

## Potential of Lignin as Antioxidant for Thermoplastics and Other Materials

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### Abstract

The antioxidant properties of technical lignins have been extensively investigated but there are still gaps of knowledge that should be filled to facilitate the practical applications of lignins as antioxidants (AOs). In the present investigation, we compared the short-term (60 min) and long-term (48h) AO performance of lignins with different contents of functional groups and lignin model compounds (LMCs) with different aromatic ring substituents in the 2,2-diphenyl-1-picrylhydrazyl radical (DPPH\*) antioxidant assay. We found some LMCs to quickly expend their AO capacity while others started off slowly but after 48h had consumed more DPPH\* per phenolic hydroxyl group. Reaction time was also a factor in the relative AO performance of lignins. For softwood lignins, a higher phenolic hydroxyl content was associated with increased DPPH\* reactivity. CatLignin, a thermally treated lignin rich in phenolic units and especially catechol groups, consumed more than twice as much DPPH\* than any other lignin during 48h (over two mol/lignin unit of 180 g/mol). CatLignin also had the lowest 60 min half-maximal effective concentration (EC50). In polypropylene, lignins provided better UV protection than commercial primary antioxidants applied at similar loadings. Similarly, the better performance of lignin over commercial AOs was observed against thermal oxidation.

**Keywords:** Antioxidant; DPPH\*; Lignin; Thermoplastics

### INTRODUCTION

Antioxidants (AOs) are commonly used in many polymer products such as polyolefins that are prone to weathering and loss of mechanical properties when exposed to heat or light <sup>1</sup>. Two different types of antioxidants are typically applied. Primary antioxidants (PAO) act as radical scavengers and are often phenolic compounds, while secondary antioxidants (SAO) stabilise the product by reducing the formed hydroperoxyl structures into hydroxyl groups <sup>2</sup>. Only small quantities (0.05-0.2%) of antioxidants are needed, but the AOs tend to be the most costly additives.

Lignin is the most important by-product from the lignocellulosic biorefineries, and a renewable resource for chemical industry for applications such as bio-based binders, resins, composites and plastics, most of which exceed its fuel value <sup>3</sup>. An increase in the utilisation of lignin for higher value products could significantly improve the cost-competitiveness of the lignocellulosic biorefineries, and create new lower-cost, sustainable raw materials for the chemical industry. It can be used as a matrix polymer or filler to improve stiffness of relatively soft plastic thermoplastic materials like polyolefins <sup>4</sup>. Unfortunately, this occurs at the expense of tensile and impact strength, which is typical of all fillers with low aspect ratios. However, one of the interesting features of lignin is its ability to act as a free radical scavenger, making it a potential low-dose substitute for synthetic PAOs in thermoplastic products. In this regard it is important to assess the antioxidant activity (AA) of various technical lignins. The 2,2-diphenyl-1-picrylhydrazyl radical (DPPH\*) assay <sup>5</sup> that is independent of sample polarity has

been applied to investigate the AA of lignins and lignin model compounds (LMCs) as PAOs<sup>6-10</sup>). In a homolytic dissociation of the phenolic O-H bond, a DPPH\* is reduced as it abstracts the hydrogen atom while lignin is oxidised to a phenoxy radical ( $\text{DPPH}^* + \text{PhOH} \rightarrow \text{DPPH} + \text{PhO}^*$ ). The type and number of substituents on the phenolic unit determine the dissociation enthalpy of the O-H bond and the stability of the resulting phenoxy radical and therefore the rate of the reaction.

Based on LMC studies<sup>6,10</sup>), the inductive effects of electron-donating functional groups (e.g.  $\alpha\text{-CH}_2$ ) favour the formation of phenoxy radical as they decrease the polarisation of the phenolic O-H bond, whereas the inductive effects of electron-withdrawing substituents (e.g. -OH, -OCH<sub>3</sub>, -C=O) work in the opposite direction. However, substituents with free pairs of electrons (-OH<sub>phen</sub> and -OCH<sub>3</sub> *ortho* to the phenolic hydroxyl at C<sub>4</sub>) or ring-conjugated C=C or C=O bonds in the lignin side chain stabilise the phenoxy radical by extending its resonance. In most cases the resonance and inductive effects clash but the net AA effects are such that phenolic hydroxyl and methoxyl groups are strongly activating while  $\alpha\text{-C=O}$  groups are strongly deactivating. For ring-conjugated C=C bonds, carbonyl groups not at C <sub>$\alpha$</sub>  and aliphatic hydroxyl groups the situation is complex – their individual effects seem interrelated and the net effects on AA vary. The AAs of lignins<sup>7-11</sup>) and LMCs in DPPH\* assays are highly correlated, although the correlations probably suffer due to the quantitation of lignin side-chain structures by pyrolysis GC/MS<sup>7</sup>) (the lignin degradation products are difficult to trace back to original lignin structures such as double bonds, C <sub>$\alpha$</sub> -CH<sub>2</sub> groups and oxygen-based functional groups). Other potential sources of discrepancy include the heterogeneity of lignins and their impurities such as carbohydrates as well as steric effects due to the three-dimensional structure of lignin.

Many LMCs and lignins are able to reduce more than one mole of DPPH\* per phenolic hydroxyl group<sup>6-10</sup>), indicating that initially formed phenoxy radicals can be regenerated to phenolic hydroxyls via secondary reactions. This suggests that when time is not a limiting factor the actual AO capacity of lignins and LMCs may be significantly greater than their short-term AA that is usually determined within reaction times of less than 1h even for substrates whose DPPH\* consumption has not yet plateaued. Studies on oligomerisation of phenoxy radicals produced by laccase-mediated oxidation<sup>12,13</sup>) showed that the regeneration of monomeric guaiacylic radicals may occur either by dimerization (C<sub>5</sub>-C<sub>5</sub> coupling exclusively) or hydrogen atom transfer from a hydroxyl substituted C <sub>$\alpha$</sub>  to phenoxy radical and its oxidation to an  $\alpha\text{-C=O}$  group. If both modes of regeneration are possible, the thermodynamic stability of the product and any hydrogen bonding occurring during its formation determine the product distribution. For instance, because of the solvation promoting effect of hydrogen bonding, vanillyl alcohol radical regenerated in water preferably by giving the less thermodynamically favoured C<sub>5</sub>-C<sub>5</sub> product rather than the more favoured product of hydrogen atom transfer, vanillin. However, further oligomerisation reactions gave rise to C<sub>5</sub>-C<sub>5</sub> products with benzaldehyde groups. Syringylic radicals are unable to form C<sub>5</sub>-C<sub>5</sub> coupling products and e.g. syringyl alcohol radicals may regenerate the phenolic hydroxyl via syringaldehyde or 2,6-dimethoxy-*p*-benzoquinone<sup>14-16</sup>).

Regular technical lignins contain few if any catechol units and related LMCs have therefore not been included in earlier AA studies of lignins. However, some of the pyrolysis lignins investigated by Ponomarenko et al<sup>9</sup>) had clearly undergone significant demethylation, and showed a high DPPH\* reactivity on a mass basis although their reactivity in terms of DPPH\* reduced per phenolic hydroxyl was 0.6-0.8. The conversion of a methoxyl group to a second phenolic hydroxyl group not only adds to the sites where a phenoxy radical may form but may also boost the rate of reaction by activating the adjacent phenolic hydroxyl more than a methoxyl groups does. In addition to pyrolysis lignin, the CatLignins produced by heat treatment of kraft black liquor,<sup>17</sup>) can also offer a catechol rich technical lignin with enhanced antioxidative properties. Besides demethylation, new phenolic units are formed in alkaline heat treatment conditions via cleavage of alkyl-aryl ether bonds, resulting in a significantly higher total content of phenolic units than in any currently available technical lignin. Due to demethoxylation, also the *p*-hydroxyphenyl content of CatLignin is higher than in conventional kraft lignins.

The present paper deals with short-term (60 min) and extended DPPH\* assays (up to 48h when necessary and corrected for natural DPPH\* decay) on several conventional technical lignins (kraft, soda, organosolv and lignosulphonate), as well as novel CatLignin<sup>17</sup>), EcoHelix lignin-carbohydrate complex and kraft lignin fractions obtained by sequential solvent (ethanol/water) fractionation<sup>18</sup>). Before lignin

analyses, LMCs with 1-3 phenolic hydroxyls and/or 1-2 methoxyls were studied. As the DPPH\* reaction time may be relevant to AO applications of lignins, our goal was to elucidate not only the short-term AA of the substrates but also to explore their longer-term AA by allowing sufficient time for slow-reacting substrates to plateau. In addition, some of the lignins were investigated as PAOs (with and without a SAO) in polypropylene to improve its resistance to heat and light.

## EXPERIMENTAL

### Materials

The lignins studied and their structural features are given in Table 1. Two softwood (SW) kraft lignins, (SW-Kraft1 gifted by Metsä-Fibre and SW-Kraft2 purchased from UPM Biochemical (Helsinki, Finland), were used. Ethanol/water based solvent fractionation was performed on SW-Kraft1 according to Jääskeläinen et al.<sup>18)</sup>, providing an insoluble (SW-Kraft1-HighMW) fraction at 80% ethanol content, and fractions precipitated (SW-Kraft1-MedMW) or remaining soluble (SW-Kraft1-LowMW) at 50% ethanol content. SW-CatLignin was separated from industrial SW black liquor, using a novel process based on thermal treatment<sup>17)</sup>. Beech organosolv lignin (HW-Organosolv) was produced by Fraunhofer CBP (Leuna, Germany), commercial wheat straw soda (WS-Soda) Protobind™ 1000 lignin by GreenValue S.A. (Granit, Switzerland), SW-Lignosulphonate by Domsjö Fabriker AB (Örnsköldsvik, Sweden) and SW-EcoHelix<sup>19)</sup> (batch DH13F) lignin-carbohydrate complex by EcoHelix AB (Stockholm, Sweden). Chemicals and solvents were purchased from Sigma-Aldrich.

### Determination of Lignin Functional Groups

The hydroxyl and carboxyl contents of lignins were determined according to Granata and Argyropoulos<sup>20)</sup> from freshly phosphitylated lignins by <sup>31</sup>P NMR on a Bruker 500 MHz NMR spectrometer at room temperature using a previously published method<sup>20)</sup>. Methoxyl groups were determined using the method of Baker<sup>21)</sup> with some modifications.

### Determination of Lignin Substructures

*p*-Hydroxyphenyl:guaiacyl:catechol:syringyl (H:G:C:S) ratio of lignins was determined according to the method of Ohra-aho et al.<sup>22)</sup> with some modifications. About 0.1 mg of sample was pyrolysed at 580 °C for 2 seconds with a filament pulse pyrolyzer (Pyrola2000, Pyrol AB, Sweden). Degradation products were directly led with carrier gas (helium) to gas chromatograph (Agilent 7890B) capillary column DB-1701 (30 m × 0.25 mm, film 1 µm) for separation. The compound detection was performed with an Agilent 5977A mass selective detector with mass scan range of *m/z* 25-500 (EI 70 eV). Detector responses for lignin substructures were determined using selected model compounds.

### Size-Exclusion Chromatography (SEC)

For the molar mass measurements, the samples were dissolved in 0.1 M NaOH and filtered (0.45 µm). The molar mass measurements were performed with size exclusion chromatography (SEC) using 0.1 M NaOH eluent (pH 13, 0.5 ml/min, T = 25 °C) and PSS MCX 1000 & 100000 Å columns. The elution curves were detected using Waters 2998 Photodiode Array detector at 280 nm. The weight average molar mass (*M<sub>w</sub>*) was calculated against polystyrene sulphonate standards (eight standards with a range of 3420–148500 g/mol) and using Waters Empower 3 (Milford, MA, USA) software.

### Antioxidant Assays

DPPH\* assays were conducted according to the method of Dizhbite et al.<sup>10)</sup> with some modifications. All lignins and LMCs were fully soluble in 80/20 (v/v) aqueous propylene glycol methyl ether/water (PGME) used as the solvent. Absorbance of lignin (10 mg/l) and DPPH\* (starting concentration 80 mg/l) solutions was measured at 515 nm on a Perkin Elmer Lambda 650 UV/VIS spectrophotometer (Perkin Elmer, Waltham, MA, USA) for reaction times ranging from 2 min to 48h. The DPPH\* consumption by lignins was corrected for the absorbance of lignin at 515 nm and the natural decline of DPPH\* concentration during the measurement time span, determined separately using pure

lignin and DPPH\* solutions, respectively. 60 min half-maximal effective concentration (EC50) calculations were also performed<sup>23</sup>).

### Testing of Lignin as AO in Polypropylene

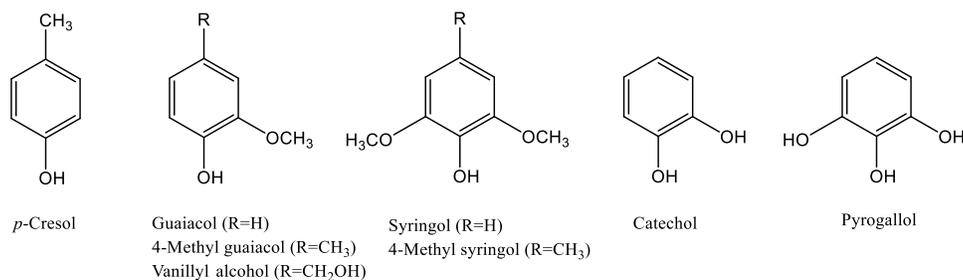
The antioxidative properties of lignins were studied in AO-free polypropylene (PP Borealis Borclean™ HB311BF). Commercial antioxidants from BASF, Irganox 1010 (pentaerythritol tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] (PAO) and Irgafos 168 (tris[2,4-di-tert-butylphenyl]phosphite) (SAO), were used as reference. Lignin dose was equal with the PAO (0.09 wt-%), and it was used with and without 0.05% of SAO. The lignin fractions and the AOs were compounded with PP by co-rotating twin-screw extruder (Berstorff GmbH ZE 25x33 D, Berstorff GmbH, Hanover, Germany), and the dog-bone shaped test pieces (ISO 527) for the mechanical testing were injection moulded with an injection moulding machine (Engel ES 200/50 HL, Engel Maschinenbau Gesellschaft m.b.H, Schwefberg, Austria). The samples were aged in QUV Accelerated Weathering tester (Q-LAB Corporation, Westlake, OH, USA) according to ASTM G154, using UVA-340 fluorescent lamps and a test cycle of UV-A irradiation at 50°C for 22 h and 2 h water condensation at 38°C. Tensile strength was evaluated before and after 500h treatment. Tensile testing was performed according to ISO 527 using Instron 4505 Universal Tensile Tester (Instron Corp., Canton, MA, USA) mechanical test equipment. The results represent the average of a minimum of six replicate samples. All the tested samples were conditioned at 23°C and 50% relative humidity for a minimum of five days before testing. Thermal stability of unaged samples was evaluated according to the oxidative induction time (OIT) determined by DSC (DSC204 F1 Phoenix®, Netzsch, Germany) according to ASTM® D 3895 and DIN EN 728 for polyolefins. The test procedure involves heating of the sample to a temperature beyond its melting point under a protective gas (nitrogen). After that, the sample atmosphere is transformed from inert to oxidative (O<sub>2</sub>) at a constant temperature of 200°C. The time elapsing until the onset of the exothermal oxidation of the sample is the OIT.

## RESULTS AND DISCUSSION

### Antioxidant Activity of LMCs in the DPPH\* Assay

LMCs were selected to reflect the structural diversity of the technical lignins investigated, known to comprise guaiacyl, syringyl, *p*-hydroxyphenyl and catechol units and different side-chain structures. Gallyol units are probably not present in the lignins but pyrogallol was nevertheless included to glean more information on the effects of multiple phenolic hydroxyl substituents.

The antioxidant activity of LMCs (Fig. 1) depended on the type and number of electron-donating substituents (phenolic hydroxyl, methoxyl, (hydroxy)alkyl) on the aromatic ring (Fig. 2), in agreement with earlier investigations<sup>6,8,10</sup>. The redox potential of DPPH\* was too low for *p*-cresol that was not oxidised at all.



**Fig. 1.** LMCs used in this study.

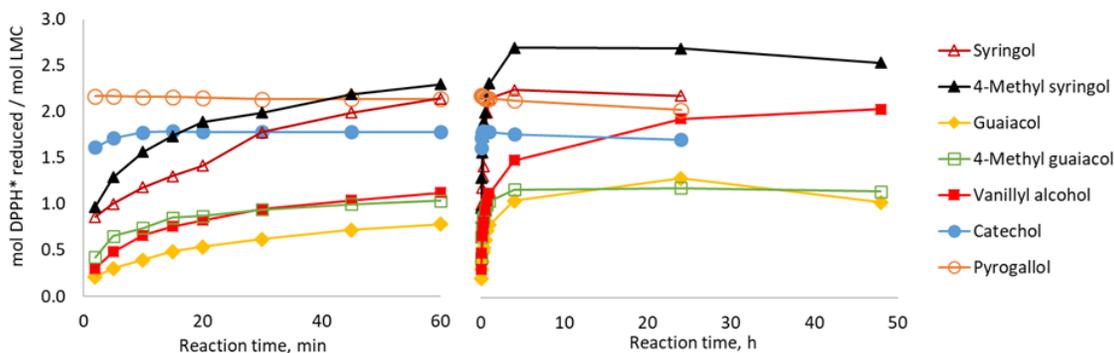
Of the three guaiacyl-type compounds with different *para*-substituents, 4-methyl guaiacol and vanillyl alcohol consumed DPPH\* somewhat faster than guaiacol during the first 60 minutes. While plateaus were reached for 4-methyl guaiacol and guaiacol within 240 min (4h), for vanillyl alcohol

longer than 1440 min (24h) were needed. Also, vanillyl alcohol consumed two molar equivalents of DPPH\* and the other two compounds just one. A plausible explanation is that the C $\alpha$ -H in vanillyl alcohol can regenerate the phenoxy radicals, while this mechanism is not active in methyl guaiacol.

The syringyl-type compounds syringol and 4-methyl syringol were clearly more reactive than guaiacol and 4-methyl guaiacol, respectively, showing the activating effect of the second methoxyl group. As with the guaiacyl-type compounds, the *para*-methyl group was reaction-promoting, allowing 4-methyl syringol to consume 2.7 molar equivalents of DPPH\* vs the 2.2. equivalents consumed by syringol. The reactions of both compounds plateaued during 1-4h but 4-methyl syringol had a faster rate of reaction.

The reactions of catechol and pyrogallol with two and three phenolic hydroxyls, respectively, were completed within two minutes (pyrogallol) and ten minutes (catechol). These rates of reaction were very high compared to those of the other compounds; however, after 50-60 min their DPPH\* consumption was surpassed by that of the syringyl-type compounds. The second and third phenolic hydroxyls increased the molar equivalents of DPPH\* consumed but not in direct proportion to their number.

The LMC studies show that electron-donating substituents increase not only their rate of reaction but, in most cases, also the molar equivalents of DPPH\* reduced. At least LMCs bearing a single phenolic hydroxyl can only consume more than one molar equivalent of DPPH\* if their phenoxy radicals are able to regenerate, e.g. by radical coupling<sup>13,16</sup>, and react again. The results also show that the choice of reaction time can have a significant effect on the relative AAs of phenolic antioxidants in the DPPH\* assay.



**Fig. 2.** Antioxidant activity of LMCs in the DPPH\* assay during 60 min (left) and 48h (right).

### Antioxidant Activity of Technical Lignins in the DPPH\* Assay

The DPPH\* investigation covered a diverse range of technical lignins, derived from different botanical origins (softwood, hardwood and grass), pulping processes (kraft, soda, organosolv, liginosulphonate and EcoHelix) and post-treatments of lignins (CatLignin process<sup>17</sup>) and solvent fractionation). As a result, the lignins show considerable differences in their functional group contents (Table 1).

The short-term (60 min) AA of technical lignins (Table 1) in the DPPH\* assay are expressed as their EC<sub>50</sub> values in Fig. 3 (the lower the EC<sub>50</sub> value, the higher the AA). Most of the values fall within a relatively narrow range, with 1.57-1.92 moles of lignin (assuming MW of lignin = 180 g/mol) required to reduce one mole of DPPH\*. The EC<sub>50</sub> values of the SW lignins within this range decrease with increasing phenolic hydroxyl content, consistent with earlier reports<sup>8,24</sup>. For SW-Kraft1 and its three MW fractions, the AAs also decline with increasing MW (their MW is highly correlated with their phenolic hydroxyl content). However, the HW-Organosolv and WS-Soda lignins in this range, whose phenolic hydroxyl contents are lower than those of the SW lignins, may have derived benefit from their syringyl units<sup>8</sup>, as was observed in the LMC studies (in particular, the high methoxyl content of HW-organosolv lignin indicates a high content of syringyl units). The low AA of the SW-Liginosulphonate

and SW-EcoHelix lignins is most likely due to their low phenolic hydroxyl contents. The highest AA was shown by SW-CatLignin. In light of the LMC study, the catechol units (LMC studies showed catechol to react faster than guaiacyl-type compounds) and high total phenolic hydroxyl content<sup>8)</sup> of SW-CatLignin offer themselves as the explication for its high AA - according to pyrolysis-GC results, SW-CatLignin is the only lignin with a significant content of catechol units (Table 2).

**Table 1.** Studied lignins and their structural features.\*

	M <sub>w</sub> , (g/mol)	Functional groups (mmol/g)				Aliph. OH	OCH <sub>3</sub>	COOH	Lignin (%)
		Phenolic OH							
		H	G+Cat	C+S	Total				
SW-Kraft1	5000	0.24	2.56	2.34	4.94	2.07	4.74	0.45	96.0
SW-Kraft1-HighMW	9600	0.22	1.91	1.92	4.05	2.10	3.78	0.32	95.4
SW-Kraft1-MedMW	3400	0.25	2.22	1.92	4.40	1.39	4.12	0.50	98.9
SW-Kraft1-LowMW	1600	0.29	3.67	1.76	5.71	1.65	4.40	0.59	97.3
SW-CatLignin	3700	0.71	2.45	2.45	5.60	0.92	2.23	0.71	98.2
SW-Kraft2	3700	0.27	2.22	1.78	4.27	2.02	4.18	0.51	97.3
HW-Organosolv	1900	0.08	0.93	2.49	3.50	1.84	6.45	0.12	98.0
WS-Soda	2500	0.48	0.99	2.00	3.46	1.46	4.68	0.98	98.2
SW-Ligno-sulphonate**19)	10500	0.04	0.78	0.21	1.03	4.06	2.22	0.92	80.5
SW-EcoHelix**19)	31400	0.04	0.00	0.15	0.19	7.47	2.58	0.55	72.8

\*Lignin included Klason + acid-soluble components. The functional group contents are expressed on lignin basis. H = *p*-hydroxyphenyl, G = guaiacyl, Cat = catechol, C = condensed, S = syringyl

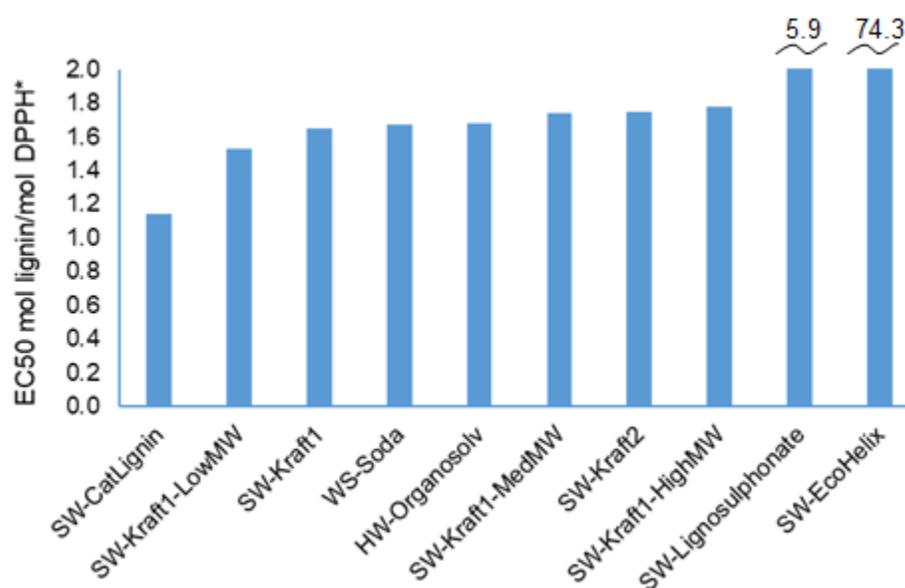
\*\*Data from ref 19)

**Table 2.** Ratio of lignin substructures.

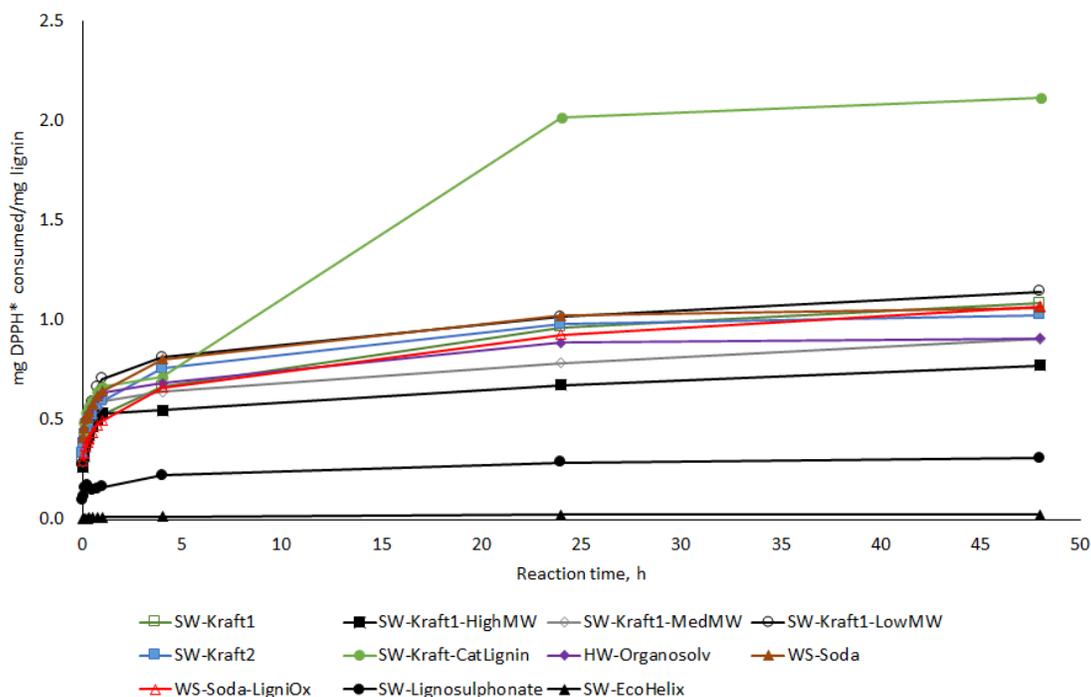
	H:G:Cat:S
SW-Kraft1	0.05: 1.00: 0.08: 0.03
SW-Kraft1-HighMW	0.04: 1.00: 0.06: 0.03
SW-Kraft1-MedMW	0.05: 1.00: 0.08: 0.03
SW-Kraft1-LowMW	0.03: 1.00: 0.04: 0.05
SW-Kraft2	0.06: 1.00: 0.09: 0.01
SW-CatLignin	0.10: 1.00: 0.36: 0.02
HW-Organosolv	0.03: 1.00: 0.00: 1:57
WS-Soda	0.15: 1.00: 0.03: 1.00
SW-EcoHelix*	0.08: 1.00: 0.00: 0.01
SW-Lignosulphonate	0.06: 1.00: 0.00: 0.00

H = *p*-hydroxyphenyl, G = guaiacyl, Cat = catechol, S = syringyl

In general, the relative long-term (48h) AAs of the lignins correlate well with the corresponding 60min-EC50 values. The main exception was the SW-CatLignin that after 4h had consumed less DPPH\* than many of the other lignins but ended up with a much higher consumption by 48h. The DPPH\* consumption was initially rapid but continued at a slower pace for 48h and possibly longer. Assuming an MW of 180 g/mol for a mole of lignin, the molar consumptions of the lignins ranged from 0.03 to 2.5 mol of DPPH\* per mol of lignin.



**Fig. 3.** EC50 values (60 min) of technical lignins in the DPPH\* assay. The values are calculated based on the lignin contents in Table 1. Lignin MW = 180 g/mol per phenylpropane unit.



**Fig. 4.** DPPH\* consumption of lignins during 48h. The values are calculated based on the lignin contents in Table 1. Lignin MW = 180 g/mol per phenylpropane unit.

### Lignins as PAOs in Polypropylene Composites

The antioxidative properties of kraft lignins (SW-Kraft1, SW-CatLignin) and the SW-Kraft1 fractions obtained by solvent fractionation were studied in PP composites. As shown in Table 3, the low lignin amount (0.09 %-w) had no effect on initial mechanical properties before UV ageing. After very severe 500h UV ageing, the mechanical properties could be retained significantly better with all the studied lignins compared to the commercial PAO. SAO did not add to the UV resistance provided by

lignin. The antioxidant performance of all studied lignins was equally good.

Lignins also outperformed commercial AOs in protecting PP against thermal oxidation (Table 4). In this case, SW-CatLignin showed better antioxidative properties than SW-Kraft1, providing PP with a higher oxidation induction time (OIT). The low- and medium-MW fractions of SW-Kraft1 (SW-Kraft1-LowMW and SW-Kraft1-MedMW) afforded similar OIT values. With these three best performing lignins, the co-use of SAO further reduced the thermal oxidation tendency, which was not observed with SW-Kraft1 or its high-MW fraction (SW-Kraft1-HighMW). The high antioxidative properties correlated with the high amount of free phenolic hydroxyl groups of SW-Kraft1-MedMW, SW-Kraft1-LowMW and SW-CatLignin samples (Table 1) and their reactivity in the DPPH\* assay.

## CONCLUSIONS

1. The DPPH\* consumption of most lignins and some lignin model compounds continued for >24h and the short- and long-term assays (60 min and 48h) occasionally gave different results for their relative reactivities.
2. For softwood lignins, an increase in phenolic hydroxyl content was associated with greater DPPH\* reactivity. SW-CatLignin containing a significant proportion of catechol units had the highest reactivity over 48h and the lowest 60 min half-maximal effective concentration (EC50), which agrees with the very high rates of reaction showed by catechol and pyrogallol model compounds.
3. Many lignins and lignin model compounds consumed more than their molar equivalent of DPPH\*, showing that phenolic hydroxyls oxidised to phenoxy radicals are able to regenerate, depending on the lignin structure.
4. Lignins were better primary antioxidants for polypropylene subjected to UV ageing or thermal degradation than commercial reference antioxidants. Especially the medium-MW kraft lignin fraction seemed to inhibit UV induced degradation in PP.

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