940	299.0914	$C_{17}H_{14}O_5$	3.587	12.9	100	11	3-[1-(furan-2-yl)-3-oxobutyl]-4-hydroxychromen-2-one
301.1080	301.1071	$C_{17}H_{17}O_5$	5.667	360.2	0	2, 3	(2S, 3S) −3,5,7-trihydroxy-6,8-dimethylflavanone
331.1195	331.1176	$C_{18}H_{19}O_6$	5.595	577.1	100	1, 2, 3, 4	methyl 2,5-dihydroxy-4 - [(1S) -1- (3-hydroxy-4-methoxiphenyl) prop-2-en-1-yl] benzoate
357.1313	357.1313 (356.126)	$C_{20}H_{21}O_6$	5.328	6	100	4	3-(4-Hydroxy-3-methoxyphenyl)allyl 3-(4-hydroxy-3-methoxyphenyl)acrylate
359.1452	359.1489	$C_{20}H_{22}O_6$	3.858	69.1	100	11	(10S)-1-hydroxy-3-(hydroxymethyl)-10-[(2S,3R,4S,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)oxan-2-yl]-8-[(2S,3R,4S,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)oxan-2-yl]oxy-10H-anthracen-9-one
361.1652	361.1646	$C_{20}H_{25}O_6$	5.52	19	100	12	3-Benzofuranmethanol, 2,3-dihydro-2-(4-hydroxy-3-methoxy-phenyl)-5-(3-hydroxy-1-propenyl)-7-methoxy-dehydrodiconiferol
373.1296	373.1293	$C_{20}H_{21}O_7$	4.371	18	100	10	2-[2-[2-(3,4-dimethoxyphenyl)acetyl]-4,5-dimethoxyphenyl] acetate
384.1453	384.1442	$C_{21}H_{22}NO_6$	3.165	7	78.75	11	1-[2-[(6-oxo-7,8,9,10-tetrahydrobenzo[c]chromen-3-yl)oxy] acetyl]piperidine-4-carboxylate
401.1608	401.1595	$C_{22}H_{25}O_7$	4.163	6.9	100	1, 2, 3, 4	2-[[3-(2,3-dihydro-1,4-benzodioxin-6-yl)-4-oxo-6-propan-2-yl-4a,5,6,7,8,8a-hexahydrochromen-7-yl]oxy]acetate
405.1521	405.1544	$C_{21}H_{25}O_8$	4.869	6.7	45.59	9	Mallatophenone
419.1707	419.1700	$C_{22}H_{27}O_8$	4.163	9.4	100	1, 3	4-[6-(4-hydroxy-3,5-dimethoxyphenyl)-1,3,3a,4,6,6a-hexahydrofuro[3,4-c]furan-3-yl]-2,6-dimethoxyphenol
271.0961	271.0965	$C_{16}H_{15}O_4$	5.767	52.71	100	11	4-[(3-methylbut-2-en-1-yl)oxy]-7H-furo[3,2-g]chromen-7-one

[6,27,30].

At 1330 cm^{-1}, the bands represented the C-O stretching of the syringyl structure [27]. Bands for C-O-C segments appeared at 1215 cm^{-1}. The C-H stretching of the deformation of the phenylpropane unit is observed at 1115 cm^{-1}. A system of small bands presents a maximum between 1127 cm^{-1} and 1125 cm^{-1}, characteristic of G and S lignin unities [30]. There are small peaks at 908 cm^{-1} and 823 cm^{-1} that represent out-of-plane C-H for the G unit and at position 2 and 6 of the S unit, respectively [27,28].

Samples separated by chromatography were subjected to mass spectrometry analysis in positive and negative mode. However, the results indicated that the analysis using the ESI(+)-MS mode had greater intensity and capacity for detecting phenolic compounds, so this was the method chosen in the present work. The molecular formula of the compounds was determined, and the probable structures were identified with the help of the KEGG and CheBI databases, some containing more than one structural possibility, based on the data obtained for the *m/z* ratio, correlation between theoretical mass and experimental mass (error of measured masses, ppm) and mSigma (related to the isotopic profile), presented in Table 2.

From the material obtained in the hydrogenolysis reactions, 19 compounds from the isolated fractions were identified using the UHPLC-ESI(+)-MS method, demonstrating that the method used was efficient to separate and detect typically hydrophilic compounds.

Table 2 reveals the molecular formulas of the most characteristic compounds, isolated from the specific ions obtained. The ions correspond to a series of phenolic derivatives and oligomers related to the hydroxyphenyl (H), guaiacyl (G) and syringyl (S) subunits, obtained from the cracking of lignin, as stated in the literature [31,32].

The result of superimposing the chromatograms demonstrated appreciable differences between the 20 samples obtained, including the blanks. For reactions in which no catalyst was used, only the compound $C_{14}H_{17}O_5$ was identified, whose structural possibilities are *trans*-coniferyl alcohol diacetate or 1-acetoxyeugenol acetate. The products are more widely distributed in reactions in methanol and in the presence of Ru/C catalyst. This result is consistent with previous studies, which reported that reactions in isopropanol and ethanol are less effective than in methanol [33].

The type of solvent used was the effect that seemed to exert the greatest influence on the composition of the products formed. Phenolic derivatives with lower molar mass were obtained mainly for isopropanol: formic acid reactions. Formic acid acts as a hydrogen donor, as it can completely decompose into hydrogen and carbon dioxide upon heating, providing reactive hydrogens, which favor hydrogenolysis reactions [3].

It is known that the efficiency of phenolic substances as antioxidants depends largely on their chemical structure, reactive orientation and the number of hydroxyl groups linked to the aromatic ring [37]. The DPPH scavenging activity of lignin hydrogenolysis products is shown in Fig. 2.

Based on the results obtained, we can say that, as a general rule, samples 16 (In in isopropanol-formic acid; 78.88 %), 13 (Pd/$CaCO_3$ in isopropanol-formic acid; 78.20 %), 14 (Pd/C in isopropanol-formic acid; 65.17 %), 6 (Pd/C in ethanol; 61.12 %) and 15 (Ru/C in isopropanol-formic acid; 53.03 %) were the most effective in reduction of DPPH. Samples 13 to 16 were obtained from reactions using isopropanol: formic acid, which reveals that lignin hydrogenolysis reactions in this solvent favor the production of compounds that can act as antioxidants. These data are corroborated by UHPLC-ESI(+)-MS analyses, which demonstrated that phenolic species with lower molar mass were obtained in this solvent.

It was observed that the DPPH elimination capacity of the samples presented a high potential for antioxidant activity. More importantly, the antioxidant activity of samples from the Experiments 5, 6, 9, 13, 14, 15 and 16 were higher than that of the commercial antioxidant BHT – commonly used for industrial purposes -, whose percentage of DPPH reduction was presented by Magalhães et al. [34] as 40.15 % at a concentration of 100 mg L^{-1}, following a similar methodology. It was reported that the DPPH scavenging

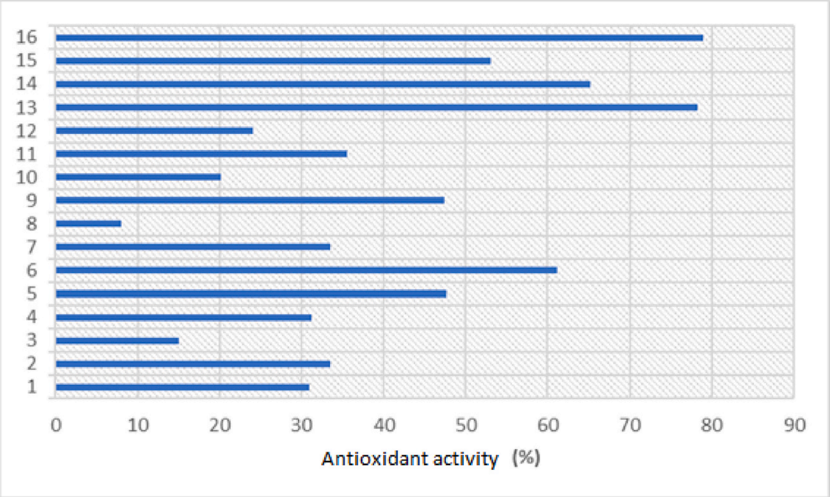

Fig. 2. Percentage of DPPH reduction of the 16 samples presented in Table 1 for each sample, expressed in antioxidant activity (% AA) for the concentration of 100 mg L^{-1}.

capacity of lignin and phenolic hydroxyl groups has a positive correlation [35], which may justify the high antioxidant activity of the lignin products found in the present work.

4. Conclusions

Kraft lignin was degraded via hydrogenolysis routes using noble metal catalysts. After catalysis, new phenolic compounds were produced. UHPLC-ESI-MS analysis revealed that the products have a phenolic nature. The samples obtained in isopropanol: formic acid were more active against the DPPH radical, and superior to kraft lignin and the commercial antioxidant BHT. The best result was obtained using the In catalyst in isopropanol: formic acid (1:1 v/v).

Thus, the scale-up of the lignin extracts obtained from this prospective study – considering their processes and their applications - should lead to the development of one or more antioxidant formulations for industrial uses. Furthermore, the results obtained from this study will be useful to develop effective sustainable strategies for lignin valorization.

CRediT authorship contribution statement

Silvio Vaz: Writing – original draft, Supervision, Project administration, Funding acquisition, Conceptualization. **Ana Elisa Barreto:** Validation, Methodology, Investigation, Formal analysis. **Bruno Leite Sampaio:** Methodology, Investigation.

Consent to participate

All authors consent to participate in the manuscript writing and publication.

Consent for publication

All authors consent to publish this manuscript.

Ethical approval

Not applicable.

Data availability

Datasets can be made available by means request to the corresponding author.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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