

Oxidation of Lignin from *Eucalyptus globulus* Pulping Liquors to Produce Syringaldehyde and Vanillin

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ABSTRACT: Lignin is one of the main components of the pulping liquors and a potential source of high-added-value chemicals. The aim of this work is to evaluate the potential of industrial *Eucalyptus globulus* sulfite liquor and kraft liquors (collected at different stages of processing before the recovery boiler) for the production of syringaldehyde (Sy) and vanillin (V) by oxidation with O₂ in alkaline medium. Oxidations were performed in a jacketed reactor with controlled temperature and pressure by (1) direct reaction of pulping liquors and (2) reaction of kraft lignins isolated from liquors. Lignins produced by LignoBoost technology were also evaluated. The products profiles were established, as well as the yields, temperature and O₂ uptake during the reaction. Sulfite liquor is the best raw material leading to the highest yield by direct oxidation (33 kg of Sy and 15 kg of V per lignin ton), followed by thin kraft liquor (KL) which, compared to evaporated and heat treated liquors, also led to lower proportion of byproducts such as syringic and vanillic acids. Lignin isolation benefits yields and selectivity but just in the case of KL, leading to 28 kg of Sy and 12 kg of V per ton of lignin. The performance of the materials studied is primarily affected by the lignin characteristics but also by the inorganic content of the pulping liquors, whereas no effect of the carbohydrates was noticed.

1. INTRODUCTION

Lignin is a three-dimensional phenolic macromolecule that has a structural function in plant cell walls. The typical hardwood lignin is a copolymer of coniferyl and sinapyl alcohols (Figure 1) being usually referred as “guaiacyl-syringyl lignin”, although

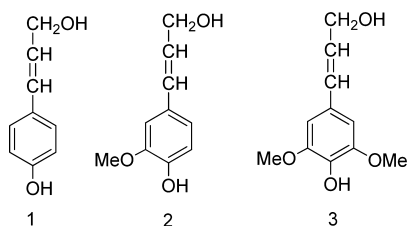


Figure 1. *p*-Coumaryl (1), coniferyl (2), and sinapyl (3) alcohols, the precursors of *p*-hydroxyphenyl, guaiacyl, and syringyl moieties of the lignin structure, respectively.

the *p*-hydroxyphenyl unit, derived from *p*-coumaryl alcohol (Figure 1), is also detected in some hardwoods such eucalyptus, birch,¹ and aspen.² Biosynthesis of softwood lignin involves exclusively coniferyl alcohol, being referred as “guaiacyl lignin”.

The aim of the pulping processes is to delignify the wood matrix by promoting the lignin dissolution in pulping liquor, liberating the cellulose and a fraction of the original hemicelluloses. The world dominant process to produce pulp for papermaking is kraft pulping, whereas the sulfite process accounts for about 5% of the world chemical pulp production.³ However, acid sulfite pulping of *Eucalyptus globulus* wood has significance in South Africa, Portugal, and Spain for production of total chlorine free bleached dissolving pulps and pulps for papermaking. Concerning *Eucalyptus* kraft pulp, the production is about 30 million ton of bleached and air-dried pulp/year (source: Pöyry, 2013).

Pulping operations are highly integrated and dependent on pulping liquor, which is concentrated and burned in the recovery boiler, supplying energy to the pulp mill operations with simultaneously recovery of pulping chemicals.⁴ In some mills, part of liquor/lignin produced is diverted to increase the pulp production capacity (situations where recovery furnace is limited) or to upgrade its organic components, mainly lignin. The largest volume of lignin produced worldwide comes from wood pulping; the lignin generated is known as liginosulfonates or as kraft lignin depending on the process used, sulfite or kraft pulping, respectively. Moreover, the emerging biorefining activity is also producing side streams containing lignin that claims for valorization due to environmental and economical issues. Lignin has a large number of practical and valuable applications.⁵ One of the most well-known lignin applications is the production of vanillin (V, 4-hydroxy-3-methoxybenzaldehyde),^{6–10} an important ingredient in highly consumed products and an intermediate of fine chemicals.^{11–13} Until about the 70s, oxidation of softwood sulfite liquor for V production was, for some pulp companies, an important practice.¹¹ However, lignin has become less attractive as a raw material for V synthesis due to the further developments in the pulp industry¹¹ such the substitution of softwoods by hardwoods as preferable raw materials. Alkaline oxidation of the hardwood lignin gives mostly syringaldehyde (Sy, 4-hydroxy-3,5-dimethoxybenzaldehyde) and lower yields of V. This was taken as a disadvantage since the process (reaction and separation schemes) and market were focused on V; separation technologies to recover V and Sy from the oxidation

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mixture were not available at that time and industry was not aware of the importance of Sy as an intermediate for specialties synthesis. Therefore, no further industrial actions were undertaken considering this subject.

Although some V is still made from lignin (Borregaard remained as a producer of V from lignosulfonates) most synthetic V is obtained from petrochemical derived guaiacol, supplying about 85% of the world needs.¹⁴ Sy has been synthesized from gallic acid, pyrogallol, and V itself.¹⁵

Recently, the demand for chemicals from renewable sources has breathed new life on the lignin route to produce V. Furthermore, there is an increasing interest also for homologous compounds such as Sy,^{16,17} for direct applications,¹⁸ or as precursors of fine chemicals and drugs.^{15,19,20}

Sy can be produced from oxidative depolymerization of lignin from hardwood^{21–23} or from annual plants.²⁴ Considering the current availability of these lignin types in the side streams of pulp industries and biorefineries, this could be an important approach in view of lignin exploitation for high-added value applications.

As far as is concerned, *E. globulus* kraft lignins (isolated and nonisolated) from different stages of the industrial kraft liquor processing have never been explored to the production of low molecular weight phenolics by oxidation with O₂.

The aim of this work is to contribute to the evaluation of the potential of *E. globulus* lignin as source of Sy and V. Lignins from two pulping processes (kraft and sulfite), three kraft liquor processing stages (at the outlet of digester, after evaporation and after heat treatment), and different isolation process (Lignoboost process²⁵ laboratory isolation and no isolation) are studied by oxidation with O₂ in alkaline medium. For each, the profiles of Sy, V, and other minor products are established, as well as the yields, selectivity, time to maximum, temperature profile, and oxygen uptake during the reaction.

2. MATERIAL AND METHODS

2.1. Pulping Liquors and Lignins. *Eucalyptus globulus* kraft liquors were collected at different stages of a Portuguese bleached kraft pulp plant: at the outlet of kraft digester (thin kraft liquor, hereby referred as KL, dry solids, 21.6% w/w_{liquor}), after the evaporation stage (EKL, dry solids, 79.4% w/w_{liquor}), and after heat treatment (HTEKL, dry solids, 83.9% w/w_{liquor}), just before the recovery furnace. Industrial spent liquor from magnesium-based acidic sulfite pulping of *Eucalyptus globulus* was collected after the evaporation step in a Portuguese sulfite pulp mill and it is hereby referred as sulfite liquor (SL, dry solids, 68.0% w/w_{liquor}).

Two hardwood kraft lignins isolated by the LignoBoost process were studied: one from *Eucalyptus globulus* (EgLBoost) was supplied by a Portuguese mill of bleached kraft pulp, and another from a mixture of Northern Europe hardwoods (HLBoost) was supplied by Innventia AB, Sweden.

2.2. Lignin Isolation. Kraft lignins were isolated from respective liquors by slow acidification with 5 M H₂SO₄ (95–97%, Fluka), until pH 5. The mixture was maintained under agitation and at low temperature (10 °C) during acidification. The precipitated lignin was recovered by centrifugation, washed two times with distilled water, and freeze-dried. Lignins isolated from kraft liquors were designated as KLLig, EKLLig, and HTEKLLig. The yields on lignin recovered from this isolation procedure were 45% for KLLig, 24% for EKLLig, and 16% for HTEKLLig, calculated with reference to the total nonvolatile solids on the respective liquors.

2.3. Characterization of Pulping Liquors and Lignins.

2.3.1. Total Nonvolatile Solids and Ash Content. Pulping liquors were analyzed for nonvolatile solids as previously described²⁶ with some modifications. Briefly, 20.0 mL of KL was added to prior dried crucibles containing calcinated and sieved sand. For the other pulping liquors, a weighted portion of liquor was diluted with water to 20.00 mL. The solution was added to crucibles with sand as described for KL. The dilution with water was performed for the high viscous liquors (EKL, HTEKL, and SL) to ensure the wetting of the sand by the liquid avoiding projection of the material during the heating period and consequent losses. The crucibles with liquors were dried at 105 °C to constant weight. After that, the crucibles were submitted to incineration (SALFOR, Salmon Fornos) at 550 °C for 8 h for ash quantification. Ashes of isolated lignins were also gravimetrically quantified after incineration of about 1 g of material. The relative error percentage was lower than 5%.

Concerning pulping liquors, a second approach was undertaken for ash quantification: the incineration of freeze-dried liquors as described for isolated lignins.

2.3.2. Carbohydrate Content. For carbohydrate content analysis, the freeze-dried sulfite and kraft liquors, and isolated lignins were submitted to acid methanolysis as previously described²⁶ with some modifications. About 10–15 mg of sample was suspended in 2 mL of 2 M HCl methanolic solution, and the acid methanolysis was performed at 100 °C. After 4 h, 100 μ L of pyridine ($\geq 99.0\%$, Sigma–Aldrich) and 1.00 mL of sorbitol solution 0.1 mg/mL ($>98.0\%$, Sigma–Aldrich) were added and the mixture was evaporated under reduced pressure. Then, the dried methanolysates were dissolved in 150 μ L of pyridine, 150 μ L of *N,O*-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA, $\geq 99\%$, Fluka) and 50 μ L of chlorotrimethylsilane (TMS, $\geq 99\%$, Fluka), maintaining the reaction mixture at 80 °C for 30 min, to convert the partially methylated monosaccharides to trimethylsilylated derivatives. The products were identified by GC-MS and quantified GC-FID with the same equipment and experimental conditions as already described in literature,²⁷ with minor modifications in the temperature program: 100–175 °C at 4 °C/min and 175–290 °C at 12 °C/min. Quantification was carried out with calibration curves built with standards for each monosaccharide: rhamnose (99%, Merk), xylose (99%, Merk), galacturonic acid ($\geq 97\%$, Fluka), glucose (99.5%, Sigma–Aldrich), galactose ($>99\%$, Acros Organics), manose ($>99\%$, Acros Organics), and arabinose ($>99\%$, Acros Organics); glucuronic acid (98%, Alfa Aesar) was the standard used for 4-*O*-methyl-glucuronic acid quantification.

2.3.3. Nitrobenzene Oxidation. Freeze-dried pulping liquors and isolated lignins were submitted to alkaline nitrobenzene oxidation (NO) at analytical scale using small stainless steel reactors, as already described in the literature concerning reaction conditions and products analysis.²⁸

2.4. Oxidation Experiments and Products Analysis. Oxidations with O₂ in alkaline medium were performed in a Büchi AG laboratory autoclave with a capacity of 1 L (model BEP280 type II, Switzerland). The heating and control of the reactor temperature was assured by a Haake thermostatic bath (model N2-B, Karlsruhe, Germany). The temperature inside the reactor was measured using thermocouples type K, and a pressure transducer (Kulite model XYME-190 M G, Leonia, USA) was used to assess total pressure. The flow rate of O₂ was measured by means a mass flow meter EL FLOW (Bronkhorst High-Tech B.V.) model F-201C-FAC-11-V and expressed as a

standard cubic centimeter per minute (sccpm). Reaction mixture samples were collected at preset time intervals by means an electro valve (Asco Netherlands) and a universal fractions collector Eldex. The signals of the thermocouple, flowmeter, and pressure transducer were recorded by means an acquisition board and a LabView program. For each oxidation essay, about 30 g of lignin or the corresponding weight of total nonvolatile solids for sulfite liquor were dissolved in 300 mL of an alkaline solution containing 40 g of NaOH. For black liquors (which are already alkaline), the weight corresponding to a total 30 g of nonvolatile solids was diluted to 300 mL with water, and the pH was measured. Since the values found were in the range of 11–13, NaOH was added (between 10 and 20 g) to reach pH values higher than 13.8. The resulting mixture was diluted to 500 mL and introduced into the preheated reactor. Pressurization of the reactor was done with nitrogen until 6.8 bar. The reaction time started when the temperature reached 120 °C. At this time, O₂ was introduced starting the data acquisition. The total pressure in the reactor was kept at 9.8 bar with a partial pressure of O₂ of 3.0 bar by continuous supply of O₂ along the time. At each sampling time, the electro valve was first opened to clean the sampling line and immediately after that 2 mL of the reaction mixture was collected in a clean tube. This operation was repeated until 110 min of reaction. The analysis of the products was performed by the procedure and equipment/conditions as previously published in the literature.^{21,28}

3. RESULTS AND DISCUSSION

3.1. Composition of Sulfite and Kraft Liquors and Lignins. Pulping liquor contains dissolved organic material (removed from the wood during pulping), namely degradation products of lignin, carbohydrates, and extractives and the residual inorganic pulping chemicals. In kraft liquor, colloidal fragments of lignin are stabilized by ionized phenolic and carboxylic acid groups (stability is pH dependent), whereas carbohydrates (mainly from hemicelluloses) are present as oligosaccharides²⁹ and as saccharinic acids. In general, lignin from sulfite liquor has high molecular weight than kraft lignin, and it is present as sulfonation products.³ Table 1 presents

Table 1. Inorganic and Carbohydrate Contents of *E. globulus* Sulfite and Kraft Liquors and Isolated Lignins

	sample	inorganic content % w/w _{solids}	total carbohydrates % w/w _{solids}
liquors	KL	45.7	6.44
	EKL	49.8	4.35
	HTEKL	49.7	4.26
	SL	8.49	9.84
lignins	KLlig	12.6	5.63
	EKLlig	8.51	6.84
	HTEKLlig	1.72	12.2
	EgLBoost	0.30	2.10
	HLBoost	0.71	3.40

inorganic and carbohydrate contents in the pulping liquors and in the isolated lignins. Inorganic content is significantly lower in sulfite liquor comparatively to kraft ones. From the technological point of view this could be an advantage if the utilization of liquor as raw material for oxidation is envisaged, due the lower probability of formation of incrustations in the reactor and tubing. However, for this liquor (as for isolated

lignins) 40 g of NaOH must be added per 60 g of solids to achieve the pH for enolization of phenolic groups (necessary for the oxidation to occur).

Besides inorganics, sugar and lignosulfonates, other components such as pyrogallol, gallic acid, and β -sitosterol were previous reported in SL in very low percentage.³⁰ In black liquors,⁴ and particularly in kraft liquor from *E. globulus*,³¹ the solids are also composed by aliphatic carboxylic acids, some of those volatile (acetic acid, for example) and, therefore, not accounting for solids as quantified in this work. Lignins isolated by the LignoBoost process showed a rather low content of inorganics and carbohydrates, which is one of the main features of this technology.²⁵ Comparatively to original kraft liquors, the lignins isolated at the laboratory reveal a lower content of inorganic material, in particular HTEKLlig. However, for carbohydrate content the same trend is not observed.

Two remarks can be draw from the results on carbohydrate content: first, a considerable carbohydrates fraction of kraft liquor remains with lignins isolated at the laboratory, which could be attributed to a coprecipitation of the liquor polysaccharides, already reported in the literature.²⁹ Second, the carbohydrate contribution for precipitated material (isolated lignins) increase about twice with liquor heat treatment (Table 1, HTEKLlig). The aim of the heat treatment is the viscosity reduction of the evaporated liquor (around 80% dry solids) by partially disrupting the lignin structure, enhancing the rheological proprieties of the liquor at the recovery furnace.³² Therefore, smaller fragments of lignin are certainly generated, increasing its solubility in water and promoting its removal during the precipitated lignin washing (at the isolation procedure). In accordance, the yield of HTEKLlig was the lowest of the three (about 16%, section 2.2). However, the carbohydrate content of this material is about twice that of KLlig and EKLlig, suggesting that a resistant fraction of carbohydrates remains coprecipitated or even linked with lignin. In accordance, carbon–carbon linkage between sugars and lignin promoted by alkali was previously reported in literature.³³

3.2. Characterization of Lignins by NO. The results of analytical NO of pulping liquors and isolated lignins are depicted in Figure 2. NO analysis is based on the yields and types of simple phenolic aldehydes and acids produced. Results for *p*-hydroxybenzaldehyde (Hy), V, vanillic acid (VA), Sy, and syringic acid (SA) are reported to nonvolatile solids weight after deducting ashes and carbohydrates, hereafter designated as “lignin”. The contribution of lignin condensed structures (those ones with C–C linkages between aromatic rings) to the production of aldehydes toward NO is very limited.^{34–36} Guaiacyl units give V, and syringyl units give Sy as major products; *p*-hydroxyphenyl units yield Hy. Therefore, NO provides information on the relative amounts of the uncondensed *p*-hydroxyphenyl, guaiacyl, and syringyl units that constitute the original lignin, an important parameter for lignin characterization.³⁴ High yield and high aldehyde/acid ratio are advantages in the perspective of this route of lignin valorization.

Among pulping liquors, KL presents the highest Sy yield followed by SL. However, KL also gives a higher relative content of SA. This result is probably related with a higher content of carbonyl group at C α (benzyl carbon) of lignin which leads to the corresponding carboxylic acid.³⁷ It may be suggested that, in the case of SL, there is a lower probability of this occurrence due to the sulfonation of C α of phenyl-

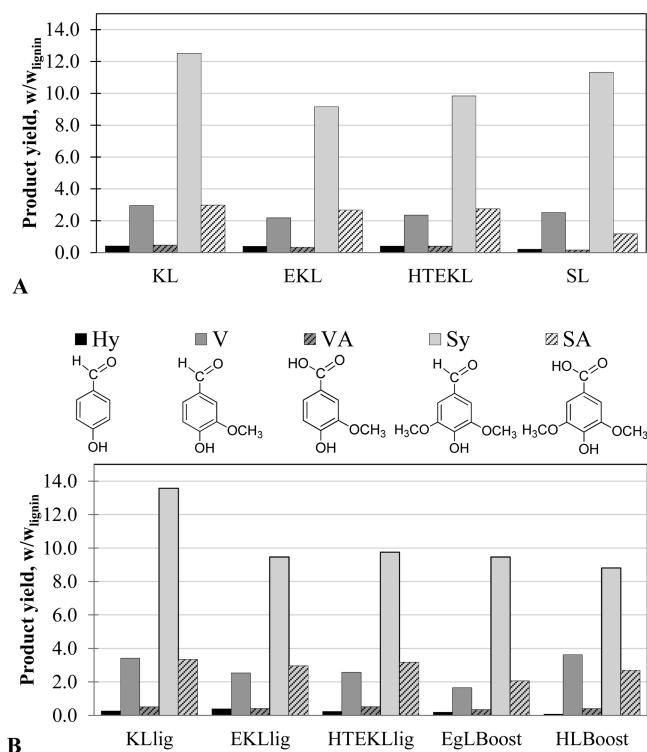


Figure 2. NO results of pulping liquors (A) and isolated lignins (B).

propanoid unit of lignins during pulping (one of the main reactions of sulfite pulping).³ The ratio Sy/SA is near 9 for SL, whereas for all other liquors and lignins the value is between 3 and 4.6. As far as NO could anticipate the results on oxidation with O₂ in alkaline medium, from the point of view of selectivity for aldehydes, the SL is advantageous over kraft liquors and isolated lignins.

After the evaporation process of KL, the content of aldehydes markedly decreases, while acids remain nearly constant for liquors (Figure 2A) and respective lignins (Figure 2B). The highest decrease on NO yield occurs from KL to EKL and KLlig to EKLLig confirming that lignin condensation was promoted during evaporation process, whereas no change was noticed with the heat treatment (HTEKL and HTEKLlig). This observation suggests that the resulting splitting of lignin occurring during liquor heat treatment would balance any eventual heat-promoted increase on condensation. Small differences on total yields were noticed between each kraft liquor and its respective isolated lignin.

Comparatively to LignoBoost lignins, KLlig presents a higher total yield (21% against 14% for EgLBoost and 16% for HLBoost), indicating higher content on noncondensed structures, which is considered an advantage for oxidation with O₂. This difference is probably related with isolation process rather than with pulping and species, since KLlig and EgLBoost are both *E. globulus* kraft lignins. On the other hand, HLBoost shows the lowest syringyl/guaiacyl ratio (near 3) reflecting the nature of Scandinavian hardwoods, which typically present a lower proportion of syringyl units than *Eucalyptus* species.¹

From the overall results, carbohydrate and ashes fraction in pulping liquors and isolated lignins does not seem to affect the conversion by NO.

3.3. Oxidation of Liquors and Isolated Lignins with O₂ in Alkaline Medium.

The oxidation of pulping liquors and

lignins were carried out in 2 M NaOH or the equivalent to pH ≥ 13.8 in the case of pulping liquors. All of the oxidation experiments began at 120 °C and pO₂ 3 bar (total pressure of 9.8 bar) with constant oxygen supply along the reaction time. The product yields (weight of compound per 100 g of lignin after deducing ashes and carbohydrates) and the pH profiles are presented for *E. globulus* liquors in Figure 3, panels A and B and for lignins in Figure 4, panels A and B. The results on the main compounds are summarized in Figure 5.

The main phenolic products identified in the oxidation mixture were Sy, V, and the respective carboxylic acids, SA and VA, all arisen from the splitting of Ca-C β ³⁷ of lignin syringyl and guaiacyl units, respectively. Moreover, the products from C β -C γ cleavage, acetovanillone (VO), and acetosyringone (SO)³⁸ were also identified, as well as Hy, in minor quantity. The progress of the products yield with reaction time does not significantly differ among the liquors and lignins: during oxidation Sy reaches to a maximum yield at reaction time between 15 and 20 min followed by a decrease for longer reaction times. For V, the time to maximum is in general, superior and, after the maximum, a smooth drop occurs when compared with Sy. These observations are in accordance with the different reactivity of syringyl and guaiacyl nuclei already stated in literature³⁹ and confirmed for other lignins.²¹ The oxidation yield obtained for each product is the net result of its production and degradation.

Data depicted in Figures 3C and 4C show also the temperature and O₂ uptake profiles in the oxidation for liquors and lignins, respectively. As a general trend, the maximum temperature and O₂ uptake during oxidation is higher for isolated lignins than for the respective liquors, probably due to the higher extent of lignin reaction in the formers, revealed in the yield (as depicted in Figure 5). Concerning the temperature profile, it is clear that the maximum is coincident with those of phenolics production rate in both liquors and lignins. However, a lower uptake of O₂ is observed in the direct oxidation of kraft liquors, which could be a consequence of its high content on inorganic compounds (Table 1). Inorganic components of kraft liquors are mainly NaOH, NaHS, Na₂CO₃, K₂CO₃, and Na₂SO₄, contributing to high ionic strength of the solution, thus decreasing the solubility of O₂ in the reaction medium^{40,41} and finally reducing the consumption during oxidation and limiting, by this way, the products formation. In the corresponding isolated lignins, ashes content are considerably lower: 4, 6, and 29 times for KLlig, EKLLig, and HTEKLlig, respectively. Moreover, it is quite probable that low molecular weight organic compounds, including lignin derivatives (always present in pulping liquors, but certainly at very lower level in isolated lignins) quickly undergo degradation in alkaline media with the concomitant CO₂ production. This would contribute to the total pressure of the system, hindering the introduction of additional O₂ and, finally, lowering the O₂ uptake.

During oxidation it is likely that carbohydrates undergo degradation reactions, consuming alkali and O₂ and thus leading to low molecular aliphatic compounds and CO₂, contributing to the total pressure. Additionally, carbohydrates can react with benzaldehyde structures via alkali-promoted reaction.³³ These facts lead us to postulate that the carbohydrate presence is unfavorable to the process. However, the results suggest that other factors (such the already mentioned inorganic content and also lignin structure) seem to overcome the eventual impairment of lignin oxidation to aldehydes caused by carbohydrates, since no effect of these

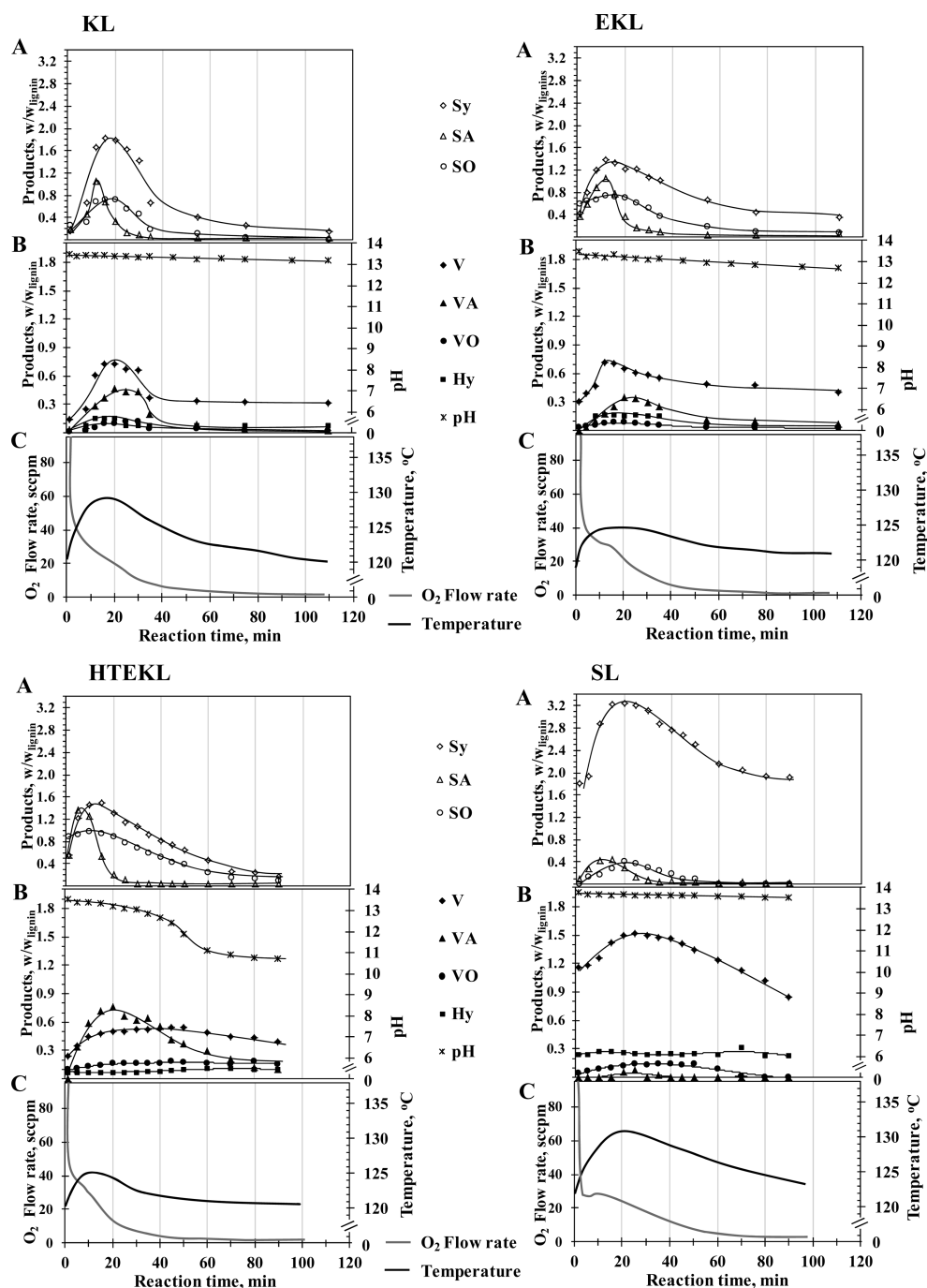


Figure 3. Profiles of monomeric products during the oxidation of *E. globulus* pulping liquors KL, EKL, HTEKL, and SL. (A) S, SA, and SO; (B) V, VA, VO, Hy, and pH of reaction medium; (C) O₂ uptake and temperature along the reaction time. General conditions: solids concentration 60 g/L, pH_i ≥ 13.8, pO₂ = 3 bar, P_t = 9.8 bar, T_i = 120 °C.

compounds were noticed (as already stated for NO). Indeed, the product yields, the O₂ uptake, and even the pH profile of HTEKLlig and EgLBoost (Figure 4) are very similar, in spite of the differences on the carbohydrate content (Table 1).

In the oxidation conditions of this work no visible effect was noticed due to alkali competing reactions (such as the above-mentioned carbohydrate reactions) on pH along the reaction: the profiles were similar for liquors and respective lignins. However, for HTEKL and the respective lignin, as well as for EgLBoost, after 50 min of reaction an intense decline is observed reaching a final value of 10 (Figures 3B and 4B), whereas final pH for the other materials is within 12 and 14.

This occurrence might be caused by lignin itself, since EgLBoost contaminants are scarce.

More than the carbohydrate and inorganic contents, in conditions where alkali and O₂ are not limiting factors, the lignin structure is undoubtedly the main factor for the final yield. NO results have demonstrated that KL has lower content on condensed structures and more potential for aldehyde production. In spite of the different reaction mechanisms involved in NO and oxidation with O₂, NO is frequently considered as an “evaluator” of lignins, representing the maximum yields that could be achieved in oxidation. Usually, yield of O₂ oxidation is about 30–50% of NO. The amount of

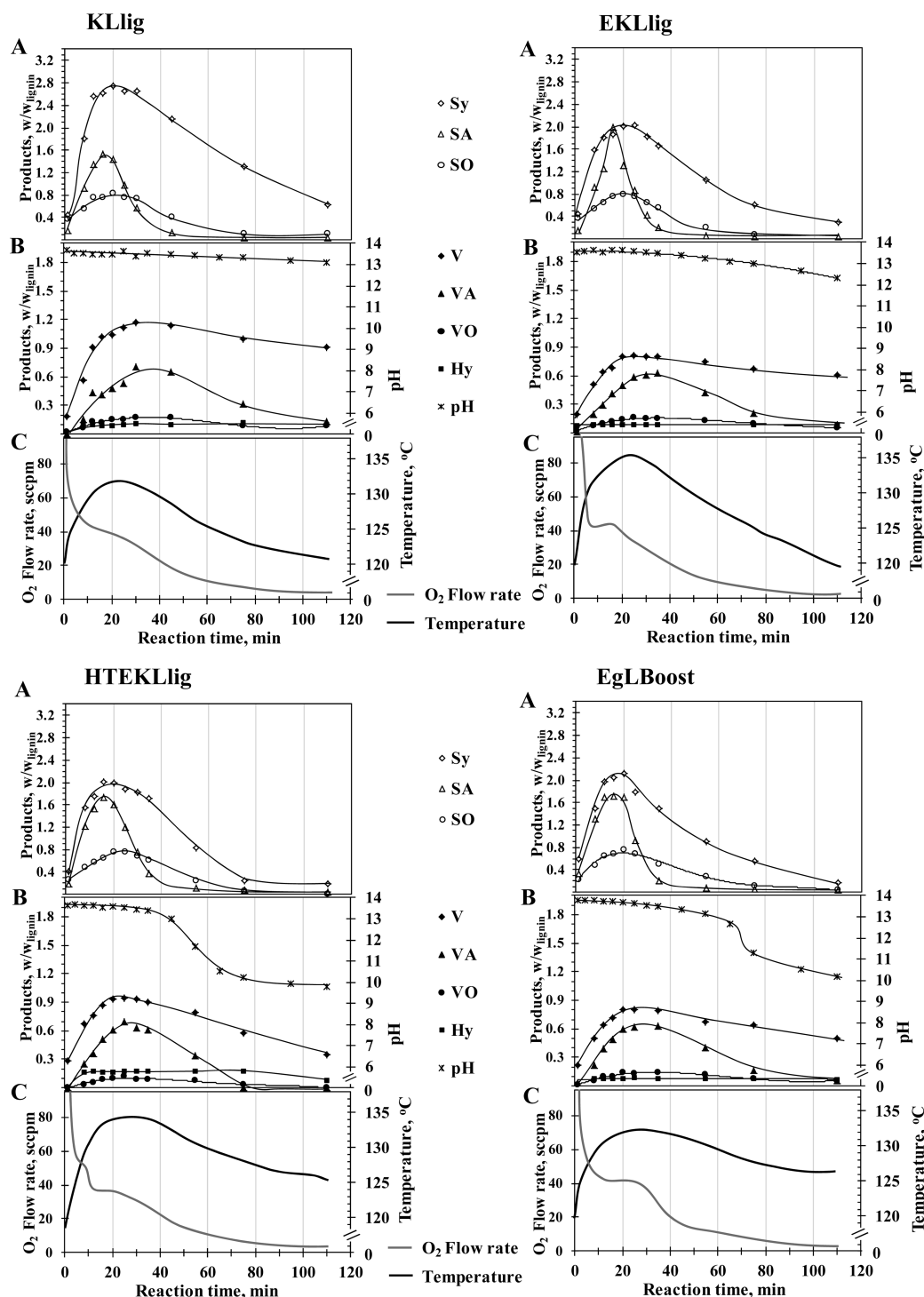


Figure 4. Profiles of monomeric products during the oxidation of isolated lignins KLlig, EKLLig, HTEKLLig, and EgLBoost from *E. globulus* kraft liquors. (A) S, SA, and SO; (B) V, VA, VO, Hy, and pH of reaction medium; (C) O₂ uptake and temperature along the reaction time. General conditions: 60 g/L, pH_i ≥ 13.8, pO₂ = 3 bar, P_t = 9.8 bar, T_i = 120 °C.

Sy and V produced from SL by oxidation with O₂ is considerable higher than for the other materials, reaching 29% and 60% of the NO value, respectively. The most probable reason for this is the structure of the noncondensed fraction of liginosulfonate: the most reactive structures toward oxidation with O₂ are those carrying conjugated double bonds (at lateral chain); under alkaline conditions, these structures are promptly produced by the elimination of the sulfonic group at Cα in SL lignin. Kraft lignin also contains these unsaturated structures as

well as the precursors; however, due to the more intensive lignin fragmentation in kraft pulping than in sulfite pulping, the availability of these reactive structures in the noncondensed fraction is probably lower in kraft lignins. In short, within all tested materials, SL was those with better overall performance considering yields, selectivity (ratio aldehydes/acids) and O₂ uptake, in spite of its contents in inorganic and carbohydrates.

Finally, minor compounds detected and quantified in the oxidation mixture for all of the pulping liquors and lignins were

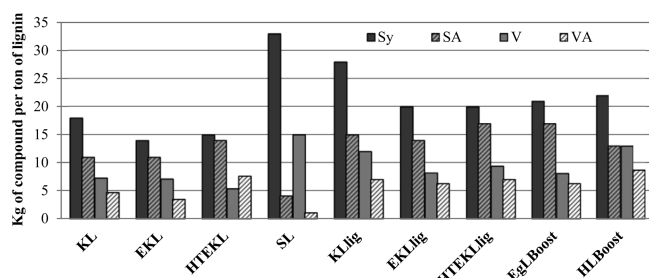


Figure 5. Yields of Sy, SA, V, and VA, the main phenolic compounds produced in the oxidation of pulping liquors and lignins with oxygen in alkaline medium (60 g/L, pH ≥ 13.8 , $pO_2 = 3$ bar, $P_t = 9.8$ bar, $T_i = 120$ °C).

Hy (product of *p*-hydroxybenzyl units) (<0.2%), VO (0.1–0.2%), and SO (0.4–1%). As stated before, acetoderivatives are products of the C β -C γ cleavage³⁸ competing with cleavage of C α -C β (leading to Sy, V, SA, and VA).

Figure 5 summarizes the results on the main products identified as oxidation products of pulping liquors and all isolated lignins. The yields, on lignin basis, are higher for isolated kraft lignins than for kraft liquors.

Data presented in Figure 5 show that SA and VA content is higher for kraft liquors and respective lignins than for SL. The ratios Sy/SA and V/VA are a measure of process selectivity for aldehydes. Sy/SA ratio for SL is about 10 times higher than the average of the other materials. These ratios slightly decrease with liquor processing (from KL/KLlig to EKL/EKLlig, and to HTEKL/HTEKLlig) denoting a decrease on selectivity, but are higher in the isolated lignins than in the respective liquors. This last observation suggests that the lab isolation (with its washing process) remove a fraction of lignin that would contribute for the acids production. Rather than being a product of further oxidation of corresponding aldehydes, the acids are more likely a byproduct of oxidation related with the content of some particular lignin structures, namely those carrying a carbonyl group at C α .³⁷ Oxidation mechanisms in complex mixtures are difficult to rationalize, and therefore, the real source of VA and SA remains not clearly assigned. The knowledge about these mechanisms at high temperature and pressure would be important from the point of view of process control, aiming to improve selectivity and yield on aldehydes.

HLBoost yields are within the values found for isolated lignins EKLlig, HTEKLlig, and EgLBoost but with higher V production. Indeed, the syringyl/guaiacyl products ratio is lower for HLBoost (1.6) than for *E. globulus* liquors and lignins (≥ 2.2), which is related with lignin origin as stated before.

Among all of the studied materials, SL clearly stands out as the raw-material with highest potential for Sy and V production: in the conditions of this study, SL produces about 33 kg of Sy and 15 kg of V per ton of lignin by direct oxidation of the liquor. These values represent about 20% more than the yield obtained by oxidation of the KLlig.

The Sy and V values obtained for both liquor and lignins were converted for the basis of kraft liquor nonvolatile solids, as presented in Table 2. From the technological point of view it is important to understand the benefit of lignin isolation on product yields, considering that the pulping liquors could be directly oxidized.

The results depicted in Table 2 show that the isolation of lignin is advantageous only in the case of the KL, leading to an increase of about 20% for Sy and 25% for V. Also, the selectivity

Table 2. Syringaldehyde and Vanillin Yields Per Ton of Nonvolatile Solids

	sample	kg of product per ton of solids	
		Sy	V
liquors	KL	8.6	3.5
	EKL	6.4	3.3
	HTEKL	6.9	2.5
lignins	KLlig	10.3	4.4
	EKLlig	4.1	1.6
	HTEKLlig	2.8	1.3

is higher due to the lower proportion of SA and VA produced from isolated lignins (Figure 5). By comparing the yields for EKL with EKLlig and HTEKL with HTEKLlig (Table 2), it is possible to conclude that the additional yield accomplished by oxidizing the isolated lignins is not enough to overcome the low recovery yield of lignin in the preceding isolation process (yields of isolation 24% and 16% for EKL and HTEKL, respectively; see section 2.2). Therefore, the productivity by ton of solids is rather lower than the values found for direct oxidation of kraft liquors. In the case of KL, the balance between the cost of isolation and the extra value obtained from the higher yields should be decisive if this route for lignin valorization is envisaged.

4. CONCLUSIONS

SL is the raw-material with better performance toward oxidation, producing 33 kg of Sy and 15 kg of V per lignin ton. Among kraft liquors, KL shows higher potential than the processed kraft liquors. If isolated lignin from KL is used as the raw material for oxidation, an increment in each compound could be achieved, reaching to 28 kg of Sy and 12 kg of V per lignin ton, with advantage also for selectivity reported as aldehyde/acid ratio. The benefit of prior lignin separation should be carried out for each case taking the yields, selectivity, O_2 consumption, and time as assessment factors.

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Notes

The authors declare no competing financial interest.

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