

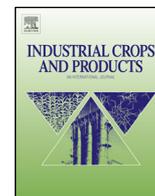
PUBLICATION IV

**Alkali-O<sub>2</sub> oxidized lignin –  
A bio-based concrete plasticizer**

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# Alkali-O<sub>2</sub> oxidized lignin – A bio-based concrete plasticizer



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## ABSTRACT

Commercial wheat straw soda lignin was used to develop an alkali-O<sub>2</sub> oxidation method to produce a ready-to-use solution for concrete plasticizing (cement dispersing). Lignin characterization was done directly from the solution. Depending on conditions, oxidation primarily induced either condensation or degradation of lignin. Thus, both the negative charge and the molar mass of the lignin were controlled by the oxidation parameters, and especially by pH.

The oxidized lignins were evaluated for their plasticizing performance in cement pastes, mortar, and concrete. Also, their effect on cement hydration was followed and several other properties of fresh and matured concrete were tested. A commercial lignosulfonate and petroleum-based superplasticizers were used as reference products.

The results indicated that alkali-O<sub>2</sub> oxidation at moderately high lignin dry solids is a promising method to produce a novel bio-based concrete plasticizer. The oxidized lignins were superior to the lignosulfonate and showed good performance in comparison to the superplasticizers.

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## 1. Introduction

Concrete, one of the most used materials in the world is a mixture of cement, water, and fine and coarse stone aggregate. Means of improving its strength, durability, and fresh stage flow-properties for better workability are constantly under research. Plasticizers, such as water-soluble lignosulfonates, or synthetic superplasticizers (organic polyelectrolytes) are often added into the concrete mixture to disperse cement particles to enhance flow-properties while using low water contents. By using less water, it is possible to have stronger concrete. Especially, the use of superplasticizers is growing in all types of concrete applications (Ramachandran et al., 1998). Annual demand of the plasticizing admixtures can be estimated to be 1.5–15 million tons if assuming that half of the annual concrete production of 18,000 million tons (GEreports, 2014) is prepared using a plasticizer dosage of 0.06–0.6 wt-% on cement (Ramachandran et al., 1998).

By far, the largest utilization of lignosulfonates, including the traditional sulphite pulping by-product lignin and the post-sulfonated alkali lignins, is in concrete admixtures with an estimated volume of 700,000 tons annually (Plank, 2004; Lora, 2008). Lignosulfonates are forecasted to have strong demand in regions that are expected to invest in significant infrastructure building in the next few years (Lora, 2008; IHS Chemical, 2012).

However, in last decades, polycarboxylate-based superplasticizers specially developed for concrete plasticizing purposes have been displacing lignosulfonates especially in Western Europe and other developed regions (Stern and Schwarzbauer, 2008; IHS Chemical, 2012). The polycarboxylates offer superior flow-properties without affecting much of the other qualities of concrete (Plank, 2004). Lignosulfonates tend to cause some retardation of concrete setting (i.e., cement hydration) particularly when their sugar content is high, and they may also cause air entrainment (Chang and Chan, 1995; Lora, 2008).

In highly alkaline concrete mixture, the working mechanism of the superplasticizers is based on both electrostatic and steric repulsion between individual cement particles to achieve a full dispersion. The negatively charged functional groups of the superplasticizer, sulfonic and carboxylic groups, adsorb on the active sites (calcium aluminate) of the cement particles giving them a negative charge, which leads to the electrostatic repulsion between the particles. The branched structure of the superplasticizer achieves steric repulsion by forcing the cement particles apart (Ramachandran et al., 1998; Yamada et al., 2000). In the case of lignosulfonates, it is postulated that the dispersing effect is mainly due to the electrostatic repulsion between the cement particles (Taylor, 1997).

Alkaline pulping originated lignins are industrially significant biomass side components (Gosselink et al., 2004) whose commercial utilization is constantly searched for (Doherty et al., 2011). It is well known that soda and kraft lignins are soluble in water only at a high pH mainly due to the ionization of the phenolic

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groups (Norgren and Lindström, 2000; Ragnar et al., 2000) and often require altering of the physico-chemical properties prior to potential applications (Lora, 2008). For the substitution of lignosulfonates by applying alkali lignin other than post-sulfonated lignin only few studies concerning cement dispersing exist. Ozonation of kraft lignin (Detroit, 1973) has been stated to result in a water-soluble product that has shown better dispersing performance than lignosulfonate products in a wide variety of organic and inorganic suspensions including cement paste. Unmodified alkali lignins (Nadif et al., 2002) or fractions thereof (Takahashi et al., 2014) have shown dispersing performance of cement particles in mortar accompanied with satisfying strength properties of the cured material. Alkali lignins have also been reacted with epoxyated polyethylene glycol derivatives and tested in cement to yield slightly better dispersing performance and bending strength than when using lignosulfonates (Uraki et al., 2012; Aso et al., 2013). However, the commercial utilization of a new plasticizer is always a combination of price and performance.

Oxygen is an environmentally friendly oxidizing agent and widely utilized in modern pulp bleaching technology to degrade residual lignin. At alkaline conditions, molecular oxygen is able to react with phenolic lignin (phenolate) to form phenoxyl radical. The radical is further oxidized to form a short living key intermediate, hydroperoxide anion structure (pKa 12–13) that rearranges to primary oxidation products (i.e., oxirane, muconic acid ester, or carbonyl structures). This leads to lignin depolymerization and introduction of acidic groups in lignin, both of which increase its water solubility (Chang and Gratzl, 1980; Sixta et al., 2006; Ji et al., 2009). The secondary oxidation of the primary oxidation products also takes place leading to small molecular degradation products (Gierer and Imsgard, 1977; Chang and Gratzl, 1980; Kuitunen et al., 2011). Below pH 12, the hydroperoxide intermediates tend to protonate and decompose homolytically back to phenoxyl radicals, which without further oxidation may spontaneously combine leading to lignin condensation (Chang and Gratzl, 1980; Kalliola et al., 2014).

Alkali-oxidation of lignins by  $O_2$  under conditions favoring lignin condensation has not been widely studied as a means to valorize lignin. On the contrary, the studies have mainly been conducted from the lignin degradation point of view in solution with rather low lignin content, very aggressive pH conditions, and high temperatures (Fargues et al., 1996; Araújo et al., 2010). Yet three old patents wherein lignin  $O_2$  oxidation was done at lignin contents up to 20 wt-%, beneficial for down-stream processing, exist. One of them reports production of polycarboxylic lignin rich in carboxylic functionality in lignin backbone (Lin, 1975). The other two report polymerization of lignin using  $O_2$  and formaldehyde (Benko and Daneault, 1976; Lin, 1980). The modified lignins were mainly tested to have good dye dispersing properties.

In the present study, oxidation by  $O_2$  in alkaline conditions was applied to increase the water solubility of a commercial wheat straw soda lignin by introduction of acidic groups in the polymer. The aim was to use the oxidized lignin solution as such for concrete plasticizing, and thus the oxidation treatment was performed at moderately high lignin content. The feasibility of the oxidized lignin solutions for concrete application was evaluated using several testing methods in comparison to commercial lignosulfonate and synthetic polycarboxylate-based superplasticizers.

## 2. Methods

### 2.1. Alkali- $O_2$ oxidation

Protobind 1000, a wheat straw soda lignin (SL) purchased from GreenValue SA (Alpnach Dorf, Switzerland) was used as raw

material. Prior to the oxidation, lignin was dissolved in a mixture of 5 M NaOH and preheated de-ionized water.

Preliminary oxidation experiments were done to understand the impact of the oxidation parameters, especially lignin content on the molar mass and charge. As the aim was to produce a ready-to-use plasticizer with a substantially high active matter content, a moderately high lignin content was intended. The experiments were done using lignin content 0.75–25.0 wt-% of the reaction solution. Under higher lignin content the solution becomes more and more viscous, which makes dispersing of  $O_2$  gas harder. The quantity of NaOH was adjusted to obtain an initial pH ( $pH_{\text{Init.}}$ ) of 13 (12.7–13.4) in the solution.

The oxidation was performed in a 1-L stainless steel pressure batch reactor (Parr Instrumental Co., Moline, IL, USA) equipped with baffles and a six-bladed turbine-type impeller stirrer, an electric heating jacket, a gas inlet, and a gas release valve.

The lignin solution was preheated in the reactor to reach a target initial temperature ( $T_{\text{Init.}}$ ). The head space was flushed with pure oxygen to replace air. Thereafter, the reactor was pressurized and this was set as the starting point of the oxidation reaction. The quantity of the lignin solution in the reactor (300–800 g) and the partial  $O_2$  pressure (5–40 bar) were varied in order to control the  $O_2$  load (12–35 wt-%) on lignin. In general, the higher the lignin content the higher the  $O_2$  pressure. The impeller was operated at 600 rpm. Reaction period of 30 min was used. Pressure and temperature in the reactor were recorded during the whole reaction period. After the oxidation, pH of the reaction solution ( $pH_{\text{Final}}$ ) was measured at room temperature.

The oxygen consumed in the experiments was computed from the reactor pressure data by applying the ideal gas law equation and the values of water vapor pressure for each data point recorded. The dissolved oxygen was taken into account accordingly. A molar mass ( $M_w$ ) of  $180 \text{ g mol}^{-1}$  was used for the lignin phenyl propane (C9) unit. The operating conditions and the total  $O_2$  uptake ( $O_2$  uptake) of the oxidations are presented in Table 1. The oxidized lignin solutions were determined for molar mass and negative charge at pH 6 (the former in the case of selected samples). Also their ability to plasticize cement paste was tested (method described below).

Based on the results of the preliminary oxidation experiments, the alkali- $O_2$  oxidation was further developed to optimize the properties of the oxidized lignin for cement plasticizing performance. Here, sequential oxidation was performed to first polymerize and then oxidize. Both stages (1ox and 2ox) of this 2-stage oxidation were carried out using the 1-L batch reactor. The initial pH of both stages was adjusted to 13. Thus, after the 1ox the oxidized lignin solution with the initial SL content of 25 wt-% was diluted to 15 wt-% using a mixture of 5 M NaOH and preheated de-ionised water. Also, a constant pH oxidation of SL at pH 11.5 was carried out in a 1.8-L batch reactor, iControl RC1e™ HP100Hastelloy (Mettler-Toledo GmbH, Switzerland) equipped with baffles, gas stirrer, a pH control loop and a pump to introduce 5 M NaOH to the reaction solution under the  $O_2$  excess. Initial SL content was set to 15 wt-%. SL content in the solution was decreased (Table 1) during the oxidation due to the addition of 5 M NaOH, which neutralized the acidity generated in the reactions and kept the pH at desired level. The last modifications of the alkali- $O_2$  oxidations included the initial oxidation at lignin content of 25 wt-% (1ox) in the 1-L reactor followed by a constant pH oxidation at pH 13 in the 1.8-L reactor, iControl RC1e™ HP100 Hastelloy.

### 2.2. Lignin characterization

#### 2.2.1. Molar mass

Average molar masses ( $M_n$  and  $M_w$ ) of the lignin material in the solutions were measured by size exclusion chromatography (SEC), using PSS MCX 1000 and 100,000 columns in 0.1 M NaOH eluent

**Table 1**  
Operating conditions for the alkali-O<sub>2</sub> oxidation of soda lignin (SL) and O<sub>2</sub> uptake of SL. Upper panel: preliminary oxidations, lower panel: improved oxidations. Reaction period of 30 min was used in all oxidations. Samples marked in bold were selected for further characterization and evaluation.

Sample	Lignin (wt-%)	NaOH on lignin (wt-%)	pH <sub>init.</sub> (-)	T <sub>init.</sub> (°C)	O <sub>2</sub> load on lignin (wt-%)	O <sub>2</sub> uptake on lignin (wt-%)
Preliminary oxidations						
SL 0.75%60C ox	0.75	53	13.1	60	20	8
SL 0.75%80C ox	0.75	53	13.1	80	23	11
SL 2.5%60C ox	2.5	31	12.7	60	14	8
SL 2.5%80C ox	2.5	31	12.7	80	14	9
SL 5% ox	5	38	13.3	80	12	10
<b>SL 15% ox</b>	15	23	13.1	55	17	8
<b>SL 15% i.ox</b>	15	23	13.1	60	35	10
SL 25% ox	25	30	13.4	50	30	13
<b>SL 25% 1ox<sup>a</sup></b>	25	24	13.0	40	15	9
Improved oxidations						
<b>SL 15% 2ox</b>	15	17 (41)*	13.0	75	34 (49)*	8 (17)*
<b>SL constant pH ox<sup>b</sup></b>	15, 11.4 <sub>Final</sub>	65	13.1	70	35	23
<b>SL constant pH 2ox<sup>c</sup></b>	15, 10.5 <sub>Final</sub>	75 (99)*	13.0	70	35 (50)*	18 (27)*

\*In parenthesis the total NaOH load, O<sub>2</sub> load and uptake in the case of sequentially oxidized SL. The letter i within SL 15% i.ox refers to increased temperature and O<sub>2</sub> load in comparison to the other experiment (SL 15% ox) done at same lignin content.

<sup>a</sup> Initial oxidation stage prior to SL 15% 2ox and SL constant pH 2ox.

<sup>b</sup> Oxidation at pH 11.5.

<sup>c</sup> Oxidation at pH 13.

(25 °C) with UV detection (280 nm).  $M_n$  and  $M_w$  were calculated in relation to polystyrene sulfonate standards using waters empower 2 software.

### 2.2.2. Charge

A modification of a potentiometric acid-base titration method used for dry lignin samples (Rahikainen et al., 2013) was applied to determine the charge of the oxidized lignin solutions (or SL in alkaline solution in the case of un-oxidized lignin). In the modified method, a given quantity of the oxidized lignin solution containing initially 75 mg of lignin (e.g., 0.5 g in the case of solution containing initially 15 wt-% lignin) was diluted to 5 g using 0.2 M NaOH. Thereafter, the CO<sub>2</sub> species were removed from the sample by acidification and the procedure was continued as described by Rahikainen et al. (2013). The blank sample included both the alkali quantity initially existing in the lignin solution and the additional quantity of the 0.2 M NaOH. The blank was prepared and titrated similarly to the oxidized lignin solution. Linear estimation was used to obtain a titrant volume, V(HCl) for a given pH level, pH<sub>i</sub> (*i* = 11.7, 11.6, 11.5, ..., 2.0). The titrant volume consumed during the blank titration at a given pH level, V(HCl)<sub>blank</sub> at pH<sub>i</sub>, was subtracted from that consumed during the sample solution titration, V(HCl)<sub>sample</sub> at pH<sub>i</sub>. The corresponding negative charge of lignin (mmol g<sup>-1</sup>) at pH<sub>i</sub> was computed using the information of the volume difference, V(HCl at pH<sub>i</sub>), titrant concentration, and lignin mass in the sample solution. Negative charge at pH 6 is reported as an indication of anionic character.

### 2.2.3. Aromatic lignin

Aromatic lignin content of selected samples was detected as UV-lignin at 280 nm based on absorptivity value of 25.0 L g<sup>-1</sup> cm<sup>-1</sup> determined for SL.

### 2.2.4. Solubility

A simple procedure was used to evaluate the water solubility of the oxidized lignins. In the procedure lignin recovery (yield, %) from the solution by acidification and centrifugation was quantified as a function of pH range from 2.5 to 7. The acidification was done using 1 M HCl, where after the precipitate was separated by centrifugation at 10,000 g for 30 min and dried overnight at 105 °C. The recovery yield was computed based on the initial lignin content in solution.

## 2.3. Application testing

### 2.3.1. Flow properties

Two cement types, Megasementti CEM I 42,5 R (Finnsementti) and Plussementti CEM II B-M (S-LL) 42,5 N (Finnsementti) (shortly CEM I and CEM II) were used. CEM II is a blended cement containing 21–35% of limestone and slag whereas, CEM I does not contain any of those.

As a reference for the oxidized lignins the following commercial plasticizer products were used: WRDA 90D (Grace construction products), a conventional lignosulfonate plasticizer with dry solids of 30 wt-%; Glenium C151 or Glenium 51 (BASF) (shortly Glenium) and VB-Parmix (Finnsementti), all three polycarboxylate-based superplasticizers with dry solids of active matter of 15, 17 and 12 wt-%, respectively. A defoamer agent, tributylphosphate (TBF) with dosage of 2.5 wt-% on oxidized lignin was used in one of the concrete tests.

Plasticizing performance of the oxidized lignin solutions was evaluated by testing the flow properties of cement pastes, mortar and concrete. Cement pastes, containing 66 or 75 wt-% of CEM II or CEM I in water, respectively, were prepared with the oxidized lignin solutions or the commercial plasticizer products using efficient mixing by Heidolph D1AX 600 for 2+2 min. Lignin solutions or the commercial products were added last in the paste. Several dosages, in a range of 0.06–0.24 wt-% of the active matter on cement were used. The fluidity of cement pastes was studied by measuring the shear stress as a function of shear rate by using a rheometer, Bohlin Visco. Mortar was prepared using a standard sand mixture, CEM II, and water with the following mass ratio; 48.6:36.0:15.4. The fluidity of the mortar was studied using the Haegermann flow table (Ø 300 mm) method (DIN 1060) and a mold with a diameter of 100 mm. Concrete, 30-L (approx 60 kg) for each experimental point, was prepared according to EN1766 type C(0,40) with CEM II. This type of concrete has low content of fines, which makes the plasticizing challenging. Slump test was applied to evaluate the workability of the concrete (SFS-EN 12350-2).

### 2.3.2. Air content, hydration, and compression strength

Air content of fresh mortar and concrete was determined according to SFS-EN 12350-7. Cement hydration kinetics were followed by measuring the heat flow of the plasticized cement paste by a conduction calorimetry (TAM-Air). Compression strength and density of the matured concrete was measured after 28 days

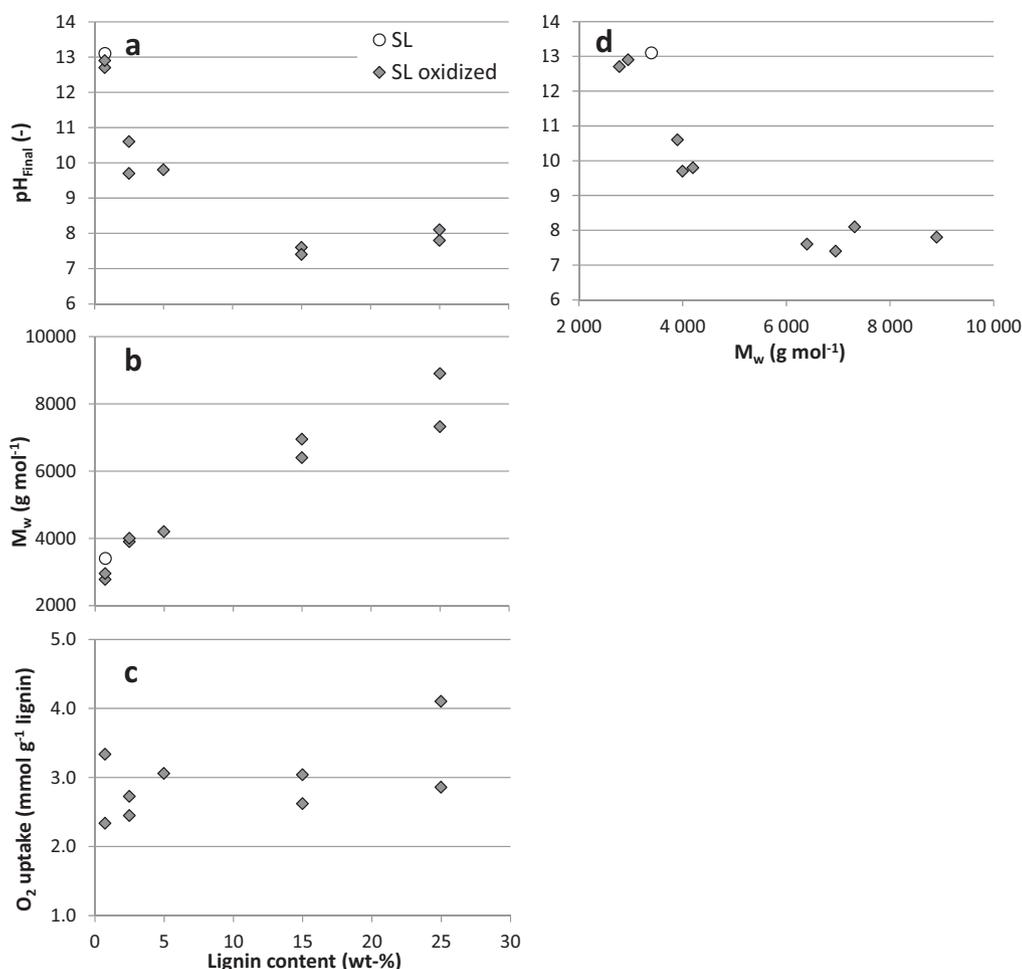


Fig. 1. (a) pH after the oxidation ( $\text{pH}_{\text{Final}}$ ), (b) molar mass ( $M_w$ ), and (c)  $\text{O}_2$  uptake as a function of lignin content in oxidation. (d) Relation between  $\text{pH}_{\text{Final}}$  and  $M_w$ .

according to EN 196-1. The air content of fresh concrete should be at minimum, since it reduces the density and strength properties of the matured concrete. The impact of one of the samples (SL constant pH 2ox), with and without a defoamer (TBF), on the air content and fluidity of concrete was tested.

### 3. Results and discussion

#### 3.1. Alkali- $\text{O}_2$ oxidation

The effect of the reaction parameters, lignin content (0.75–25 wt-%),  $\text{O}_2$  load (12–35 wt-% on lignin), and temperature (50–80 °C) was first screened by the preliminary experiments. Table 1 shows data of the preliminary oxidations. In Fig. 1a–c pH after the oxidation ( $\text{pH}_{\text{Final}}$ ), molar mass ( $M_w$ ), and  $\text{O}_2$  uptake are plotted as a function of lignin content. Fig. 1d illustrates the relation between  $\text{pH}_{\text{Final}}$  and  $M_w$ .

From Fig. 1a it can be seen that the higher the lignin content the lower the  $\text{pH}_{\text{Final}}$  until it is settled to a near neutral level (7.5–8) in the case of oxidation done at 15 and 25 wt-%. The decrease in pH is caused by the degrading reactions starting from the phenolates and consuming the major part of the oxygen in formation of the main products, muconic acid and oxirane structure, which are also very vulnerable to further oxidative degradation (Kuitunen et al., 2011). The decrease in pH is more pronounced the higher the concentration of the acidic products in a given volume of the lignin reaction solution.

In addition to the degrading reactions indicated by the pH drop, it was noted that the higher the lignin content the more condensed the lignin after oxidation (Fig. 1b). Increase in the molar mass was stronger the greater the decrease in pH, yet, the increase being further accelerated by the 25 wt-% lignin content (Fig. 1d). Only oxidation at very low lignin content (0.75 wt-%), typical for pulp oxygen delignification (Kalliola et al., 2011), led to actual depolymerization of lignin measured as reduced molar mass.

Despite the rather varying conditions applied to the preliminary oxidations,  $\text{O}_2$  consumption was fairly constant, 8–13 wt-% on lignin, which corresponds to uptake of 2.3–4.1 mmol g<sup>-1</sup> lignin (0.42–0.74 mol  $\text{O}_2$  mol<sup>-1</sup> lignin). Under the selected oxidation conditions there was no clear relation between the  $\text{O}_2$  uptake and lignin content (Fig. 1c) or accordingly between the  $\text{O}_2$  uptake and  $\text{pH}_{\text{Final}}$  or molar mass.

It appears that the most important factors contributing to lignin condensation and increase in molar mass are lignin concentration and the prevailing pH conditions in the oxidation. This is also supported by the fact that below pH 12, the hydroperoxide intermediates tend to protonate and decompose homolytically back to phenoxyl radicals, which can spontaneously combine by 5–5 coupling reaction (Chang and Gratzl, 1980; Kalliola et al., 2014). Already, moderately high lignin concentration favors the coupling reactions because the phenoxyl radicals are close to each other. In addition, the dissolution and diffusion of oxygen is hindered in viscous lignin–alkali solutions, which restricts the availability of oxygen species taking part in the degradation reactions. Condensation in viscous lignin solution by  $\text{O}_2$  under alkali conditions was

**Table 2**  
Impact of oxidation on soda lignin (SL) characteristics. Molar mass characteristics of commercial plasticizers.

Sample	$M_w$ ( $\text{g mol}^{-1}$ )	$M_n$ ( $\text{g mol}^{-1}$ )	$M_w/M_n$	$\text{O}_2$ uptake ( $\text{mmol g}^{-1}$ )	Negative charge at pH 6 ( $\text{mmol g}^{-1}$ )	UV-lignin (%) $a = 25^a$
SL	3880	2070	1.9	0.0	1.5	100
SL 15% ox	6400	3000	2.1	2.6	3.2	–
SL 15% i.ox	6950	2690	2.6	3.0	3.5	–
SL 25% 1ox	7320	2600	2.8	2.9	3.4	–
SL 15% 2ox	6270	2390	2.6	5.5	5.1	82
SL constant pH ox	4580	2020	2.3	6.9	6.5	64
SL constant pH 2ox	3200	1650	1.9	5.7	6.9	71
WRDA 90D	3000	1700	1.8	–	–	–
Glenium C151	15900	5100	3.1	–	–	–

<sup>a</sup> Absorptivity value of  $25.0 \text{ L g}^{-1} \text{ cm}^{-1}$  determined for SL.

already reported in an old patent (Lin, 1975) and could be partly reduced by optimizing the  $\text{O}_2$  load and reaction temperature.

It has also been observed that pH is the most important variable when producing vanillin from kraft lignin (Araújo et al., 2010). High alkaline pH, close to 14 is required both for the formation of vanillin and to maintain its yield, since at lower values of pH (<11.5) the vanillin oxidizes and degrades at a considerable rate. This observation also shows that it is crucial to maintain a highly alkaline pH to ensure the dissociation of the hydroperoxide intermediate. Only the hydroperoxide anion structure (pKa 12–13) rearranges to primary oxidation products, phenolic aldehyde/carbonyl structure (e.g., vanillin) being one of those (Chang and Gratzl, 1980; Sixta et al., 2006).

Since the negatively charged functional groups of the plasticizers induce the electrostatic repulsion between the cement particles, the alkali- $\text{O}_2$  oxidation was further developed in order to increase the negative charge, most preferable in a form of muconic acid structures in lignin polymer. Constant pH oxidation at pH 11.5 and sequential oxidation without or with the constant pH control in the second stage were applied for this purpose. The aim in the sequential oxidations was to first induce lignin condensation at 25 wt-% content during the initial stage (SL 25% 1ox) and thereafter at 15 wt-% content during the following more aggressive stage (SL 15% 2ox or SL constant pH 2ox) to increase the negative charge. Condensation by 5–5 coupling does not consume the phenolic groups (PhOH) in lignin, which are thus able to react with  $\text{O}_2$  in the next oxidation stage while being dissociated.

Data of the improved oxidations is shown in Table 1. In the case of SL 15% 2ox the total consumption of NaOH increased up to 41 wt-% on lignin when considering the NaOH requirements of both stages. The consumption of NaOH during the constant pH oxidations performed at 11.5 (SL constant pH ox) and at 13 after the initial oxidation (SL constant pH 2ox) was surprisingly high. The consumption of NaOH does not; however, necessarily reflect the real formation of carboxylic acids in the lignin polymer. Acidic, secondary oxidation products including  $\text{CO}_2$  are formed and they contribute to pH (Kalliola et al., 2011; Kuitunen et al., 2011) and consume NaOH. It is probably impossible to totally avoid the further oxidation of the primary oxidation products. The  $\text{O}_2$  uptake on lignin was also increased by the constant pH oxidations as the highly alkaline pH favored the oxidation of lignin rather than the secondary reactions.

### 3.2. Lignin characteristics

#### 3.2.1. Molar mass and charge

Selected oxidized lignin solutions, which showed good plasticizing performance in cement paste (results below) were characterized more carefully. Molar masses of the two commercial plasticizers were also determined (Table 2).

The results indicate that the characteristics of SL can be controlled by the oxidation parameters, and especially by pH. Thus, different kind of SL based plasticizer solutions in terms of molar mass ( $M_w$  3200–7320  $\text{g mol}^{-1}$ ) and negative charge (3.2–6.9  $\text{mmol g}^{-1}$ ) were produced (Table 2). All the other oxidation treatments except the 2-stage oxidation wherein the second oxidation was performed at constant pH 13 increased the molar mass ( $M_w$  3880  $\text{g mol}^{-1}$ ) and polydispersity (1.9) of SL. Oxidation at constant pH 11.5 hindered the condensation reactions if compared to those oxidations performed without pH control. Increase in polydispersity indicates that although the condensation reactions were prevailing some of the lignin fragments were also degraded. Molar masses of the commercial plasticizers differed greatly from each other, lignosulfonate being small ( $M_w$  3000  $\text{g mol}^{-1}$ ) and polycarboxylate being fairly large ( $M_w$  15,900  $\text{g mol}^{-1}$ ) with wide molecular weight distribution. Yet the copolymer polycarboxylates are more linear in nature than the lignosulfonates (Uchikawa et al., 1997).

The total negative charge at pH 6 in the oxidized lignin solutions determined by potentiometric titration was more than doubled when comparing to that of un-oxidized SL solution (1.5  $\text{mmol g}^{-1}$ ). As described above the negative charge can be arisen from the carboxylic functionality in lignin polymer or from the acidic, small molecular reaction products of lignin. In addition, part of the negative charge may be originated from the reduction products of  $\text{O}_2$ . Protonation of superoxide anion ( $\text{O}_2^{\bullet-}$ ) to form hydroperoxyl radical ( $\text{HOO}^{\bullet}$ ) takes place under pH 6, as the superoxide anion has a pKa value of 4.8 (Gratzl, 1992).

According to UV280 measurements, 82–71% of the aromatic structures in SL remained after the improved oxidations, thus 18–29% degraded. The content of aromatic hydroxyl groups in SL was recently quantified by  $^{31}\text{P}$  NMR to be 3.4  $\text{mmol g}^{-1}$  (Liitiä et al., 2014). Thus, assuming that the decrease in UV absorbance is due to degradation of phenolic structures, the quantity of the degraded PhOHs in SL would correspond to 0.6–1.0  $\text{mmol g}^{-1}$ . If the degradation only leads to the formation of muconic acid structures in lignin polymer, it would increase the negative charge by 1.2–2.0  $\text{mmol g}^{-1}$ . Yet the increase in negative charge measured directly from the treatment solutions of the improved oxidations was almost twofold more. This indicates that part of the primary oxidation products were further oxidized to secondary products, thus increasing the overall amount of the carboxylic acid functionalities. Since, a clear correlation is seen between the  $\text{O}_2$  uptake and negative charge at pH 6, a significant part of the charge may originate from other acidic moieties than carboxylic acids bound to lignin.

#### 3.2.2. Solubility

Fig. 2 illustrates the recovery yield of SL and oxidized SL as a function of pH. The oxidation increased lignin solubility, which is desirable for the dispersing and plasticizing applications. SL is

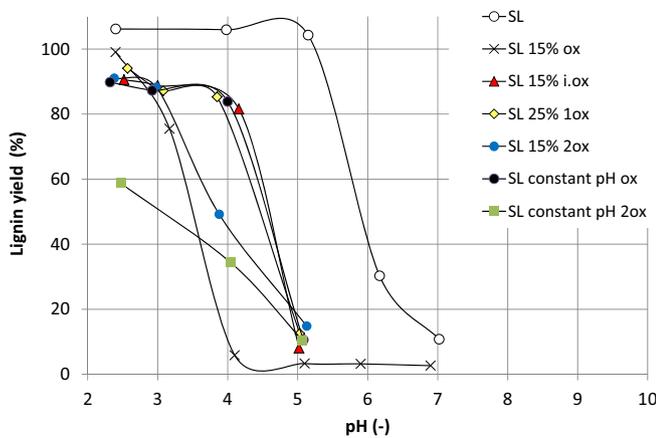


Fig. 2. Impact of oxidation on soda lignin (SL) solubility: lignin yield as a function of pH.

soluble only above pH 7, while the oxidized SL with increased molar mass is soluble above pH 4–5. Part of the lignin material in sample SL constant pH 2ox could not be recovered at pH 2.5.

It seems that the increase in charge in lignin polymer is enough to enhance its solubility considerably even though the molar mass of the polymer is high. The results also indicate that oxidized lignins would be suitable for dispersing application in slightly acidic pH range.

Recovery of lignin material by acidification may alter its structure, for example muconic acids are reported to form lactones via a ring closure reaction under neutral or acidic conditions (Gierer and Imsgard, 1977; Chang and Gratzl, 1980; Pieken and Kozarich, 1990). More specified characterization of the functionalities in oxidized lignin material was considered not to be necessary, since the solutions were to be used as such for the plasticizing applications.

### 3.3. Application testing

#### 3.3.1. Flow properties

Plasticizing performance of the oxidized lignin solutions was evaluated stepwise proceeding from the easiest media to the most demanding. The initial testing was done in cement pastes (Fig. 3), thereafter in mortar (Fig. 4) and finally the performance of selected samples was verified in concrete (Fig. 5).

Oxidized SL solutions decreased the yield stress in pastes made of both cement types, CEM I and CEM II (Fig. 3a and b) demonstrating the plasticizing performance. With a dosing of 0.20 wt-% on cement, most of the oxidized lignins provided roughly the same yield stress than the commercial polycarboxylate, Glenium with dosing of 0.06–0.07 wt-%. Differences between the oxidized SLs seemed rather small, but the constant pH oxidation indicated to be a means of producing efficient plasticizer for both cement types. The commercial liginosulfonate, WRDA 90D required approximately the same dosing than SL constant pH ox to yield an equal effect. Un-oxidized SL solution functioned as well, yet, with a twofold dosing when compared to SL constant pH ox.

The evaluation of the oxidized SLs versus the commercial products was continued in mortar (mixture of CEM II, sand, and water) using a constant dosing of 0.40 wt-% on cement. Fig. 4 presents the Haegermann flow value and air content of the fresh mortar. Now the differences between the samples are more noticeable. A higher value represents better flow properties. The production of the oxidized lignin by the 2-stage or constant pH oxidation or the combination thereof offered better plasticizing effect when compared to those produced by a single-stage oxidation. Yet all of the oxidized SLs and also the un-oxidized were superior to WRDA 90D.

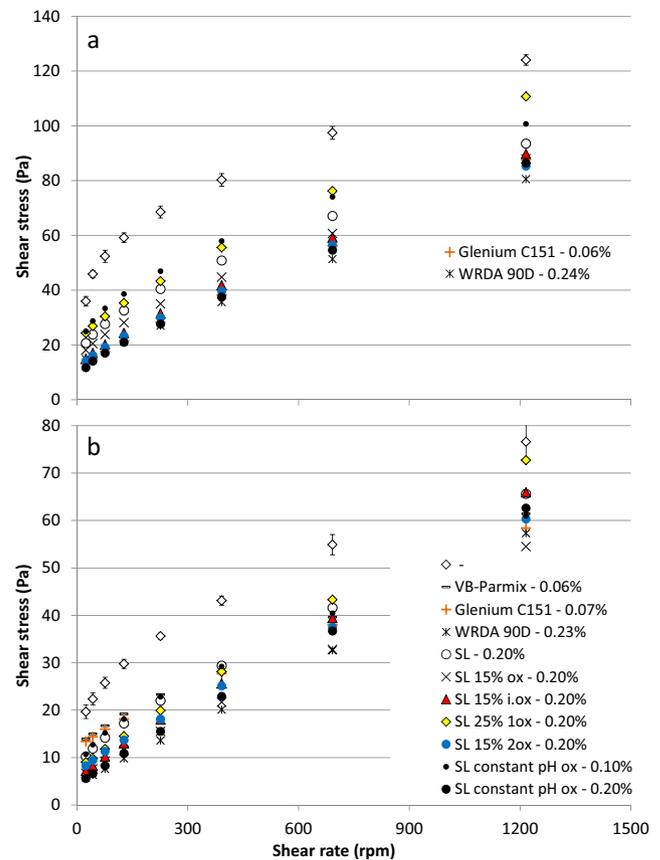


Fig. 3. Shear stress of cement pastes made of (a) CEM I (70 wt-%) and (b) CEM II (66 wt-%) as a function of shear rate. Commercial products or soda lignin (SL) solutions (un-oxidized or oxidized) used as plasticizers with dosages of 0.06–0.23 wt-% on cement. VB-Parmix tested only in the case of CEM II (b).

In addition, the performance of SL constant pH ox and SL constant pH 2ox was close to that of the other polycarboxylate-type superplasticizer, VB Parmix. The impact of the plasticizers on the air content of the testing medium is discussed below.

The performance of the three samples, produced by the improved oxidations, was finally evaluated in concrete using a slump test. The higher the slump the better the flow properties. Fig. 5a shows that these samples provided excellent plasticizing effect in concrete even with the dosage of 0.40 wt-% on cement. Their performance was again clearly better than that of WRDA 90D. The 0.40 wt-% dosage of the oxidized SL provided roughly the same

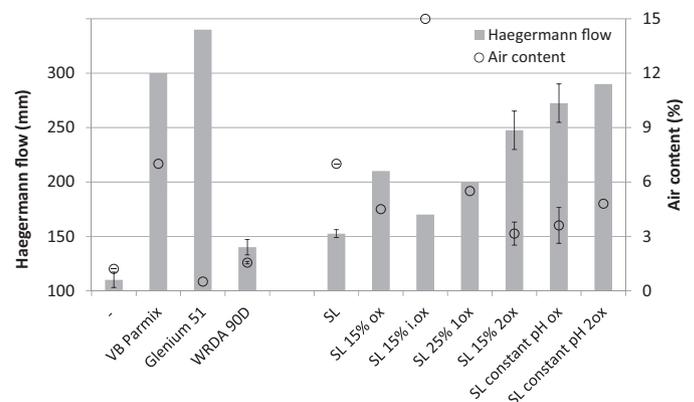
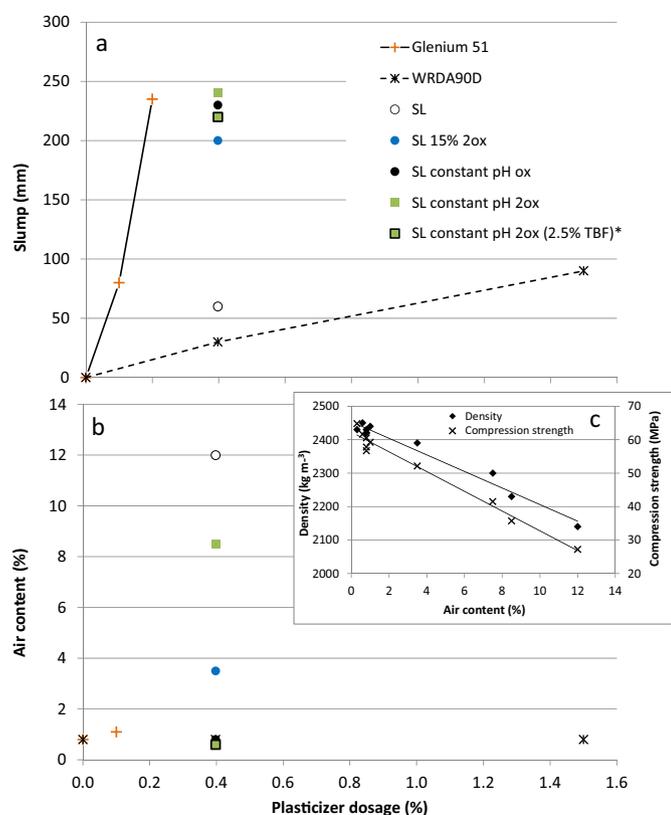


Fig. 4. Haegermann flow and air content of fresh mortar. Commercial products or soda lignin (SL) solutions (un-oxidized or oxidized) used as plasticizers with dosage of 0.40 wt-% on cement.



**Fig. 5.** (a) Slump and (b) air content in fresh stage concrete. (c) Impact of air content on compression strength and density of matured concrete. Commercial products or soda lignin (SL) solution (un-oxidized or oxidized) used as plasticizers with dosage of 0–1.5 wt-% on cement. \*Defoamer agent (TBF 2.5% on lignin) used with SL constant pH 2ox.

plasticizing efficiency as 0.20 wt-% dosage of Glenium, which can be considered to stand for an excellent performance. In one of the experiments, defoamer agent (TBF 2.5% on lignin) was used with SL constant pH 2ox. It was seen that the plasticizing effect of SL constant pH 2ox did not change even though the air introduction was prevented. This result suggests that the defoamer does not affect the plasticizing performance of the oxidized SLs, and the plasticizing performance of the oxidized SLs is not due to the increased air content.

The samples SL constant pH ox and SL constant pH 2ox showing the best performance as plasticizers had relative low  $M_w$  (4580, 3200 g mol<sup>-1</sup>) and posed high negative charge at pH 6 (6.5, 6.9 mmol g<sup>-1</sup>). Recently, different fractions of soda-AQ lignin isolated from the spent liquor were tested for their

plasticizing performance in mortar (Takahashi et al., 2014). Similarly, the results suggested that the fraction having a relatively low  $M_w$  (4000–5000 g mol<sup>-1</sup>) was the most advantageous to bring adsorption on the cement particles and showed the highest plasticizing performance. The fraction also had a high content of PhOH (2.3–2.5 mmol g<sup>-1</sup>), which hold charge while being dissociated in the highly alkaline media.

### 3.3.2. Air content, hydration, and compression strength

The oxidized SLs were observed to introduce air in mortar (Fig. 4). However, the amount was less than in the case of VB Parmix and un-oxidized SL. When evaluating the oxidized lignins in concrete, one of the samples, SL constant pH ox showed surprisingly good performance while it did not introduce air in the mixture, which was the behavior also with the commercial plasticizer products (Fig. 5b). Typically, and as well here, the air content in fresh concrete correlates with the density and strength properties of the matured concrete (28 d) (Fig. 5c). Thus, in the case of SL constant pH ox (no extra air), the compression strength was in line with that of concrete plasticized using the commercial products (Table 3). By using a small amount of a defoamer also with the other samples, the air content in concrete could be reduced ensuring sufficient properties in the matured concrete. Inclusion of defoamer is a common practice with lignosulfonate products (Taylor, 1997) which without the agent can cause air entrainment in concrete (Chang and Chan, 1995; Lora, 2008).

On contact with water, cement undergoes several reactions and forms many hydration products via complicated mechanism depending on the composition of the concrete mixture (Stark, 2011). The hydration is typically investigated by measuring the heat flow released from the material as a function of time. Typically, it is desirable that the additional agents introduced in concrete do not slow down the hydration. However, now the hydration kinetics were affected by the lignosulfonate, WRDA 90D. It was also affected by the oxidized SLs to some extent (Table 3), but there was no correlation between the retarded hydration and the compression strength of the matured concrete, which indicates that the oxidized lignin is already a promising alternative to lignosulfonate products. It was only the increased air content that had the inverse correlation with the compression strength.

The setting time of cement paste has been reported to depend roughly on the ionic functional group concentration (carboxylic and sulfonic) in the aqueous phase of the cement paste (Ramachandran et al., 1998 Yamada et al., 2000). The carboxylic functionality rich secondary oxidation products of the oxidized SL solutions likely remain more easily in the liquid phase than the polymeric lignin. In the liquid phase these small compounds could interact with the forming hydrate particles, and thus alter the cement hydration.

At the moment, any application wherein lignin has technological potential is extremely interesting. Previously, modified

**Table 3**

Test results of concrete plasticized using commercial products or un-oxidized or oxidized soda lignin (SL) solution.

Sample	Dose (%)	Heat (J g <sup>-1</sup> cement)			Density (kg m <sup>-3</sup> )	Compression strength, 28 d (MPa)
		24 h	72 h	168 h		
-	0	196	275	305	2420	56.7 ± 1.0
Glenium 51	0.20	162	258	283	2430	64.8 ± 1.1
WRDA 90D	0.40	45	76	86		
WRDA 90D	1.50				2430	60.5 ± 0.6
SL	0.40	53	108	119	2140	27.2 ± 1.7
SL 15% 2ox	0.40	22	106	123	2390	52.1 ± 0.8
SL c. pH ox	0.40	65	215	279	2420	57.8 ± 0.3
SL c. pH 2ox	0.40	53	207	263	2230	35.7 ± 1.4
SL c. pH 2ox (2.5% TBF) <sup>a</sup>	0.40	39	187	247	2450	61.6 ± 0.9

c: Refers to constant.

<sup>a</sup> Defoamer agent (TBF 2.5% on lignin) used with SL constant pH 2ox.

alkali lignins have not been reported of being tested in comparison to the polycarboxylate-based superplasticizers in concrete. The method developed in this study to produce a lignin-based plasticizer is rather simple and the results of the application testing are very promising. Yet in further investigations it is important to emphasize more on the structure–function relationship of the oxidized lignin as well as on its impact on the cement hydration.

#### 4. Conclusions

A simple alkali-O<sub>2</sub> oxidation method to control the polymerization and solubilization of soda lignin was developed. The oxidized lignin solutions were applied as ready-to-use products for concrete plasticizing. They showed superior performance to the commercial lignosulfonate and provided equal plasticizing efficiency by 0.4 wt-% dosing than the synthetic superplasticizer by 0.2 wt-%. The best performing oxidized lignin solution did not even introduce air in concrete. Hydration kinetics was affected by the oxidized lignins, but this did not reduce the compression strength of the matured concrete. Oxidized lignins may provide a sustainable and techno-economically feasible option for future superplasticizer technology.

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