

Lignin conversion into C₄ dicarboxylic acids by catalytic wet peroxide oxidation using titanium silicalite-1

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ARTICLE INFO

Keywords:

Lignin
Depolymerisation
Succinic acid
Biorefinery
Hydrogen peroxide
Titanium silicalite-1

ABSTRACT

Lignin valorisation towards added-value products has become a relevant topic to consolidate a future circular bioeconomy. In this context lignin oxidation to C₄ dicarboxylic acids (C₄-DCA) by catalytic wet peroxide oxidation is emerging as a value-added strategy, supported by the extensive use of these building blocks in several industrial fields. In this work, lignins from different sources and processes (Indulin AT, Lignol, alkali and *E. globulus* kraft lignins) were oxidised using H₂O₂ and titanium silicalite-1 catalyst (TS-1) under different operating conditions (temperature, pH, time, H₂O₂, and TS-1 load). Indulin AT was the lignin leading to the highest succinic acid yield (11.3 wt%), and TS-1 catalyst enhanced its production four times over the non-catalysed reaction. Malic acid was also produced at high yields, especially for Lignol lignin. The other lignins (*E. globulus* kraft, and alkali lignins) also produced these C₄ acids but at lower yields. The catalyst remained stable at the used experimental conditions, and showed potential to be reused for several cycles without being deactivated. Overall, the catalytic conversion of lignin to C₄-DCA can help to guide the pathway to renewable chemicals production.

1. Introduction

Lignin is obtained as a by-product in pulp mills, where it is burned in the recovery boiler to produce energy and heat. However, this step is usually considered a bottleneck in pulp production (Ahmad et al., 2020; Mathias, 1993). Consequently, using part of this residual lignin as a raw material for conversion to added-value products would improve the sustainability of the pulping industry without affecting pulp production and the energy balance of the mill (Junghans et al., 2020; Rodrigues et al., 2018; Silva et al., 2009).

The physical and chemical properties of technical lignins change depending on the feedstock source, the pulping process, and the isolation method (Kienberger et al., 2021). Lignin structure is based on three monomers: *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S), which are present in different ratios and linked differently depending on the biomass origin (Kamm et al., 2008; Upton and Kasko, 2016). Softwood lignin usually has a high G:H ratio and no S units. Units are linked by

β -O-4 (43–50 %), 5–5' (10–25 %), β -5 + α -O-4 (9–12 %) linkages, among others. Hardwood is an S:G:H lignin with a higher S content. Units are linked by β -O-4 (50–65 %), 5–5' (4–10 %), α -O-5 (4–8 %), and α -O-5' (6–8 %) linkages, among others (Rodrigues Pinto et al., 2011). These structural differences introduce challenges for the depolymerisation and upgrading of the recalcitrant lignin matrix. Cooking methods focused on high-quality cellulose, such as kraft, sulfite, and alkaline processes, use harsh conditions to achieve their objective, causing strong modifications in the lignin structure (Sun et al., 2018). The alkali process cleaves many of the ester and ether bonds between lignin and carbohydrates, and also some of the lignin C-C bonds (Kim et al., 2016). Kraft process produces a highly modified and partially fragmented lignin, with α -aryl ether and β -aryl ether linkages cleavage, recondensation reactions, and sulphur incorporation (Li et al., 2015; Sun et al., 2018). Other milder extraction processes, such as ionic liquid extraction, organosolv, and milled-wood lignin, cause fewer modifications to the lignin structure. Organosolv uses organic solvents, such as primary

Abbreviations: ALK, alkali lignin; ATR-FTIR, Attenuated total reflectance- Fourier transform infrared spectroscopy; CA, carboxylic acids; DCA, dicarboxylic acids; EDS, Energy-dispersive X-ray spectroscopy; EKL, *E. globulus* kraft lignin; EOL, Lignol organosolv lignin; GPC, Gel permeation chromatography; IAT, Indulin AT lignin; HPLC, high-performance liquid chromatography; MCA, monocarboxylic acids; SEM, Scanning electron microscopy.

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<https://doi.org/10.1016/j.indcrop.2021.114155>

Received 15 June 2021; Received in revised form 4 October 2021; Accepted 7 October 2021

Available online 13 October 2021

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alcohols, alone or mixed with water at high temperatures and pressures, and produces lignins with structures closer to the native one, with slight modifications like cleavage of β -O-4 linkages, repolymerizations, and formation of new C-C bonds (Sun et al., 2018).

Depolymerisation is an important route to achieve new products from the lignin. Oxidative lignin depolymerisation has several advantages, leading to the incorporation of new functional groups (e.g., alcohol, aldehydes, and carboxylic groups) and production of low-molecular-weight fractions, giving rise to added-value products such as phenolics, dicarboxylic acids, and others. However, it remains challenging to overcome the low selectivity towards target products and circumvent the over-oxidation to gaseous compounds (Ahmad et al., 2020; Liu et al., 2019). C₄ dicarboxylic acids, currently derived from petrochemical sources and carbohydrates fermentation routes, are used in several fields as final products (e.g. food additives) and as raw materials for pharmaceuticals and polymer industries (Zhang et al., 2020). They are also pointed out as the biomass-derived building blocks for the future development of a greener chemistry (Jong et al., 2011; Werpy and Petersen, 2004). Therefore, achieving C₄ dicarboxylic acids from lignin would allow the attainment of added-value products without competing with food and fossil resources.

Non-catalytic lignin oxidative depolymerisation has been previously reported with succinic and maleic acids yields lower than 3% (Abdelaziz et al., 2019; Demesa et al., 2015; Figueirêdo et al., 2019; Hasegawa et al., 2011; Vega-Aguilar et al., 2021). Better results were obtained with catalytic oxidation, especially in the presence of heterogeneous catalysts, such as perovskite-type oxides, chalcopyrite, and heteropoly acids (i.e., phosphotungstic and phosphomolybdic acids) (Ansaloni et al., 2017; Bi et al., 2018; Cronin et al., 2017; Demesa et al., 2017; Ma et al., 2014). The use of Fenton reagent (Fe²⁺/H₂O₂) gave rise up to 8% maleic acid with phenol (Faisal, 2009), although with other lignin model compounds, the yield was lower than 2% (Kang et al., 2019). When lignin was used, no C₄-DCA were obtained (Zeng et al., 2015), suggesting that this oxidation methodology is not an efficient strategy for lignin depolymerisation towards C₄-DCA. Perovskite-type oxides have also been tested due to their oxidative activity and the presence in their structure of transition metals with two different oxidation states. However, catalysts like LaFeO₃, LaMnO₃, and CeFeO₃ showed no improvement for C₄-DCA production comparatively with non-catalysed experiments (Ansaloni et al., 2017). Chalcopyrite (CuFeS₂) has been used with lignin and lignin model compounds with good results. Namely, catechol oxidation yielded 6% malic acid and 8% succinic acid, and diluted-acid corn stove lignin oxidation yielded 7% succinic acid and 1% malic acid (Ma et al., 2014). Chalcopyrite nanoparticles in acidic pH enhanced succinic acid yield up to 12 % when an industrial lignin was oxidised, accompanied by low fumaric and maleic acids yields (Bi et al., 2018), confirming that acid yields are dependent on the used oxidation reaction conditions. Heteropoly acids (i.e., phosphotungstic acid (H₃PW₁₂O₄₀) and phosphomolybdic acid (H₃PMo₁₂O₄₀)) showed low improvement for succinic acid yield, with disadvantages such as higher costs and recovering difficulties (Demesa et al., 2017). Other catalysts based on V and Mo oxides or pyrophosphates (deposited in materials like Al₂O₃, TiO₂, and HZSM-5), used in lignin gas-phase oxidation gave rise to no more than 2% of succinic acid (Lotfi et al., 2016, 2015). In most of these studies, significant amounts of oxalic, formic, and acetic acids were obtained (as degradation products of lignin over-oxidation). Still, the final yield and C₄-DCA type varied according to the used catalyst and applied reaction conditions. In most of these works, succinic acid yield varied between trace levels up to 2–3 wt% (lignin-basis), while maleic and fumaric acids were reported to be obtained at contents less than 1%.

Different oxidants, such as O₂, H₂O₂, O₃, and peroxy acids, have enough oxidative power to break down most ether linkages and some C-C linkages (Ma et al., 2018a). However, a strong oxidant is needed to cause ring-opening reactions to achieve dicarboxylic acids (Sun and Argyropoulos, 1996). Molecular oxygen oxidation occurs only in

alkaline conditions and is usually intended for mild oxidation to achieve aldehydes. Its oxidative power is relatively low to origin ring-opening reactions at high yields (Cabral Almada et al., 2020; Li et al., 2015). Peroxide oxidation is more active than O₂ oxidation by eliminating liquid/gas mass transfer barriers and releasing free radicals, allowing faster oxidations in milder and cleaner conditions (Bhargava et al., 2006; Cheng et al., 2017). Hydrogen peroxide oxidation causes the cleavage of β -O-4 linkages, forming non-condensed structures, especially in softwood lignins, demethoxylation of S units to G units happens, which could be repolymerised, increasing the condensed OH structures (Ahmad et al., 2020). These small fragments can further have the aromatic ring cleaved to dicarboxylic acids. Ozone can also be used for lignin oxidation, leading to ring-opening reactions and generating C₄-DCA (Figueirêdo et al., 2019). However, O₃ handling can be complex since it has to be generated *in situ* (Ahmad et al., 2020). Recently, electrochemical depolymerisation was used for lignin oxidation, releasing O₂ and H₂O₂ *in situ*; however, this technique leads to small amounts of C₄-DCA (Di Marino et al., 2019).

Among the catalysts enhancing H₂O₂ oxidative power, titanium silicalite-1 catalyst (TS-1) has been used for lignin model compounds peroxide oxidation to C₄-DCA with good results. Namely, it was reported that guaiacol is oxidised mainly to maleic acid, while vanillic acid is primarily converted to succinic acid, an important feedstock for renewable polymer production (Su et al., 2014; Vega-Aguilar et al., 2020). This catalyst has an MFI zeolite structure, with less than 3% TiO₂ and hydrophobic properties, allowing the oxidation of non-polar compounds in aqueous medium, such as phenolic compounds (Clerici, 2015; Gamba et al., 2009). The active species in the TS-1 catalysed peroxide oxidation is the Ti-OOH group, which shows better reactivity than H₂O₂ (Clerici, 2015).

Under the current state of the art, the catalytic peroxide oxidation of lignin to C₄-DCA using TS-1 catalyst is still lacking. Given the reported advantages of this catalyst towards the production of C₄-DCA, namely the previous studies conducted with model compounds, its use to improve the production yield of target acids (e.g., succinic acid) from lignin is a promising strategy towards a circular economy. Therefore, in this work, lignins from different origins (Indulin AT, Lignol, alkali, and *E. globulus* kraft lignins) were oxidised using H₂O₂ and TS-1 catalyst focusing C₄-DCA production, especially succinic acid. Moreover, the stability of the TS-1 catalyst to the applied reaction conditions, taking as reference five consecutive utilizations, was also be studied.

2. Methodology

2.1. Materials

All chemical reagents were purchased from commercial sources and used without further purification: formic acid (Chem-labs, >99 %), sulfuric acid (Chem-labs, 95–97 % p.a.), sodium hydroxide (Merck, p. a.), hydrogen peroxide solution (Fluka, >30 % p.a.), *N,N*-dimethylformamide (VWR, ≥99.9 %) and lithium chloride (VWR, AnalaR NORMAPUR). Catalyst TS-1 (ref. #: MST1001, lot number: 130,117; H⁺ cation) was acquired from ACS Materials, LLC.

Four different lignins were studied: alkali lignin (ALK), commercialised by Aldrich (product number 471003, batch #09724CE); Indulin AT (IAT), commercialised by MeadWestvaco Corporation, USA; a lignin isolated from an industrial black liquor obtained from a Portuguese *Eucalyptus globulus* kraft pulping mill (The Navigator Company, Portugal) (EKL); and a lignin produced by an ethanol organosolv process from *Eucalyptus globulus* (EOL), supplied by Lignol Innovations, Canada.

2.2. Oxidation procedure

Lignins were oxidised in closed steel reactors (20 mL), described elsewhere (Vega-Aguilar et al., 2020), using 5.00 mL of a 10.0 g/L lignin solution (dissolved in ultra-pure water), 0.500 mL of a 30 wt% H₂O₂

solution, and 5.0 mg of TS-1 catalyst (10 wt%, lignin-basis). The effect of pH (4.0–10.0), temperature (100–160 °C), reaction time (0–8 h), catalyst amount (0–15 wt%), and H₂O₂ volume (0.25–0.75 mL) on the selected DCA (succinic, fumaric, maleic, malic, tartaric, acetic, oxalic, and formic acids) yield was studied. Experiments were done in duplicate. The study of the effect of each parameter was performed under the following specific reaction conditions: pH effect (2 h, 140 °C, 10 % catalyst, 0.50 mL H₂O₂), temperature effect (2 h, pH 7, 10 % catalyst, 0.50 mL H₂O₂), reaction time effect (pH 7, 140 °C, 10 % catalyst, 0.50 mL H₂O₂); catalyst amount effect (2 h, pH 7, 140 °C, 0.50 mL H₂O₂), and H₂O₂ volume effect (2 h, pH 7, 140 °C, 10 % catalyst).

Reutilization of the TS-1 catalyst was done through its use in consecutive experiments. For that, the catalyst was washed with acidified water, centrifuged at 3500 rpm for 30 min, and then transferred, dispersed in 1.0 mL of water, to the reaction flask for the subsequent reaction. After the 5th run, the catalyst was dried at 100 °C overnight and then analysed by SEM.

2.3. Lignin quantification

Oxidized lignin samples were acidified to pH~2, heated at 40 °C to coagulate the acid-insoluble lignin, then centrifuged at 3500 rpm for 30 min. The acidic supernatant was used for carboxylic acid and acid-soluble lignin quantification. The insoluble lignin was resolubilised in an alkaline solution. Acid-soluble and insoluble lignin solutions were analysed by UV spectrophotometry at 240 nm and quantified based on a calibration curve done with the acid-soluble and insoluble lignin obtained from the respective original lignin, respectively. Lignin conversion was calculated as the sum of the acid-insoluble and the acid-soluble lignins. Calibration curves for acid-soluble and insoluble lignins can be found in Fig S1.

2.4. Carboxylic acids quantification

Carboxylic acids were quantified by high-performance liquid chromatography (HPLC) analysis using a Shimadzu UFLC, equipped with a Diode Array Detector (210 nm), a refractive index detector (RI), and a Phenomenex® Rezex™ ROA H⁺ column (300 mm x 7.8 mm) and pre-column (50 mm x 7.8 mm). The analysis was performed at 50 °C using isocratic mode (4 mmol/L H₂SO₄) at a 0.5 mL/min flow rate and an injection volume of 20 µL. Carboxylic acids were identified and quantified using calibration curves prepared from individual standards. Samples were diluted as needed and filtered through a 0.22 µm pore-size filter before injection. Calibration curves can be found in Table S1.

Quantified acids are expressed as C₄-DCA (succinic, malic, maleic, fumaric, and tartaric acids), Total DCA (C₄-DCA + malonic acid + oxalic acid), and MCA (monocarboxylic acids: acetic and formic acid).

2.5. Lignin molecular weight determination

Gel permeation chromatography (GPC) was used to evaluate lignin molecular weight and polydispersity index. Calibration was done using polystyrene (PS) standards, in the molecular weight range comprised between 162 and 50 000 g/mol (calibration curve can be seen in Fig S2). A Shimadzu UFLC, equipped with a Diode Array Detector (280 nm) was used with two Agilent columns in series: first an OligoPore column (300 × 7.5 mm, 6 µm nominal particle size) and then a MesoPore column (300 × 7.5 mm, 3 µm nominal particle size). Prior to this arrangement, a OligoPore pre-column (300 × 7.5 mm) was used. Analysis was performed at 70 °C, using dimethylformamide with 0.5 wt% LiCl, at 0.8 mL/min. More details about the applied method can be found elsewhere (Costa et al., 2018).

2.6. ATR-FTIR spectroscopic analysis of lignin

Attenuated total reflectance- Fourier transform Infrared

Spectroscopy (ATR-FTIR) measurements were carried out using a JASCO FT/IR-6800 spectrometer (JASCO Analytical Instruments, USA), equipped with a MIRacle™ Single Reflection (ZnSe crystal plate; PIKE Technologies, USA). The analysis was performed using 256 scans, in the 4000–700 cm⁻¹ region, with a 4 cm⁻¹ resolution.

2.7. Catalyst characterization

Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) were used to analyse the physical structure of the catalyst before and after oxidations, especially when it was reused. The analysis was performed in the Materials Centre of the University of Porto (CEMUP), following the procedure and equipment reported elsewhere (Vega-Aguilar et al., 2020). Briefly, samples were coated with Au/Pd (15 mA, 80 s), then analysed in a Quanta 400 FEG ESEM/EDAX Genesis X4M equipment, using high vacuum, 15 keV, 10 mm working distance and a 50 Lsec collection time.

3. Results and discussion

3.1. Lignin characterisation

The studied lignins correspond to products available from commercial processes. Alkali (ALK), Indulin AT (IAT), and ethanol organosolv lignin (EOL) were received in powder form, and no further purification or treatments were done. Regarding *E. globulus* kraft lignin (EKL), received as black liquor, it was isolated by the acid precipitation method (Costa et al., 2018).

The selected lignins are products of different pulping processes and proceed from distinct biomass feedstocks. Lignins IAT and EKL are softwood and hardwood kraft lignins, respectively. Lignin ALK is an alkali softwood, and EOL is a hardwood organosolv (ethanol) lignin. The different pulping processes and feedstock origin affect lignin's physical and chemical properties, influencing their reactivity towards oxidation and thus the production (type and yield) of C₄-DCA.

The main characteristics of the used lignins are reported in Table 1. Molecular weight (in weight and number; M_w and M_n, respectively) and polydispersity index (M_w/M_n) were obtained in the present work. The other features, namely S:G:H ratio, lignin content, and ash content, are reference values obtained from literature. Concerning molecular weight, all the studied lignins have similar M_w (around 8300–13600 g/mol) but variable M_n and polydispersity index. Lignin EKL has low polydispersity, while EOL was the lignin with the highest value. ALK lignin was the only water-soluble lignin, while IAT, EOL, and EKL needed an alkaline medium to get fully solubilised. Thus, to achieve a stable 10 g/L aqueous solution, lignins were firstly solubilised at pH 11 and then carefully acidified to pH 7. No precipitation of insoluble lignin fractions was noticed for all studied samples.

The ATR-FTIR analysis showed typical bands for softwood and hardwood lignins, as observed in Fig. 1. The bands are described

Table 1
Properties of the studied lignins (ALK, IAT, EOL, and EKL).

| Lignin | M _w (g/mol) | M _n (g/mol) | M _w /M _n | S:G:H ratio | Lignin content (%) | Ash content (%) |
|--------|------------------------|------------------------|--------------------------------|--------------------------|---------------------|---------------------|
| ALK | 9646 | 1807 | 5.34 | 0:98:2 ^(●) | 93.7 ^(●) | 1.30 ^(●) |
| IAT | 11,521 | 3027 | 3.81 | 0:97:3 ^(■) | 92.2 ^(■) | 2.6 ^(■) |
| EOL | 13,678 | 1849 | 7.40 | 70:30:0 ^(*) | 98.5 ^(*) | 0.11 ^(*) |
| EKL | 8354 | 8096 | 1.03 | 65:29:0.6 ^(▲) | 59.0 ^(▲) | 37.5 ^(▲) |

Note: marked data was obtained from: ^(●)Ma et al., 2018b; ^(◆)Sigma-Aldrich, 2006; ^(*)Costa et al., 2014; ^(■)Constant et al., 2016; ^(▲)Costa et al., 2018. Abbreviations: ALK: alkali lignin, IAT: Indulin AT, EOL: Lignol organosolv lignin, EKL: *E. globulus* kraft lignin, S: syringyl group, G: guaiacyl group, H: *p*-hydroxyphenyl group, M_w: weight average molecular weight, M_n: number average molecular weight.

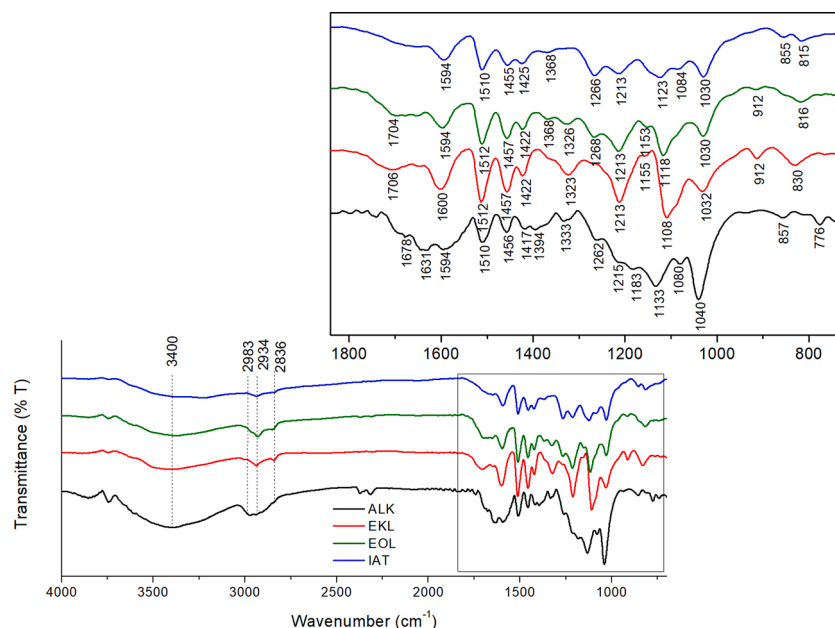


Fig. 1. ATR-FTIR analysis for the studied lignins. Abbreviations: ALK: alkali lignin, IAT: Indulin AT, EOL: Lignol organosolv lignin, EKL: *E. globulus* kraft lignin.

according to Faix (1992) and Cateto et al. (2009). All lignins show a broad band at $\sim 3400\text{ cm}^{-1}$ corresponding to the O–H stretch of O–H groups. Bands at $2983\text{--}2834\text{ cm}^{-1}$ appear for all lignins, related to C–H stretch of $-\text{CH}_3$ and $-\text{CH}_2-$ groups. The band at 1594 cm^{-1} is related to aromatic skeletal vibration plus C=O stretch, higher for hardwood lignins (EOL and EKL). Band at 1510 cm^{-1} correspond to aromatic skeletal vibrations. The band at 1456 cm^{-1} correspond to C–H asymmetric deformations in $-\text{CH}_3$ and $-\text{CH}_2-$ groups. Bands below 1430 cm^{-1} should be interpreted carefully, since there is a contribution of various vibration modes for each band in this region. At 1422 cm^{-1} the aromatic skeletal vibration is combined with C–H in-plane deformation. Band at 1213 cm^{-1} corresponds to C–C, C–O and C=O stretches. Guaiacyl units (G) characteristic vibrations (primarily in softwood ALK and IAT) include 1266 cm^{-1} (G ring and C=O stretch) and 855 cm^{-1} (C–H out-of-plane vibration in G) (Boeriu et al., 2004). Syringic units (S) vibrations (only in hardwood EOL and EKL) include 1323 cm^{-1} (S ring joined to G ring condensed) and 830 cm^{-1} (C–H out-of-plane in S) (Ma et al., 2018b). At $1108\text{--}1133\text{ cm}^{-1}$, aromatic C–H in-plane deformation appears, combined with secondary alcohols and C=O stretch (higher values for G lignins). The 1080 cm^{-1} band is related to C–O deformation in secondary alcohols and aliphatic ethers, particularly in ALK. Band at $1030\text{--}1040\text{ cm}^{-1}$ corresponds to aromatic C–H in-plane deformation with higher prevalence in G lignins, combined with C–O deformation in primary alcohols and C=O stretch (unconjugated).

3.2. TS-1 catalysed lignin oxidation

Hydrogen peroxide oxidation is reported to depend on several factors, such as pH conditions, temperature, reaction time, and H_2O_2 load, directly impacting the conversion rate and the obtained target compounds (type and yield) (Bi et al., 2018; Vega-Aguilar et al., 2020). To evaluate how these factors influenced the catalytic wet peroxide oxidation of the studied lignins, different oxidation tests were conducted by modifying each factor at a time.

3.2.1. Lignin conversion

Lignin has a complex structure that must be depolymerised, i.e., broken into smaller fragments, to be converted into $\text{C}_4\text{-DCA}$ and other compounds. Therefore, it is necessary to evaluate lignin conversion under different parameters, such as temperature, pH, time, and H_2O_2

load. In this study, lignin conversion was determined by quantifying the remaining lignin after oxidation, which can be decomposed after adding diluted acid and centrifuged, remaining in solution the soluble lignin. Insoluble lignin was re-solubilized in an alkaline solution, and both lignins were quantified by UV spectrophotometry. Lignin conversion was calculated against the original lignin placed in the reactor.

It is known that high temperatures affect the oxidative power of H_2O_2 , allowing the release of hydroxyl radicals, which can be decomposed at these high temperatures (Xiang and Lee, 2000). The temperature effect was quite notable on lignin conversion, as can be seen in Fig. 2(a), with conversion increasing with temperature increase for all lignins, up to 140°C where the maximum conversion was achieved (80.3% , 91.9% , 93.6% , and 97.5% , respectively for ALK, EOL, EKL, and IAT). When 160°C was used, no significant differences were noticed. The molecular weight decrease with temperature rise can be observed in Fig. 3, compatible with depolymerisation occurrence (structure reduction to smaller fragments). At higher temperatures, a prevalence of low molecular weight lignin fragments was perceived comparatively with the original lignin, especially for AKL and IAT, pointing out that the molecular weight profile for 140 and 160°C is quite similar, corroborating the maintenance of the lignin conversion after 140°C . Moreover, for the EOL lignin signs of repolymerization at high temperatures are noticed. Data for EKL at 100°C is not shown since the lignin was not well dissolved in the solvent.

Peroxide oxidation also has a high dependence on the pH medium; H_2O_2 is a weak acid, and thus its reactivity changes with pH. It is stable at acidic pH, while it quickly decomposes at alkaline conditions to molecular O_2 and H_2O . It can act as a nucleophile under alkaline conditions and electrophile in acidic medium (Xiang and Lee, 2000; Yin et al., 2015). pH conditions also affect the oxidation pathway of the phenolic structures, namely by the attack to hydroxyl radicals with the formation of an anionic radical (alkaline pH), a cationic radical (acidic pH), or a neutral radical, releasing an OH^- , H^+ or H_2O group, respectively (Gierer et al., 1992).

Alkaline pH gave rise to lower lignin conversions (especially for ALK lignin) (Fig. 2b). The lignin phenolic structures were stable to H_2O_2 oxidation at this pH, inhibiting radicals formation from the H_2O_2 homolytic decomposition, which is responsible for aromatic moieties degradation (Gierer, 1986). Recoupling of aromatic structures was also favoured, generating larger aromatic compounds with high absorptivity

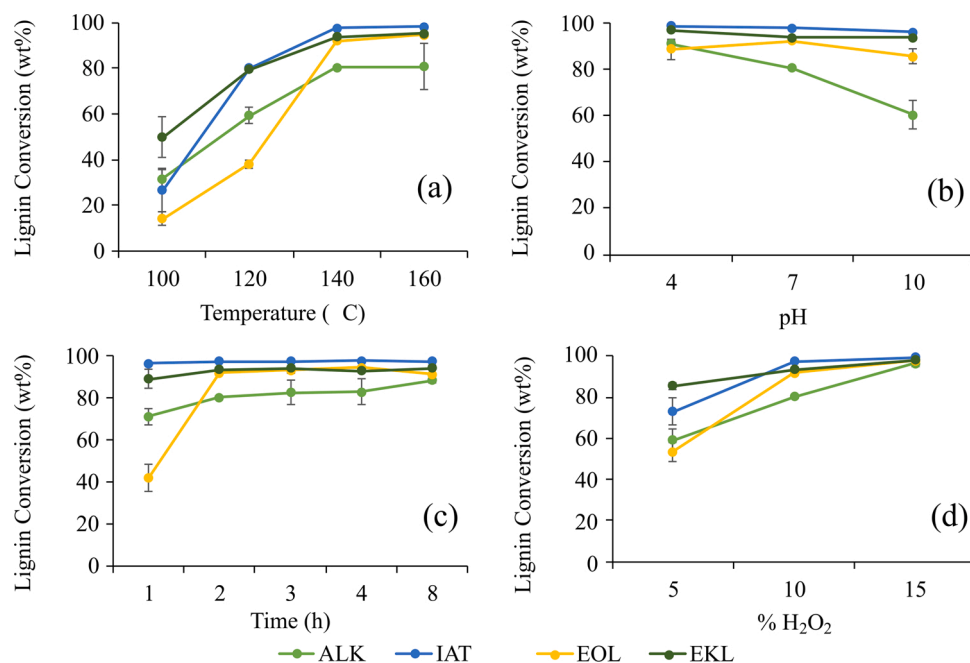


Fig. 2. Lignin conversion by catalytic wet peroxide oxidation. Effect of: (a) Temperature; (b) pH; (c) time; (d) H₂O₂ percentage. Abbreviations: ALK: alkali lignin, IAT: Indulin AT, EOL: Lignol organosolv lignin, EKL: *E. globulus* kraft lignin.

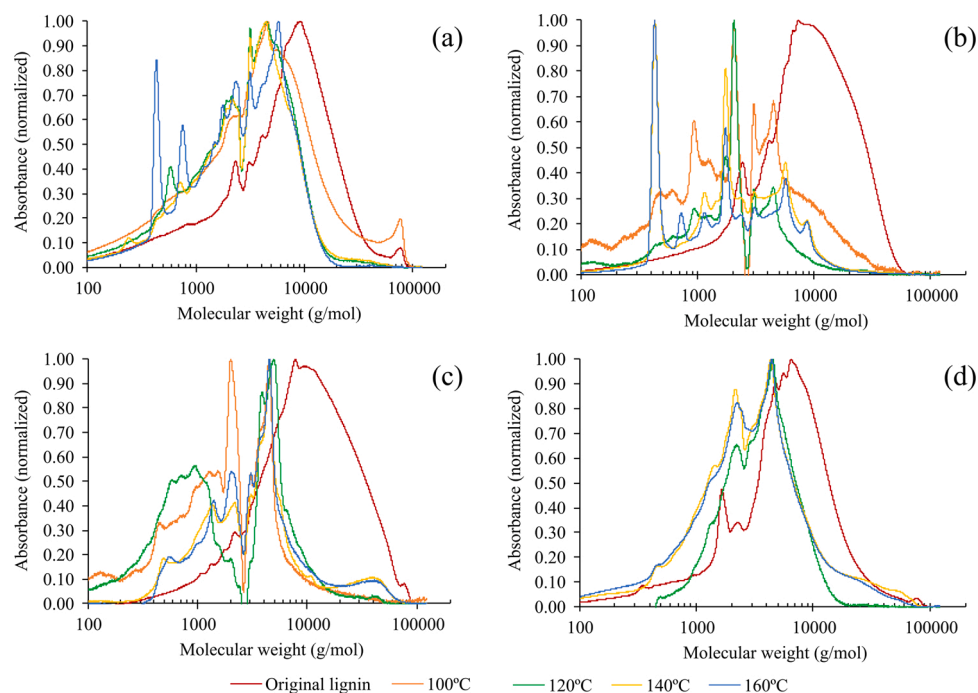


Fig. 3. Gel permeation chromatograms for lignins ((a) ALK, (b) IAT, (c) EOL, (d) EKL) oxidised at different temperatures (100, 120, 140, and 160 °C). Abbreviations: ALK: alkali lignin, IAT: Indulin AT, EOL: Lignol organosolv lignin, EKL: *E. globulus* kraft lignin.

(Gierer et al., 1992). This fact may explain the lower lignin conversion at alkaline pH due to repolymerization reactions. Moreover, H₂O₂ is quickly decomposed at alkaline pH to water and O₂ (Suttipornphaisakul et al., 2020). In acidic and neutral pH, redox and disproportionation reactions were more frequent, allowing the formation of hydroxylated and demethoxylated products, and, therefore, to a higher level of lignin depolymerisation to short fragments and, in a later stage, to the compounds of interest.

The testing of the lignin oxidation at different times was done at 140

°C and pH 7 in the range 1–8 hours. Lignin conversion was already observed in the first hours for kraft lignins (IAT and EKL), as shown in Fig. 2c. Lignin EOL gave rise to low conversion in the first hour, probably due to its higher condensed structure (Costa et al., 2014), which needed longer oxidation times to break the structure to smaller fragments. Comparatively, with the other lignins, ALK conducted to lower conversions, never reaching 100 %. Alkaline pretreatment depolymerised lignin by cleaving the ether linkages and leaving instead available OH phenolic groups, which are the main cause for lignin re-condensation,

reaching a very condensed and recalcitrant structure (Bao et al., 2020; Ma et al., 2018b). Analysis using ATR-FTIR confirmed the presence of the available OH groups by the presence of different bands. Band at 1040 cm^{-1} shows a high intensity compared to the other lignins, being related to C—O in primary alcohols. Band at 1086 cm^{-1} is related to secondary alcohols and ethers, and it is only present in ALK and IAT. Finally, bands at 1108–1133 cm^{-1} are associated to a combination of C—H in S units and secondary alcohols and C=O (Cateto et al., 2009). This band is present in EKL and EOL (as hardwood lignins) but is also present in ALK, mainly by the presence of OH groups. Also, ALK showed a more intense band at 3400 cm^{-1} , associated to O—H groups. It has been reported that higher ether linkages content helps to activate the aromatic ring (Ma et al., 2018b). Since alkaline-pretreated lignin has a lower amount of ether linkages, the depolymerisation of the aromatic moieties become lower, causing that ALK presented a low reactivity towards oxidation. Therefore the ring-opening reaction of these aromatic compounds yields lower amounts of C₄-DCA.

The amount of H₂O₂ available for oxidation is a relevant parameter for reaching good conversions, avoiding over-oxidation of the already produced compounds. As seen in Fig. 2d, lignin conversion increased as the H₂O₂ available to react also increased. EOL and ALK lignins were the ones leading to lower conversions for low H₂O₂ contents due to their higher condensed structure (Costa et al., 2014; Ma et al., 2018b), while the conversion of the EKL lignin was higher due to the higher reactivity of softwood kraft lignins in peroxide oxidations (Vega-Aguilar et al., 2021).

3.2.2. C₄-DCA yields

Once the lignin has been depolymerised into smaller fragments, ring-opening reactions occur, yielding C₄-DCA compounds. The parameters tested for lignin conversion (temperature, pH, time, and H₂O₂ percentage) were also analysed in the production yield of the acids (succinic, malic, maleic, fumaric, and tartaric acids).

The best lignin conversions to C₄-DCA were obtained for the higher tested temperatures, as seen in Fig. 4a. Namely, the best C₄-DCA yield was achieved at 140 °C for most lignins (IAT, EOL, and EKL), following the same behaviour observed for lignin conversion. Only ALK showed a slightly higher yield at 160 °C. Lignin ALK has a low reactivity towards

oxidation (Ma et al., 2018b), therefore needing a higher temperature to be depolymerised and oxidised. Malic and succinic acids were the main obtained acids, while maleic and fumaric acids were observed for all temperatures but at very low yields. Tartaric acid was obtained mainly at high temperatures. Lignin IAT provided the higher succinic acid yield, with 11.3 wt%, compared to EOL (9.7 wt%), EKL (7.6 wt%), and ALK (5.8 wt%). Regarding malic acid, EOL gave rise to the highest yield (19.5 wt%), compared to IAT (10.1 wt%), ALK (6.6 wt%), and EKL (5.5 wt%). In all cases, the succinic acid yield was higher for the catalysed reaction when compared to the non-catalysed one, being up to four times higher in the best-case scenario (as compared with the non-catalysed reaction, see Fig S3). In contrast, for malic acid, the results were similar for the two oxidation methods (Fig. S3a). Moreover, in most cases, acetic acid yields were similar for the non-catalysed and catalysed reactions, with formic acid yields being higher for the catalysed reaction (Fig S4 and S5).

It can be concluded that the best temperature to achieve succinic and malic acid at the highest yields was 140 °C, which is in agreement with the previous studies using lignin model compounds (Vega-Aguilar et al., 2020). A temperature higher than 140 °C over-oxidised the products, causing degradation of the produced C₄ acids, mainly the succinic acid, which had been reported to be oxidised to acetic acid (Suzuki et al., 2006), whose yield was much higher at 160 °C.

Alkaline pH led to lower C₄-DCA yields, especially for ALK lignin (Fig. 4b). In acidic and neutral pH, the yields were similar. It has been reported that the amount of demethoxylation increased with pH decreasing (Gierer et al., 1992). Since the demethoxylation is one of the first steps to the further aromatic ring oxidation and ring-opening reactions (Vega-Aguilar et al., 2021), the use of a lower pH increased lignin conversion to lower-molecular weight compounds, confirmed by the higher lignin conversion and C₄-DCA yields in acidic pH. However, since lignin is usually insoluble in acidic pH, performing the oxidation under these conditions can put constraints to the production process since lignin deposits in the catalyst and mass-transfer limitations can appear. Neutral pH led to similar C₄-DCA yields, comparatively to acidic pH, with the advantage that lignin is much more soluble in this medium. Individual C₄-DCA yields showed no significant differences between acidic and neutral conditions.

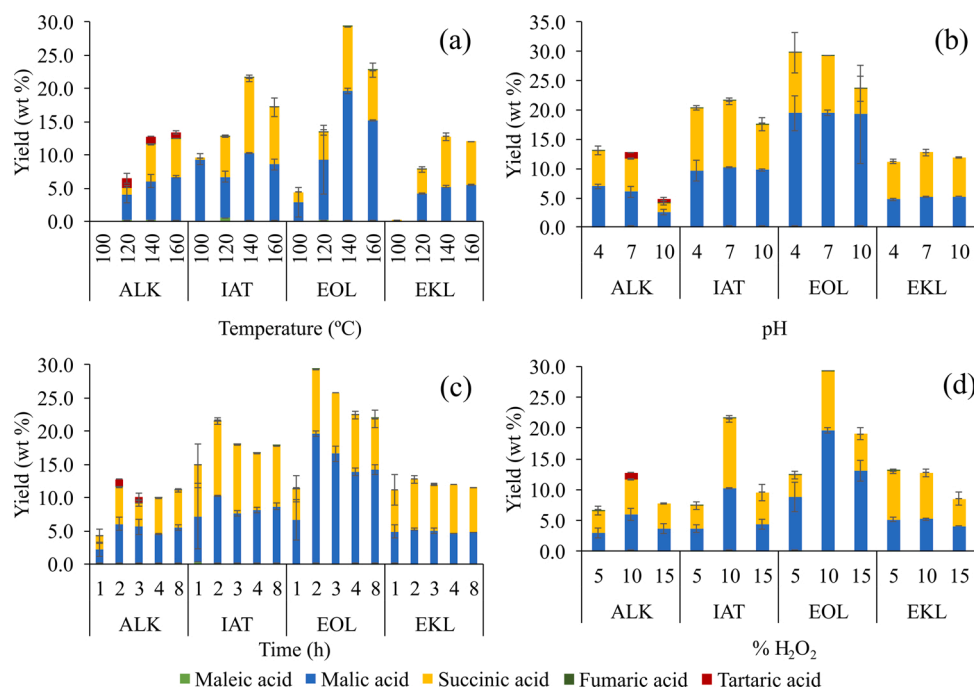


Fig. 4. C₄-DCA yield in catalytic wet peroxide oxidation. Effect of: (a) Temperature; (b) pH; (c) time; (d) H₂O₂ percentage. Abbreviations: ALK: alkali lignin, IAT: Indulin AT, EOL: Lignol organosolv lignin, EKL: *E. globulus* kraft lignin.

The main reaction sites of the TS-1 catalyst are the Ti atoms, whose reactivity is modified by changing the pH. It has been reported that, at neutral pH, TiO_2 has zero charge (pH 6.25–6.8), having at this point the best adsorption capability for the reactants due to the neutral surface (Suttipornphisakul et al., 2020). Even lignin conversion was higher at acidic pH, C_4 -DCA yield was similar to the one achieved at neutral pH, confirming that enhanced oxidation at a neutral pH was achieved with the catalyst. It is also important to note that the presence of TS-1 catalyst improved succinic acid yield for all studied lignins at the three evaluated pH conditions. For the non-catalysed reaction, the presence of succinic acid was negligible (Fig. S3b).

For the four analysed lignins the highest C_4 -DCA yields were achieved after 2 h, as can be seen in Fig. 4c. However, the formed acids showed a different stability pattern against time. Malic acid yield decreased due to their oxidation to low-molecular compounds, such as acetic acid, whereas succinic acid revealed to be stable throughout time, showing very low degradation levels, which can be helpful in a future biorefinery process.

A high amount of H_2O_2 caused mineralisation of the C_4 -DCA, avoiding their production at valued yields. As seen in Fig. 4d, the best yields were obtained for 10 % H_2O_2 , while the extra adding of peroxide caused a decrease in the obtained acids yield. The same effect was observed for the degradation products (formic and acetic acids), showing that they were utterly mineralised to CO_2 using high H_2O_2 concentration. This behaviour was also observed with lignin peroxide oxidations using different TiO_2 based catalysts (Suttipornphisakul et al., 2020). Therefore, it is necessary to evaluate and optimize the amount of H_2O_2 added to the reaction in lignin oxidation leading to C_4 -DCA. The use of an oxidiser amount higher than the needed one would make the process more costly without any valuable advantages.

The best lignin for succinic acid production was IAT, but EOL conducted to the higher total C_4 -DCA yields, while ALK and EKL showed similar low yields. As previously stated, technical lignins with a higher content of aryl-ether bonds indicate a not too aggressive pulping process, avoiding re-condensation reactions. Once the aryl-ether bonds are cleaved in the oxidation reaction, the aromatic rings are oxidised and opened, leading to C_4 -DCA. The lignin EOL, proceeding from an organosolv process, has a structure closer to the one of the native lignin, i.e., it preserved most of the aryl-ether linkages after the pulping process. As a hardwood lignin, it has the advantage of reacting faster due to its syringyl groups. Therefore, the oxidant cleaves the ether bonds and opens the aromatic rings without being consumed in the breaking of the C—C bonds of the condensed structures. This fact may led to the existence of some extra oxidant to oxidize more aromatic rings and continue oxidizing the formed dicarboxylic acids, giving rise to high percentages of malic acids. Kraft lignins have a more recalcitrant structure due to the used harsher pulping process, causing the cleavage of aryl-ether bonds and the re-condensation of the fragments, reducing the overall C_4 -DCA yield. Lignin IAT is a softwood lignin whose guaiacyl moieties are easily oxidised to succinic acid, giving rise to a higher yield for this compound. Lignin EKL as a hardwood lignin shows higher reactivity towards oxidation, expecting that higher C_4 -DCA yields were obtained. However, since this lignin is highly reactive, during the delignification process, it becomes partially degraded and condensed, as reported in previous works (Costa et al., 2014), reducing the possibility to achieve higher C_4 -DCA yields. Finally, even though ALK is an alkali softwood lignin, and thus better yields were expected (as happened with IAT), its structure was heavily modified, with condensed structures found in this lignin, reducing the global C_4 -DCA yield. Then, it can be stated that lignins with lower chemical modification, i.e. lignins with a structure closer to the one of native lignin, would be more suitable for C_4 -DCA production, given that they still present aryl-ether linkages that can be cleaved and ring-opening before re-condensation occur, which will decrease reactivity. The fact that less modified lignins give better C_4 -DCA yields could be especially helpful for biorefinery processes, where milder extraction processes are being used.

During the HPLC analysis, phenolic compounds were not identified, corroborating that at even low concentrations of H_2O_2 , degradation of the lignin fragments through ring-opening reactions occurred, forming low-molecular-weight compounds and even reaching complete mineralisation, without leasing to individual phenolic monomers.

3.3. Evaluation of TS-1 catalyst in C_4 -DCA production

3.3.1. Catalyst loading effect

Due to the catalytic effect of TS-1 in radical species production, it is important to evaluate the minimum catalyst load to be added to the reaction flask to ensure the highest C_4 -DCA yields, avoiding increasing costs in the oxidation process. Titanium silicalite-1 has the advantage of not having noble metals in its structure, having a lower cost than other precious-metal-based catalysts. To examine the optimum catalyst load, oxidation reactions were performed using different amounts of catalyst, as seen in Fig. 5.

Generally, all lignins were better converted using a lower amount of catalyst (Fig. 5a), as the observed differences for the observed conversion data were statistically significant (confirmed by a one-way ANOVA test, $P = 0.05$, Table S2). However, when the C_4 -DCA yield is analysed for the studied lignins, the non-catalysed reaction gave rise to lower yields, especially for succinic acid (Fig. 5b). The higher succinic acid yield, for all lignins, was obtained using a 10 % catalyst load (lignin-basis). The behaviour for malic acid was similar, except for EOL, where it was produced at a higher yield when less catalyst was presented. Loads higher than 10 % caused a decrease in C_4 -DCA yields, suggesting that the ideal load is 10 %. Previous works where furfural was oxidised using TS-1 showed an ideal load of ~5 wt%, allowing a better maleic acid yield, while loads higher than 10 % load intensified the over-oxidation (Alonso-Fagúndez et al., 2014). However, due to the lignin complex structure, in this work the over-oxidation was only observed after a catalyst load of 10 % wt.

3.3.2. TS-1 reusability

To examine the reusability of the TS-1 catalyst in the C_4 -DCA production, the same catalyst sample was consecutively used in five runs under the same experimental conditions. For these oxidation tests, the chosen conditions led to the best succinic acid yield in the individual parameter evaluation, which were achieved with IAT lignin, at pH 7, 140 °C, 2 h, 10 % H_2O_2 , and 10 % TS-1.

After each oxidation run, the reaction mixture was centrifuged, and the liquid was removed using a pipette. Some of the catalyst remained suspended in the solution leading to a loss every run. This problem was due to the small size of the catalyst particles (0.3–0.5 μm), impeding sedimentation even after long centrifugation times (30 min at 3500 rpm). After five runs, the remaining catalyst was quantified as 46 % of the original amount, confirming that the small size affected its recovery by centrifugation. A higher particle size catalyst is recommended for further studies, facilitating its full recovery after centrifugation.

As seen in Fig. 6a, lignin conversion was preserved through the continuous runs, while the total CA (which involves C_4 -DCA, acetic, oxalic and formic acids) yield decreased from 43 wt% to 36 wt%. Specifically, C_4 -DCA yield decreased from 19 wt% to 15 wt%. A variation in the different acid yields in each run (Fig. 6b) was observed, with more significant changes for maleic, fumaric, and formic acids. After five runs, malic and succinic acids yields were still 89 % and 70 % of the first run value, respectively. This variation could be explained by the catalyst loss as previously described. At the 5th run, the amount of TS-1 was practically half of the original amount, and the results matched the experiments where 5% TS-1 catalyst was used compared to 10 % TS-1 (Fig. 5).

Deactivation has been reported for TS-1 catalysed oxidations, mainly due to the deposition of the reaction by-products over the surface and within the pores, even when using pure and simple feedstocks such as furfural (Rodenas et al., 2018). In this work, after the first run, a slight change of colour was observed, which was expectable due to the

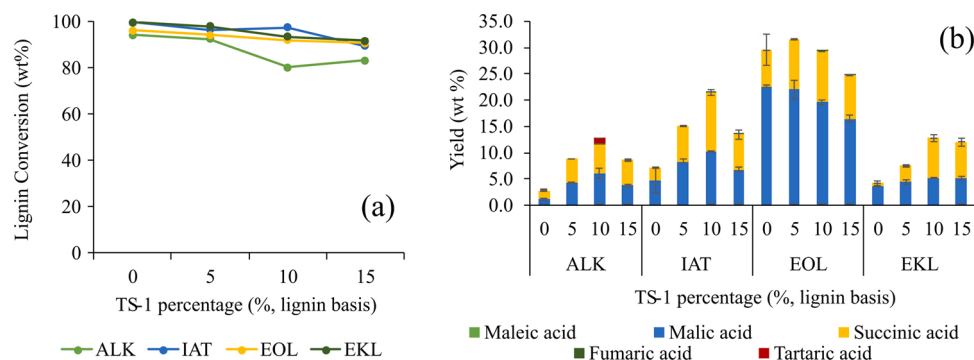


Fig. 5. Effect of TS-1 load on: (a) lignin conversion and (b) C₄-DCA yield. Abbreviations: ALK: alkali lignin, IAT: Indulin AT, EOL: Lignol organosolv lignin, EKL: *E. globulus* kraft lignin, TS-1: titanium silicalite-1.

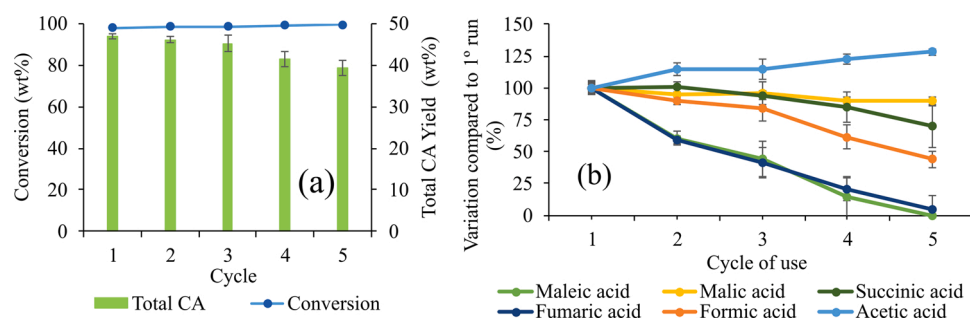


Fig. 6. Catalyst reusability after five successive oxidation runs. (a) Lignin conversion, (b) Carboxylic acids (CA) yield evolution along the five consecutive runs, comparatively with the first oxidation. Abbreviations: CA: carboxylic acids.

deposition of lignin fragments associated with its complex reactivity and structure. These deposits can affect catalyst activity since they can block the pores and catalyst's surface, which is the main factor for TS-1 deactivation (Shi et al., 2013; Wang et al., 2007). Regeneration of catalysts contaminated with carbonaceous species can be done by calcination, being reported as a solution for deactivated TS-1 after several cycles (Alba-Rubio et al., 2017; Rodenas et al., 2018). In this work, the catalyst was only washed with acidified water between cycles. In other studies, the catalyst was repeatedly washed with organic solvents and dried before use, therefore removing more effectively the deposited contaminations from the pores (Alba-Rubio et al., 2017; Rodenas et al., 2018). As seen in Fig. 7, the physical structure of TS-1 was not modified after one cycle. After five runs, some slight physical modifications are perceived on the particle's surface, with their whole structure remaining intact. Analysis using EDS showed that the atomic Si/Ti ratio (44.9 ± 0.7) remained stable with one cycle (45 ± 3). A change to 34 ± 3 was observed after five cycles, suggesting a decrease in the Si content,

probably due to some damages in the MFI surface structure. However, the activity experiments indicate that the main reason for C₄-DCA yield decrease was the loss of catalyst during the washing step and not the deactivation of the catalyst itself.

4. Conclusions

Lignin catalytic peroxide oxidation using TS-1 catalyst proved that C₄-DCA could be obtained at attractive yields. Succinic and malic acids were the main products, while maleic, fumaric, and tartaric acids were present in small amounts. Compared to the alkali lignin, kraft and organosolv lignins lead to higher conversion towards C₄-DCA. Succinic acid, a valuable product for bio-based polymers, was obtained at higher yields for the catalysed reaction than the non-catalysed one, being Indulin AT lignin the best-studied case, leading to a yield four times higher than the one achieved without catalyst. Overall, the succinic acid yield followed the order IAT > EOL > EKL > ALK, while the best C₄-DCA

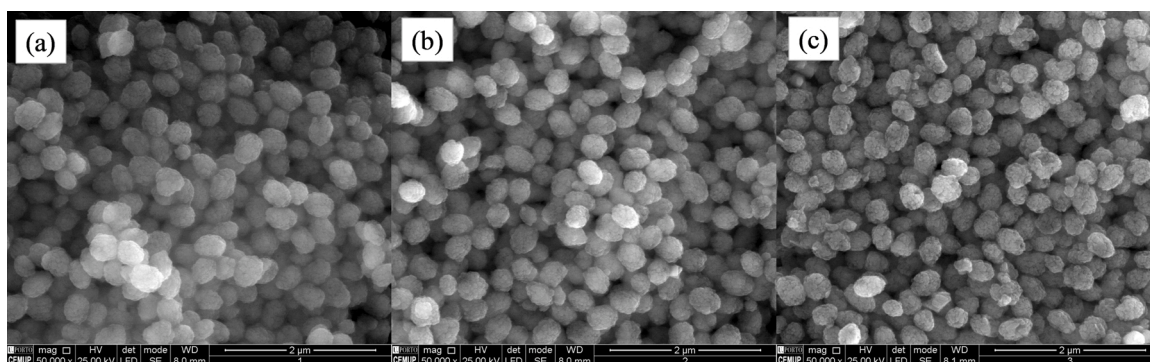


Fig. 7. Scanning electron microscopy (SEM) images of the original and reutilized catalyst: (a) original titanium silicalite-1 (TS-1) catalyst, (b) after 1 oxidation cycle, (c) after five oxidation cycles.

total yields were achieved by EOL, suggesting that organosolv lignins (and lignins with a structure closer to native lignin) would have a more efficient oxidation activity towards C₄-DCA. Evaluating oxidation reaction key parameters was determinant to achieve good conversions without reaching over-oxidation, with the best conditions achieved for each individual parameter study, for the considered lignins, being 140 °C (temperature effect), neutral pH (pH effect), 10 % TS1, lignin basis (catalyst effect), and 10 % H₂O₂ load (oxidant load effect). Values differing from these give rise to low lignin conversions, or over-oxidation products, like acetic and formic acids. This study considered the study of one parameter at a time and thus the overall best conditions were not achieved. Even so, the data presented here can be the basis for a deeper study, namely by using different statistical tools, like surface response methodology.

The optimum amount of TS-1 was determined to be 10 wt% (lignin-basis) and the catalyst was found to be reusable. In the analysed consecutive cycles, a decrease in succinic and malic acids yield was observed, justified mainly due to the catalyst loss during the centrifugation step, which was linked to its small particle size and not to the deactivation caused by the carbonaceous deposits.

Funding sources

This work was financially supported by: Base Funding - UIDB/50,020/2020 of the Associate Laboratory LSRE-LCM - funded by national funds through FCT/MCTES (PIDDAC); Base Funding - UIDB/00,690/2020 of CIMO - Centro de Investigação de Montanha—funded by national funds through FCT/MCTES (PIDDAC). COST Action LignoCOST (CA17128). Costa Rica Science, Technology and Telecommunications Ministry for the PhD. Scholarship MICITT-PINN-CON-2-1-4-17-1-002.

CRediT authorship contribution statement

Carlos A. Vega-Aguilar: Conceptualization, Methodology, Investigation, Formal analysis, Data curation, Writing - original draft. **M. Filomena Barreiro:** Conceptualization, Resources, Writing - review & editing, Supervision. **Alírio E. Rodrigues:** Conceptualization, Resources, Writing - review & editing, Supervision.

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.

Acknowledgments

This work was financially supported by: Base Funding - UIDB/50020/2020 of the Associate Laboratory LSRE-LCM - funded by national funds through FCT/MCTES (PIDDAC); Base Funding - UIDB/00690/2020 of CIMO - Centro de Investigação de Montanha—funded by national funds through FCT/MCTES (PIDDAC). COST Action LignoCOST (CA17128). Carlos Vega-Aguilar thanks the Costa Rica Science, Technology and Telecommunications Ministry for the PhD. Scholarship MICITT-PINN-CON-2-1-4-17-1-002. The authors thank Dr. Maria José Sampaio and Prof. Dr. Joaquim Faria (LA LSRE-LCM) for the help with the ATR measurements.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.indcrop.2021.114155>.

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