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# Production of phenolic compounds from catalytic oxidation of Kraft black liquor in a continuous reactor

*Antonio Hernández-Mañas,<sup>[a,b]</sup> Nicolas Chaussard,<sup>[a,b]</sup> Frédérique Bertaud,<sup>[c]</sup> Léa Vilcocq,<sup>\*[b]</sup>  
Pascal Fongarland,<sup>[b]</sup> and Laurent Djakovitch<sup>\*[a]</sup>*

<sup>[a]</sup> IRCELYON – UMR 5256 – Université de Lyon, Université Claude Bernard Lyon 1, CNRS; 2  
avenue Albert Einstein, F-69626 Villeurbanne cedex, France

<sup>[b]</sup> CP2M – UMR 528 – Université de Lyon, Université Claude Bernard Lyon 1, CNRS, CPE-  
Lyon; 43 Bd du 11 Nov. 1918 - B. P. 82007, F-69616, Villeurbanne, France

<sup>[c]</sup> CTP (Centre Technique du Papier) – Domaine Universitaire CS90251, 38044 Grenoble cedex  
9, France

## Abstract

Black liquor is a side stream from pulp and paper industry containing lignin and other organic and inorganic materials. Catalytic alkaline oxidation of black liquor was carried out employing CuO/TiO<sub>2</sub> catalyst in a trickle bed reactor employing mild reaction conditions (150-200°C, 80 bar) and short contact times (4-9 minutes). The effects of temperature, contact time, and presence of catalyst were investigated. In our best operating conditions, i.e. 200°C, 4 min contact time, lignin conversion was complete and phenolic monomers were obtained (maximum total yield 6.2 wt.%), among which vanillin (maximum yield 3.3 wt.%). Vanillin represented 53 wt.% of phenolic monomers. At longer contact times, the degradation of phenolic compounds was observed. The application of a continuous trickle bed reactor, allowing short reaction times and limiting degradation reactions, is particularly appropriate for this reaction. Vanillin productivity in this reactor is 936 g.m<sup>3</sup>.h<sup>-1</sup>.

## Introduction

Black Liquor is an aqueous effluent massively produced in the pulp and paper industry. It is a by-product of wood transformation in cellulosic fibers, employing Kraft pulping process.<sup>1</sup> It contains mainly lignin with an important fraction of aliphatics, and a significant charge of inorganics (NaOH, NaHS, Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>).

Historically and still now, the valorization of this by-product is mostly limited to combustion for energy production and inorganic chemicals recovery purposes.<sup>2</sup> Some papers also studied the pyrolysis of black liquor,<sup>3,4</sup> its use as a pretreatment medium for lignocellulose fractionation,<sup>5</sup> or its potential for the production of short organic acids.<sup>6,7</sup> Hydrothermal treatment of soda black liquor under inert atmosphere was recently investigated and produced low yields of aromatic

compounds (total yield 5%).<sup>8,9</sup> In the search for new renewable sources for high-value-added chemicals, black liquor appears as an interesting candidate for the production of phenolic compounds by aerobic oxidation, since it presents a high content of lignin, a natural polymer with aromatic moieties. Extensive researches were conducted on the conversion of lignin to aromatics through various pathways.<sup>10–16</sup> Nevertheless, the complexity of black liquor composition makes its conversion process a hard task that is still in primary research.<sup>17</sup>

Vanillin is a phenolic compound widely used as an aroma ingredient.<sup>18</sup> It can be extracted from natural vanilla but also produced from guaiacol oxidation (petrochemical pathway), from glucose via ferulic acid, or from lignin oxidation (biosourced pathways). The latter is exploited industrially for decades and supplies 15% of vanillin market, for example with the process Borregaard, where lignosulfonate from paper industry is oxidized over a copper catalyst in basic aqueous medium.<sup>19</sup> Besides F&F (fragrances & flavor) industry, vanillin attracts the attention of polymer industry for the synthesis of phenolic resins.<sup>20</sup> In literature, modest yields of vanillin from lignin oxidation were obtained, usually ca. 6-12 wt.%.<sup>18</sup> Borregaard claimed to reach 13 wt.% vanillin yield from lignosulfonate using CuSO<sub>4</sub> as a catalyst.<sup>21</sup> Kraft lignin is the most difficult substrate for vanillin production because of the degradation of lignin ether bonds during Kraft cooking. Maximum yield of vanillin ever reported from Kraft lignin was around 10 wt.%.<sup>22</sup> Usual yields in vanillin from Kraft lignin range between 3 to 7 wt.%.<sup>14</sup>

Just a few studies focused on black liquor valorization by direct oxidation. Pioneer work by Pearl in 1942 described vanillin production from industrial black liquor in the presence of air in hydrothermal conditions.<sup>23</sup> Then in 1977, two patents by Katzen et al.<sup>24</sup> and Mutton et al.<sup>25</sup> highlighted the advantages of continuous gas-liquid reactors for the oxidation of black liquor. However, in these early studies, the quantification of vanillin and lignin was ambiguous. More

recently, wet oxidation of black liquor was proposed as a pretreatment for pulp industry that would reduce viscosity, organic sulfur and pH.<sup>26</sup> The authors also observed an increase in CO<sub>2</sub>, acetic and lactic acids production with oxidation and suggested that carboxylic acids could be recovered and valorized before total oxidation. In the last decades, Pinto et al. reported the oxidation of various pulping liquors in alkaline conditions without catalyst.<sup>17</sup> Maximum yields of 3.3 wt.% syringaldehyde, 1.5 wt.% vanillin and 5.3 wt.% total phenolic monomers were obtained from eucalyptus sulphite liquor; maximum yields of 1.8 wt.% syringaldehyde, 0.7 wt.% vanillin and 3.9 wt.% total phenolic monomers were obtained from eucalyptus Kraft black liquor. This shows that lignin in black liquor is more resilient than lignin in sulphite liquor, as already evidenced with purified lignins. In another study, the same team used nitrobenzene oxidation as a technique to determine the maximum yield of vanillin that could be produced from black liquor (i.e. theoretical oxidation yield).<sup>27</sup> Although this method is not an option for an industrial process, it shows that the maximum nitrobenzene oxidation yield is 7 wt.% in vanillin (obtained from giant reed or silver grass black liquors). In another study, the same group reported 12 wt.% nitrobenzene oxidation yield in syringaldehyde from Eucalyptus (hardwood) black liquor.<sup>17</sup> They also suggested that the presence of inorganics in black liquor could prevent correct dilution of O<sub>2</sub> in the reaction media, limiting thus the yields of vanillin and syringaldehyde during black liquor oxidation. Additionally, carbohydrates could play another negative factor by reacting with the aromatic aldehydes produced.<sup>17</sup>

Several aspects of black liquor oxidation can thus be elucidated. It can be carried out under mild reaction conditions (usually 2–14 bar air and 120–190 °C), and gives aromatics with a high degree of functionalization (phenols, methoxyphenols, etc.). The presence of copper seems to enhance the

production of aromatics.<sup>23</sup> Under more severe reaction conditions or at longer reaction time, degradation of these aromatic compounds into carboxylic acids occurs.<sup>28–30</sup>

Besides, there is a significant research effort employing isolated Kraft lignin, which is extracted from black liquor by acidification, precipitation and filtration beforehand.<sup>12,31–34</sup> This extracted lignin is generally re-diluted in organic solvents or in basic aqueous solutions before being converted.<sup>35–40</sup> Usually, mild reaction conditions are applied for oxidative conversion of lignin (temperature inferior to 250°C, aqueous solvent). Oxygen can be directly employed as oxidant,<sup>14</sup> while several catalysts showed an increase in the selectivity into aromatic compounds from lignin. These catalysts include transition metal ( $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ),<sup>41,42</sup> perovskite based oxides,<sup>43–48</sup> polyoxometalates,<sup>35,49,50</sup>  $\text{Au/CeO}_2$ ,  $\text{Au/Li-Al}$ ,<sup>51–53</sup>  $\text{Co/TiO}_2$ ,  $\text{Co/CeO}_2$  or  $\text{Co/ZrO}_2$ ,<sup>54</sup>  $\text{Pd/Al}_2\text{O}_3$ .<sup>55</sup> Usually, the experiments carried out employing isolated lignin report total monomer yields below 10 wt.%, higher yields being obtained from hardwood lignins than from softwood lignins.<sup>10,56,57</sup> Despite these efforts in investigation, the yields obtained in phenolic compounds from lignin oxidation, and by extension from black liquor, are still rather low.

In our ongoing researches on lignin upgrading to aromatics,<sup>37–40</sup> we were interested by visiting the direct use of *Pinus pinaster* black liquor provided by a Kraft pulp mill (Smurfit Kappa – SKCP, Factice, France) for providing biosourced aromatics, focusing on vanillin. In this work, we engaged softwood black liquor in aerobic catalytic oxidation in a continuous fixed-bed reactor.

## Results and Discussion

Before engaging Black liquor in any experiments, several characterizations were made. Data are collected in Table 1. Details on the characterization techniques are given in ESI. The black liquor employed in all the experiments was obtained in the SKCP-Kraft pulp mill (Facture, France), which uses local maritime pine (*Pinus pinaster*) as biomass.

As it can be observed, this black liquor presents a dry matter content of around 26 wt.% and 31 wt.% of this dry matter is lignin. That makes an 8 wt.% of lignin in total black liquor in mass basis, and having in account the density of the black liquor ( $1.14 \text{ g.cm}^{-1}$ ) the concentration of lignin of such by-product is  $91 \text{ g.L}^{-1}$ . Additionally, the Na content is important, which can be associated to the high content of NaOH and  $\text{Na}_2\text{S}$  employed in the Kraft process. In order to avoid clogging effects in the flow reactor, black liquor was diluted by a factor 40 in aqueous basic media ( $\text{NaOH}_{\text{aq}}$   $10 \text{ g.L}^{-1}$ ) before any experiments so that the lignin concentration before reaction reaches  $2.27 \text{ g.L}^{-1}$ . The dilution allowed to lower the viscosity of the feed and to limit any foaming issue in the continuous reactor.

**Table 1.** Characterization analysis of the industrial black liquor entering in the evapo-concentration line and sampled in September 2019.

pH (20°C)	13.7
Dry matter content (wt.%, on crude sample)	$26.0 \pm 0.1$
Density 20°C ( $\text{g/cm}^3$ )	1.11
LHV <sup>[a]</sup> (MJ/Kg o.d. sample)	$8.11 \pm 0.6$
Lignin content (AIL <sup>[b]</sup> + ASL <sup>[c]</sup> ) (wt.%, o.d. sample)	$30.8 \pm 0.6$ (23.5 + 7.3)
Na (wt.%, o.d. sample)	$17.6 \pm 0.05$
K (wt.%, o.d. sample)	$1.35 \pm 0.05$
Total Sulphur (wt.%, o.d. sample)	$0.93 \pm 0.02$
Sulphates content (wt.%, g S eq. /100 g o.d. sample)	$0.5 \pm 0.1$
Wood extractives (wt.%, o.d. sample)	$0.56 \pm 0.05$
Ashes (wt.%, o.d. sample)	39.9

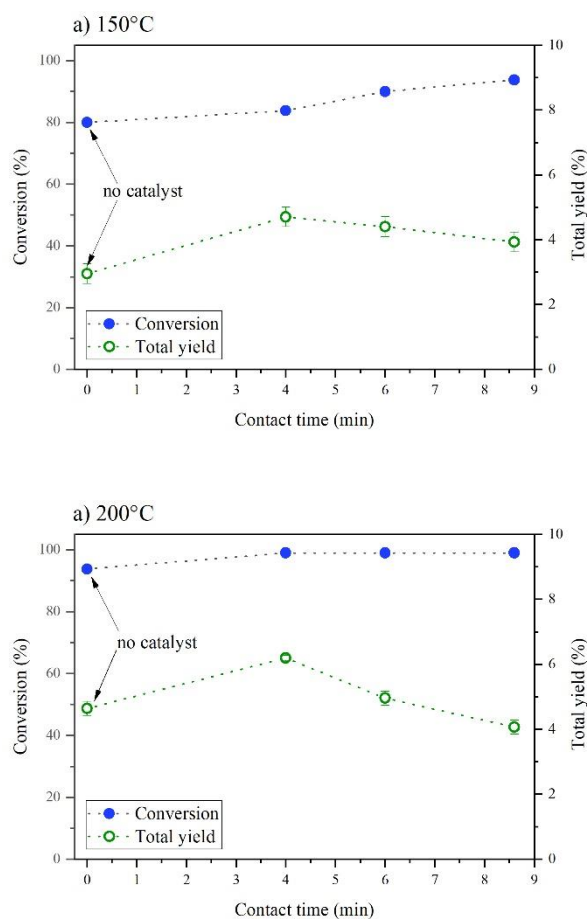
[a] Lower Heating Value; [b] Acid Insoluble Lignin, also called 'Klason lignin'; [c] Acid Soluble Lignin

The catalytic oxidation of black liquor was carried out in a fixed bed tubular reactor under air flow and liquid flow in trickle bed mode, pressurized at 80 bar (see ESI for experimental details). Black liquor was diluted in alkaline solution up to 2.27 g.L<sup>-1</sup> of lignin concentration before reaction, corresponding to 5 g.L<sup>-1</sup> of dry matter. CuO/TiO<sub>2</sub> was used as a catalyst.

During oxidation, lignin was depolymerized and oxidation products were formed. Figure 1 depicts the evolution of lignin conversion and total yield of phenolic monomers with contact time. At 150°C, lignin conversion reaches 80 wt.% without catalyst and 84 wt.% with CuO/TiO<sub>2</sub>. Then it increases until 94 wt.% when contact time increases. The high conversion of lignin is therefore mainly due to the effect of temperature and of the alkaline medium. The total yield in monomers is only 2.9 wt.% without catalyst but reaches 4.7 wt.% when CuO/TiO<sub>2</sub> is present. This shows that the presence of catalyst increases the formation of phenolic compounds by 62 %. Total phenolic yield decreases when contact time increases to reach 3.9 wt.% at 8.6 min. This decrease is attributed to the degradation of phenolic compounds into aliphatic compounds, as already observed for oxidation products of lignin oxidation.<sup>58</sup> At 200°C, lignin conversion (i.e. Klason phase conversion) is 94 wt.% in the absence of catalyst and 100 wt.% when a catalyst is present whatever the contact time, validating that lignin conversion is mostly due to the aqueous alkaline conditions and temperature effects. Higher temperature favors the complete depolymerization of lignin. The total monomers yield at 200°C is especially remarkable, since phenolic monomers production increases with the presence of CuO/TiO<sub>2</sub> from 4.6 wt.% without catalyst to 6.2 wt.% with catalyst, i.e. an increase by 35%. Hence, high temperature has a beneficial effect on total monomers yield: from 4.7 wt.% total yield at 150°C vs 6.2 wt.% at 200°C. Then the total yield of monomers decreases when contact time increases from 6.2 wt.% at 4 min to 4.1 wt.% at 8.6 min contact time.



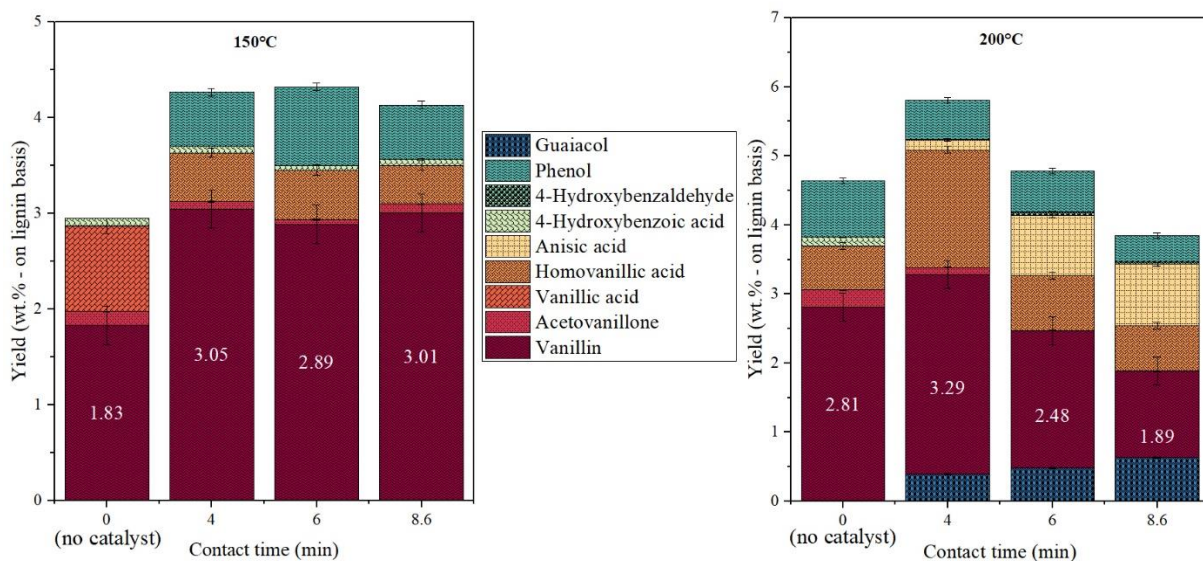
This important decrease is related with the degradation of the aromatic compounds formed, so very low contact times favor the production of phenolic monomers.



**Figure 1.** Conversion and total yield of phenolics during black liquor oxidation at (a) 150°C and (b) 200°C. *Operating conditions: 80 bar, air flow 15 NL.h<sup>-1</sup>, liquid flow varies with contact time, 20 g of catalyst CuO/TiO<sub>2</sub>. Contact time zero corresponds to a test without catalyst and a liquid flow equivalent to contact time 4 min.*

The main identified products in all the experiments were vanillin, homovanillic acid, acetovanillone, anisic acid, hydroxybenzaldehyde, guaiacol and phenol (Figure 2 and Figure S3 in ESI). Traces of vanillic acid and 4-hydroxybenzoic acid were also detected. At 200°C and 4 min contact time, when the total yield of phenolic monomers was at its maximum, vanillin and

homovanillic acid were the two major products, with 3.3 wt.% yield and 1.7 wt.% yield, respectively, i.e. 53 wt.% and 27 wt.% respectively of all phenolic monomers. In these operating conditions, the final concentration in monomers was  $0.17 \text{ g.L}^{-1}$  starting from diluted black liquor with a lignin concentration of  $2.27 \text{ g.L}^{-1}$ . At higher contact times at  $200^\circ\text{C}$ , a drastic decrease in vanillin and homovanillic acid yields was observed whereas yields in phenol and guaiacol remained stable. At lower temperature ( $150^\circ\text{C}$ ), guaiacol and anisic acid were not observed anymore, and the main products were vanillin, phenol and homovanillic acid. At  $150^\circ\text{C}$ , contact time had only a minor effect on vanillin and homovanillic yield. In the absence of catalyst, yields in vanillin and homovanillic acid were low whatever the temperature. Contrarily to what was observed at  $200^\circ\text{C}$ , at  $150^\circ\text{C}$ , vanillic acid was one of the main products after vanillin.

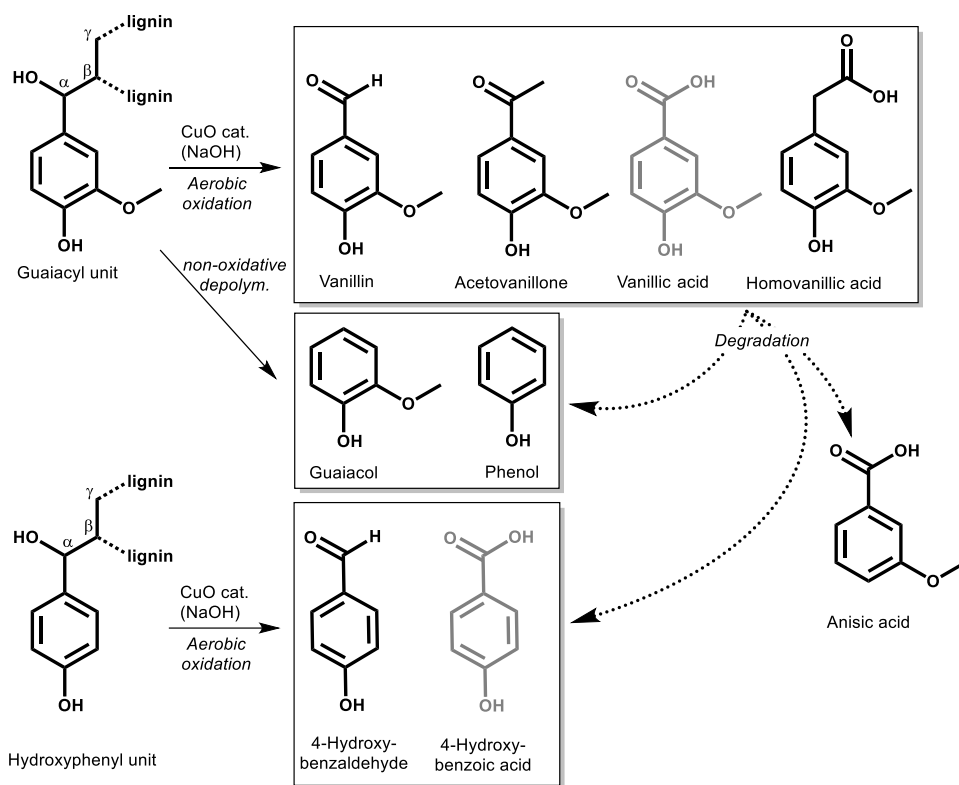


**Figure 2.** Yields of phenolic monomers during black liquor catalytic oxidation at  $150^\circ\text{C}$  and  $200^\circ\text{C}$ . Operating conditions: 80 bar, air flow  $15 \text{ NL.h}^{-1}$ , liquid flow varies with contact time, 20 g of catalyst  $\text{CuO/TiO}_2$ . Contact time zero corresponds to a test without catalyst and a liquid flow equivalent to contact time 4 min.

Products distribution in monomers (Table S3 in ESI) also evidenced a strong impact of the presence of catalyst and of reaction temperature. At 150°C, without catalyst, vanillin represented 61% of monomers, followed by vanillic acid (30%) and acetovanillone (5%). When the catalyst was present, vanillin still represented 63% of monomers, but vanillic acid only 8% and homovanillic acid 11%; phenol represented 15% of monomers. This distribution changed only marginally with contact time, vanillin representing up to 72% of monomers at longer contact times. At 200°C, without catalyst, vanillin represented 66% of monomers, followed by homovanillic acid (26%) and acetovanillone (6%). With catalyst, vanillin represented only 53% of monomers, homovanillic acid 26%, followed by phenol (9%) and guaiacol (7%). At longer contact time, the parts of vanillin and homovanillic acid decreased and anisic acid represented up to 20% of monomers. Therefore, the presence of catalyst enhanced the part of phenol (150°C) and guaiacol (200°C), as well as the part of anisic acid (200°C), but drastically decreased the part of vanillic acid. The decrease in the part of vanillin in monomers is due to the appearance of these new compounds.

Vanillin, acetovanillone, vanillic acid and homovanillic acid were produced by the oxidation of guaiacyl units of lignin, as already described in the literature of lignin oxidation (Figure 3).<sup>14,18</sup> According to Tarabanko et al., these three molecules are formed by different pathways from lignin. Vanillin production is initiated by an initial oxidation of the C $\gamma$ -OH and ended by a retro aldol cleavage. Between the two steps quinone methide intermediate is formed and then transformed into a cinnamaldehyde by an addition of OH<sup>-</sup> in the C $\gamma$ .<sup>59</sup> When the initial oxidation is produced in the C $\alpha$ -OH group, it can start the pathway towards the production of vanillic acid. On the other hand, if the OH<sup>-</sup> addition on the quinone methide intermediate is produced in the C $\alpha$  position results in acetovanillone.<sup>60</sup>

4-Hydroxybenzaldehyde and 4-hydroxybenzoic acid can be formed by a similar mechanism from the oxidation of p-hydroxyphenyl units, present in softwood Kraft lignin in minor amount (< 10%),<sup>39,57</sup> or from the degradation of guaiacyl units through demethoxylation. Moreover, guaiacol and phenol were also observed, which could be the products of non-oxidative cleavage of lignin units or formed from the degradation of other phenolic compounds (e.g. demethoxylation, decarbonylation). They are particularly present when the catalyst was used (at 150°C) or at high temperature. It is interesting to note that anisic acid is only present at 200°C in presence of a catalyst and at long contact times. This indicates that anisic acid is a degradation product, which could be formed for example by dehydroxylation/oxidation of vanillin or vanillic acid.



**Figure 3.** Reaction pathways for the oxidation of guaiacyl and p-hydroxyphenyl units.

Degradation of vanillin, acetovanillone and vanillic acid in oxidative conditions was described earlier in literature.<sup>61</sup> Degradation of vanillic acid is particularly rapid in alkaline, oxidative

conditions. Degradation products from vanillin and vanillic acid were reported to be acetic acid, formic acid, oxalic acid, methanol, CO<sub>2</sub> and heavy condensation products.<sup>62</sup> Therefore, the application of a continuous fixed bed reactor, allowing short reaction times and limiting degradation reactions, is particularly appropriate for this reaction.

This work represents the highest vanillin yield reported from black liquor so far. To the best of our knowledge, there is only one example of black liquor oxidation to phenolic compounds: Pinto et al. employed real Eucalyptus black liquor and obtained a total yield in phenolic monomers under 4 wt.% and a yield in vanillin below 2 wt.% at 120°C.<sup>17</sup>

Vanillin yield in our study is comparable with the one obtained by oxidation of isolated softwood Kraft lignin with or without catalyst (from 4 wt.% to 10 wt.%).<sup>22,57,63,64</sup> Although the yield obtained in our experiments is lower, it would be advantageous to eliminate Kraft lignin purification step in the vanillin production process and to replace homogeneous catalysts (e.g. H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>) by heterogeneous catalysts.

Vanillin productivity, i.e. the amount of vanillin produced per hour and per volume of reactor, was calculated from our data and from selected works on black liquor oxidation and Kraft lignin oxidation (Table 2, detailed calculation in ESI). High levels of productivity were obtained when process intensification was implemented: Rodrigues' team used isolated Kraft lignin in high concentration;<sup>17,65</sup> Walch et al. applied short reaction time;<sup>66</sup> we chose to use a continuous fixed bed reactor. These approaches were effective to obtain a productivity superior to 0.5 kg<sub>vanillin</sub>·m<sup>-3</sup>·h<sup>-1</sup>. This work is the first one reporting vanillin productivity as high as 0.9 kg<sub>vanillin</sub>·m<sup>-3</sup>·h<sup>-1</sup> by direct oxidation of black liquor. In the future, based on these preliminary results, vanillin productivity could be increased by increasing the concentration of black liquor in the feed, therefore reducing the use of water in the process.

**Table 2.** Vanillin production from black liquor and Kraft lignin – comparative study.

Biomass	Feed	Operating conditions	Vanillin yield (wt.%) <sup>[a]</sup>	Total phenolic yield (wt.%) <sup>[a]</sup>	Vanillin productivity (kg.m <sup>-3</sup> .h <sup>-1</sup> )	Ref.
Maritime pine (softwood)	Diluted black liquor (2 g <sub>lignin</sub> .L <sup>-1</sup> )	200°C, 80 bar, CuO/TiO <sub>2</sub> catalyst, 4 min contact time <sup>[b]</sup>	3.3	6.2	0.936	This work
Eucalyptus	Diluted black liquor (27 g <sub>lignin</sub> .L <sup>-1</sup> )	120°C, 10 bar, no catalyst, 20 min	0.7	4.4	0.284	Rodrigues team, 2013 <sup>17</sup>
Pine (Softwood)	Kraft lignin in alkaline solution (60 g.L <sup>-1</sup> )	120°C, 10 bar, no catalyst, 25 min	4.4	7.2	3.013	Rodrigues team, 2011 <sup>65</sup>
Pine (Softwood)	Kraft lignin in alkaline solution (60 g.L <sup>-1</sup> )	133°C, 10 bar, no catalyst, 60 min	10.8	n.d.	5.282	Rodrigues team, 1996 <sup>63</sup>
n.d.	Kraft lignin in alkaline solution (10 g.L <sup>-1</sup> )	150°C, H <sub>2</sub> O <sub>2</sub> , CuMn catalyst, 60 min	6.8	12	0.340	Hwang team, 2020 <sup>67</sup>
Softwood	Kraft lignin (fractions) in alkaline solution	140°C, H <sub>2</sub> O <sub>2</sub> , CuSO <sub>4</sub> , 60 min	10.9	n.d.	0.291	Repo team, 2020 <sup>68</sup>
Softwood	Kraft lignin in alkaline solution (25 g.L <sup>-1</sup> )	150°C, 5 bar O <sub>2</sub> , V-Cu catalyst, 10 min	3.5	7	1.050	Riisager team, 2021 <sup>66</sup>
Softwood	Kraft lignin in MeO/H <sub>2</sub> O (10 g.L <sup>-1</sup> )	170°C, 10 bar O <sub>2</sub> , H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub> catalyst, 20 min	3.6	7.2	0.270	Voitl & von Rohr, 2010 <sup>49</sup>

<sup>[a]</sup> Yield on dry lignin basis; <sup>[b]</sup> fixed bed continuous reactor.

## Conclusion

In conclusion, the feasibility of direct catalytic oxidation of black liquor in a continuous fixed bed reactor was demonstrated. Kraft lignin in black liquor was converted to vanillin, homovanillic acid, acetovanillone, phenol and other phenolic compounds, in alkaline medium, under air flow.

The presence of catalyst had only a minor influence on lignin conversion but a great impact on the selectivity for phenolic compounds. With or without catalyst, temperature had a strong impact on both lignin depolymerization and phenolic compounds production. It was suggested that lignin depolymerization is mostly homogeneous whereas monomers production is partly catalyzed by the solid copper catalyst during the reaction. The best operating conditions were 200°C, 80 bar, catalyst CuO/TiO<sub>2</sub>, and 4 min contact time. The maximum total yield of phenolic compounds was 6.2 wt.%, which is the highest monomer yield reported so far from black liquor. Vanillin yield was 3.3 wt.% at maximum, i.e. vanillin represented 53% of detected monomers. However, the degradation of phenolic compounds was observed when contact time increased. The use of a continuous reactor is thus particularly relevant for controlling contact time of catalytic oxidation. Solid catalyst is based on copper, an inexpensive, non noble and abundant metal. The production of phenolic compounds from black liquor oxidation is promising, since they present a first step to develop an efficient continuous process that could be employed in the integrated forest biorefineries of the future. Current work focus on studying the catalyst performances after long time on stream, the reactivity of concentrated feeds and corrosion issues to assess the industrial feasibility of such a process.

## ASSOCIATED CONTENT

### **Supporting Information.**

Experimental section; scheme of trickle bed reactor; catalyst characterization; HPLC analysis results before and after reaction; distribution of phenolic compounds; calculation of vanillin productivity ( PDF file). This information is available free of charge via the Internet at

<http://pubs.acs.org/>.

## AUTHOR INFORMATION

### **Corresponding Authors**

\*Léa Vilcocq, [lea.vilcocq@cnrs.fr](mailto:lea.vilcocq@cnrs.fr) ; Laurent Djakovitch, [laurent.djakovitch@ircelyon.univ-lyon1.fr](mailto:laurent.djakovitch@ircelyon.univ-lyon1.fr)

### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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### **Notes**

The authors declare no competing financial interest.

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## ABBREVIATIONS

LHV: Lower Heating Value

AIL: Acid Insoluble Lignin (also known as Klason lignin or Klason phase)

ASL: Acid Soluble Lignin



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## SYNOPSIS

