An integrated process to produce vanillin and lignin-based polyurethanes from Kraft lignin


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Abstract

The aim of this manuscript is to present an integrated process that includes reaction and separation steps for producing vanillin and lignin-based polyurethanes from Kraft lignin. It provides details about lignin oxidation and subsequent vanillin recovery, as well as, the synthesis of lignin-based polyurethanes. The oxidation of Kraft lignin in alkaline medium has been carried out in a batch reactor and the optimum operational conditions for vanillin production obtained. The feasibility of a continuous process for vanillin production has been analyzed using a structured bubble column reactor. The generated reaction stream (degraded lignin and sodium vanillate) was further subjected to an ultrafiltration process to recover the vanillate. An ion-exchange process allows recovering the vanillin by passing the vanillate solution through a column packed with an ion-exchange resin in H+ form. The remaining lignin can act as a raw material to produce polyurethanes and/or biofuels. In this work the first approach was explored.

Keywords: Kraft lignin; Vanillin; Polyurethanes; Oxidation; Ultrafiltration; Integrated process

1. Introduction

One of the major priorities of 21st century is the replacement of fossil carbon source by a renewable raw material (biomass). Nowadays, the international community is strongly committed with sustainable development and terms such as bioproducts, bioenergy, bioeconomy are being used frequently by politicians’ and investors’, R&D projects, companies’ reports, thus corroborating the growing concern, on sustainable growth, zero-waste industries and environmentally friendly processes (Biomass R&D Technical Advisory Committee, 2006; European Parliament and Council, 2002; Ree and Annevelink, 2007). The concept of biorefinery comes from this state of mind. Biorefineries are structures that integrate processes and technologies for an efficient biomass conversion into products such as base chemicals, platform chemicals, fuels and energy (Kamm et al., 2006; Ree and Annevelink, 2007). Hence, there is no doubt about the impact that biorefineries can bring into our lives in a near future.

Nevertheless the potential associated to industrial biorefineries, there are still uncertainties and technical difficulties (e.g., technology costs, know-how on available processes or food versus fuel dilemma) that need to be overcome in order that these novel systems become more competitive against the current industrial alternatives based on petrochemical resources. The so-called lignocellulose feedstock (LCF) biorefinery is particularly favoured by the sustainability and cost of biomass supply. Moreover, the generated conversion products are well placed comparatively in the traditional petrochemical and the future biobased product markets (Kamm and Kamm, 2004).

One of the most abundant aromatic substances in the biosphere is lignin. The main source of lignin is the pulp and paper industry, where nowadays the Kraft process prevails...
with a quote of approximately 80% of the world chemical pulp production (Saake and Lehnen, 2004). The black liquor, a by-product stream of this process, contains, typically, 30–34% of lignin. In a conventional process, this stream is burned to provide energy for mill operations, and to recover the cooking chemicals (Wallberg et al., 2005). Nowadays, this destructive way to treat the large amount of generated black liquor is not considered anymore a satisfactory solution. Moreover, it is worth mentioning that due to the complex energetic integration of the Kraft process, an expansion in the pulp production implies a revamp in the burners and also a capacity increase of the recovery boiler. This introduces a major bottleneck in the process leading to the appearing of some approaches to debottleneck the recovery boiler. Solutions such as the extraction of lignin from the black liquor proportionally to the production increase (sold as a biofuel) or upgrading of the recovery boiler and the turbine system have been proposed (Axelsson et al., 2006; Mathias, 1993).

To overcome the disadvantages associated with the conventional black liquor process treatment, alternative methods are required. One solution is the utilization of black liquor to generate high-added value products. When black liquor is burned, many organic compounds are vanished, especially lignin, from which many valuable substances or materials can be produced, such as vanillin, vanillic acid, dispersing agents, synthetic tannins, polymer filter sand binding agents, activated carbon, ion-exchanger substrates, etc. In this work, the focus is directed to the production of synthetic vanillin from lignin obtained from black liquor. The main feedstock is Kraft lignin and the end products vanillin and polyurethane materials (plus biofuel).

A flow sheet of the proposed process is shown in Fig. 1. A portion of the by-product stream, black liquor, is processed to extract the lignin. This extraction can be done by the traditional acidification/precipitation method followed by separation, or by using alternative methods such as the one developed by the Swedish group and known as LignoBoost (Öhman et al., 2006). After obtaining the purified lignin, the subsequent process is based on three main steps. The first step is the alkaline lignin oxidation performed in a bubble column reactor (Araujo, 2008). Thereafter, the obtained mixture passes through a membrane ultrafiltration system where the lignin higher molecular residues are retained. Sodium vanillate and other low molecular weight species go to the permeate stream (Zabkova et al., 2007a). Finally, the permeate containing smaller molecules and excess NaOH flows through a packed bed with an acid resin, in order to convert the sodium vanillate into vanillin (Zabkova et al., 2007b). This ion-exchange step is accompanied by a neutralization reaction thus originating an exit stream with lower pH. The degraded lignin resulting from the membrane process appears as a by-product in the flow sheet. Our purpose is to valorise this material by obtaining lignin-based polyurethane products, e.g., rigid foams, elastomers, sealants (Cateto et al., 2008a), and additionally biofuels for the related unit operations.

The aim of this manuscript is to describe an integrated process to produce vanillin from Kraft lignin oxidation. Details about each required unit operation are presented. This work is supported by a research program dedicated to vanillin production from Kraft lignin that has been conducted at the Laboratory of Separation and Reaction Engineering (LSRE) for many years. Considering the industrial importance of vanillin, a brief discussion focusing the market and general aspects of this compound are presented. In the final section, the utilization of lignin as a macromonomer in polyurethane synthesis is explored.

2. Vanillin: application and world market

Vanillin (C₈H₈O₃) is the major flavour constituent of vanilla. It has a wide range of applications in food industry as a flavour agent and in perfumery as an additive. Other applications include antioxidant additive, antifoaming agent, vulcanization inhibitor and chemical precursor for pharmaceutical and agrochemical industries (Cerrutti et al., 1997; Fitzgerald et al.,

![Fig. 1 – Valorisation of Kraft lignin by a biorefinery concept: the proposed integrated process for producing vanillin and biopolymers.](image-url)
Vanillin market is mainly constituted by large multinational holders: (i) flavour and fragrance companies (IFF, Givaudan, Quest, Danisco); (ii) chocolate and ice cream producers (Unilever, Nestle, Cadbury, Suchard); and (iii) manufacturer of pharmaceuticals (Merck).

There are two commercial types of vanillin: pure vanillin, which is obtained by chemical synthesis, i.e., derived from guaiacol or lignosulphonates of the paper and pulp industry; and vanilla extract obtained from the pod of tropical vanilla orchid (Daughsch and Pastore, 2005; Walton et al., 2003). The natural vanillin is very expensive comparatively to the synthetic counterpart. The natural vanilla market is characterized by very volatile prices (Jaeger, 2005), mainly sensitive to several events (natural, economic or political) affecting its larger producer Madagascar (FAOSTAT, 2005). The unstable market of this natural product has encouraged the development of new chemicals routes. Hence, synthetic vanillin became widely used and competition of markets is longstanding and turns more fierce when prices of natural vanilla rockets.

Vanillin was first produced by Haarrmann and Reimer in the late 1800s, using guaiacol obtained from phenol. Between 1930s and 1980s, the major synthetic vanillin supply market share was generated by lignin-containing waste produced by the sulphite pulping process (Triumph Venture Capital Ltd., 2004a). However, from 1980s, changes introduced in the pulp and paper industry processes led to a decrease of this raw material required by vanillin plants. The competing chemical pulping process, the sulphate or Kraft process, was preferred since it allowed the recycling of the waste liquors for chemical recovery. As a result, these by-product streams were not available for vanillin production and petrochemical guaiacol has gained relevance. Nowadays the synthesis of vanillin from petrochemical guaiacol accounts for 85% of the world supply, with the remaining 15% being produced from lignin (Triumph Venture Capital Ltd., 2004a). Despite the guaiacol route produces vanillin with nearly absence of by-products; this process is dependent on petroleum-derived compounds, in opposition with lignin-based biomass oxidation process.

Natural vanilla flavouring constitutes less than 5% of the world market (Triumph Venture Capital Ltd., 2004a). Considering its application as a flavouring and fragrance ingredient, the global demand for synthetic vanillin is currently around 16,000 tonnes/year (Triumph Venture Capital Ltd., 2004b). However, vanillin may be used for the synthesis of several second-generation fine chemicals and several pharmaceutical chemicals (Bjorsvik and Liguori, 2002). There are only few significant manufacturers of this product in the world. Rhodia SA dominates the vanillin market using the catechol-guaiacol process. Borregaard (Norway), the second largest vanillin producer, is one of the remaining producers of lignin-based vanillin. Essentially, Borregaard supplies the European market and its vanillin production is almost exclusively for large-scale costumers under long-term contracts.

In the middle of 2005, vanillin market prices have reached $15 kg⁻¹ (Nair, 2005). Since it is mostly produced from guaiacol, vanillin prices are sensitive to the world oil market (Haldiday, 2008). Besides, lignin-based vanillin is in high demand for certain market sectors, particularly for the perfume industry, European chocolate manufacturers, and Japanese market, and as such tends to command a price premium. The price of lignin-based vanillin has consistently maintained at about $100–200 kg⁻¹ above that of guaiacol-based vanillin (Triumph Venture Capital Ltd., 2004b).

3. Feedstock: lignin. General aspects

Lignin is a three-dimensional amorphous macromolecule made of phenylpropane units that arise from the copolymerization of three primary precursors: coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol. The chemical composition of lignin and its content in wood vary greatly with and within a plant, depending on its species, age, morphological location and growth environment. Lignin from softwoods (gymnosperms) is predominantly based on structural units derived from the coniferyl alcohol (guaiacyl units), which are the precursors for vanillin yield (Adachi et al., 1992; Higuchi, 1980). On the other hand, hardwood (angiosperms) lignins present structures with much broader chemical compositions, i.e., with various guaiacyl:syringyl ratios. Lignin from different sources can be oxidized to obtain phenolic compounds: spent pulp liquor from paper industry, native lignin, sugarcane bagasse, Klasen lignin, among others (Creighton et al., 1941; Sales et al., 2002; Villar et al., 1997).

The commercially available lignins comprise two categories: (1) the sulphur-free lignins, mainly obtained from biomass conversion technologies focused on biofuel production, organosolv pulping processes (Lebo et al., 2001; Sixta, 2006), and soda pulping based on alternative resources like agricultural residues and non-wood fibres (Lora and Glasser, 2002); and (2) the sulphur containing lignins, which result essentially from Kraft and sulphite pulping processes. This last category comprises almost the whole market of commercially available lignins. The total annual capacity of technical lignins production is around 785,000 tonnes/year of which approximately 60% corresponds to the production from Borregaard LignoTech and the remaining from other companies (as example, Tembbibre, Fraser Paper, Tolmozzo, Westvaco). The annual capacity of the major producers of technical lignins in Europe and North America can be found elsewhere (Lebo et al., 2001).

It is estimated that 98–99% of the lignin separated from wood in the sulphite pulping, and especially in the Kraft pulping, is burned for energy and chemicals recovery or disposed in waste streams (Lora and Glasser, 2002). The remaining amount is isolated from the spent pulping liquors and sold for specialty applications, which is normally around 1 million tonnes per year worldwide (Lora and Glasser, 2002; Thieleman et al., 2002). Vanillin and dimethyl sulphoxide are the only two low molecular chemicals produced in large quantities from technical lignins, particularly from lignosulphonates. Industrially, softwood spent sulphite liquors or isolated lignosulphonates are oxidized, in alkaline media, by oxygen or air to produce vanillin (Bjorsvik, 1999). Our aim fits in this type of lignin application, but instead of using lignosulphonates, the vanillin production is based on isolated lignin from the largely available Kraft pulping waste liquor. Data from the Food and Agricultural Organization of the United Nations (FAO)—revealed that, in 2006, 9.8 × 10⁶ tonnes of Kraft pulp were produced in worldwide developed countries from a total chemical pulp production of 1.03 × 10⁸ tonnes (FAO, 2008). Kraft lignins can be precipitated and extracted from the black liquor in a two-step acidification process. First, carbon dioxide is used to reduce the pH of the liquor till 9–10, and about 75% of the lignin is precipitated as a sodium salt (Lebo et al., 2001). For further purification, this lignin is suspended in water and acidified with H₂SO₄ to a pH lower than 3. The commercial Kraft lignins are generally sold in the sulphonated form or as lignin amines. The physical properties for softwood Kraft lignins and softwood lignosulphonates can be found.
Lignin oxidation route has been extensively studied since production from Reaction Engineering (LSRE) on the area of vanillin chemical. Following sections. The paper is written within the framework related to this integration concept are presented in the following steps in order to allow the isolation of vanillin from the presence of air (Triumph Venture Capital Ltd., 2004a). This is based on the alkaline oxidation of lignosulphonates in the production includes the lignin oxidation processes from black liquor, specially using precipitation (Norgren, 2001; Norgren and Edlund, 2003; Ohman et al., 2007a,b; Sun et al., 1999) and ultrafiltration methods (Bhattacharjee et al., 2006; Holmqvist et al., 2005; Liu et al., 2004a,b; Wallberg et al., 2006); and, (2) as focused earlier, development of new lignin applications. In Fig. 1, both the squares “Processing” and “Lignin Plant” represent steps where lignin can be extracted from black liquor using any suitable technology.

4. The integrated process

The general concept of the integrated process for vanillin production includes the Kraft lignin oxidation and separation steps in order to allow the isolation of vanillin from the oxidized solution. The reaction and purification procedures related to this integration concept are presented in the following sections. The paper is written within the framework of the work developed by the Laboratory of Separation and Reaction Engineering (LSRE) on the area of vanillin chemical production from Kraft lignin oxidation (Araujo, 2008; Fargues et al., 1996a,b; Mathias, 1993; Mathias et al., 1995; Mathias and Rodrigues, 1995; Mathias and Rodrigues, 1995; Zabkova et al., 2007a,b, 2006), as well as, polyurethane synthesis from lignin-based raw materials (Cateto et al., 2008a,b,c, 2007).

4.1. Lignin oxidation and vanillin production

The only lignin-based process industrially implemented is based on the alkaline oxidation of lignosulphonates in the presence of air (Triumph Venture Capital Ltd., 2004a). This lignin oxidation route has been extensively studied since the sixties (Bjorsvik, 1999; Diddams and Krum, 1970; Ness, 1983). The use of Kraft black liquor as raw material, instead of the conventional application of lignosulphonates, is lacking presently. Since, currently, Kraft process prevails in the pulp and paper industry, we focus on the Kraft lignin oxidation for vanillin production in this integrated process.

The chemical oxidation of lignin with oxygen is a reaction in which typical operating conditions involve high pH values (close to 14), high temperatures (up to 150 °C) and high total pressure (e.g., 10 bar (Mathias, 1993)). Under these conditions it is possible to cleave this large complex molecule thus creating a favourable medium for the oxidation of their fragments towards vanillin. In particular, ether bonds in the alfa- and beta- carbon positions of the phenyl propane units are cleaved, and there is also the rupture of carbon–carbon bonds in the propanoid side chains of the phenyl propane units (Lebo et al., 2001). In general, subsequent to the alkaline oxidative cleavage of lignin that provides fragments which can lead to the production of vanillin, well known stages in the field of reactivity of lignin may be assumed (Tarabanko and Petrukhov, 2003): (1) the formation of phenoxy radicals (by the detachment of one electron from phenoxy anion), (2) the formation of quinone methide (by disproportionation of phenoxy radical), (3) the formation of coniferyl alcohol (by nucleophilic addition of hydroxide ion), (4) probable formation of gamma-carbonyl (by oxidation of coniferyl alcohol); and, finally, (5) the formation of vanillin (by the retro-aldol cleavage of the alfa- and beta-un satu rated aldehydes). There are a few published works dealing with the oxidation mechanisms of lignin and, in most cases, the approaches involve lignosulphonates and are based on different assumptions (Bjorsvik, 1999; Dardelet et al., 1985; Schultz and Templeton, 1986; Tarabanko et al., 1995a,b, 2004; Tarabanko and Petrukhov, 2003). It is worth mentioning that due to the molecule complex structure, developing a reaction mechanism is not a straightforward task. Moreover, two additional reasons make this task harder: the lignin oxidation is associated to complex alkaline hydrolysis steps at high temperatures; and, under drastic oxidative conditions, peroxyl radicals (from aromatic aldehydes), which often are intermediate in the oxidation by oxygen, react fast with vanillin leading to oxidative degradation (Bjorsvik, 1999). A reaction scheme for vanillin production from lignin and vanillin oxidation in alkaline medium has been discussed previously in the work of Mathias (1993) and Fargues et al. (1996a). We have been investigating the vanillin production from chemical oxidation of Kraft lignin in order to develop kinetic models for this process and, mainly, to analyze the effect of operating process parameters on the yield of the process. It was verified that operational parameters such as temperature, lignin concentration, oxygen partial pressure and sodium hydroxide concentration have considerable influence on the produced vanillin amount (Mathias and Rodrigues, 1995). Some results of lignin oxidation experiments performed at LSRE are summarized in Table 1.

The batch experiments of lignin oxidation have been performed in a jacketed reactor with controlled temperature and pressure. The reaction mixture (solution of lignin in sodium hydroxide) was maintained under stirring and oxygen was fed to the reactor. The total pressure of the system was kept constant by continuous addition of oxygen (Fargues et al., 1996a; Mathias et al., 1995; Mathias and Rodrigues, 1995).

There is a maximum obtainable vanillin yield from a specific type of lignin. The formation of phenolic compounds like vanillin or syringaldehyde is strictly related to the available percentage of its precursor in the lignin structure. The less transformations or chemical treatments lignin suffers, the more useful it becomes for producing phenolic aldehydes (Tarabanko et al., 1995a,b; Villar et al., 1997).

Mathias and Rodrigues (1995) have reported that a 60 g/L solution of Kraft lignin from Pinus spp. can provide a maximum vanillin yield of 13% (w/w); value based on nitrobenzene oxidation (7 h of reaction, 147 °C, 2N NaOH and 0.84 mL of nitrobenzene per gram of initial lignin). Villar et al. (1997), using a lignin precipitated from Kraft black liquor with the addition of a calcium salt dissolved in a water soluble alcohol, have published a maximum yield for the total phenolic aldehydes (syringaldehyde + vanillin) of 14%, also based on nitrobenzene oxidation (40 min of reaction, 190 °C, 2N NaOH and 6 mL of C6H5NO2 per gram of initial lignin).

From Table 1, one can observe yields in the range of 3–10% for the Kraft lignin oxidation with O2 using similar operating conditions. Under these conditions, Mathias (1993) and Fargues et al. (1996a) have found a vanillin yield around 10%
Table 1 – Set of experimental conditions used in batch experiments of Kraft lignin oxidation and obtained vanillin yields.

<table>
<thead>
<tr>
<th>Lignin type</th>
<th>T&lt;sup&gt;a&lt;/sup&gt; (°C)</th>
<th>P&lt;sub&gt;O&lt;sub&gt;2&lt;/sub&gt;&lt;/sub&gt; (bar)</th>
<th>P&lt;sub&gt;a&lt;/sub&gt; (bar)</th>
<th>C&lt;sub&gt;Lignin&lt;/sub&gt; (g/L)</th>
<th>t&lt;sub&gt;max&lt;/sub&gt; (min)</th>
<th>Vanillin yield (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pinus spp. Westvaco</td>
<td>121</td>
<td>4.1</td>
<td>9.3</td>
<td>60</td>
<td>43.4</td>
<td>7.3</td>
<td>Mathias (1993)</td>
</tr>
<tr>
<td></td>
<td>119</td>
<td>6.5</td>
<td>9.5</td>
<td>60</td>
<td>27.1</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>3.7</td>
<td>9.7</td>
<td>60</td>
<td>76.5</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>141</td>
<td>3.8</td>
<td>10.0</td>
<td>60</td>
<td>64.4</td>
<td>10.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>122</td>
<td>3.8</td>
<td>9.6</td>
<td>30</td>
<td>61.4</td>
<td>10.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>3.0</td>
<td>9.7</td>
<td>60</td>
<td>60.0</td>
<td>8.3</td>
<td>Fargues et al. (1996a)</td>
</tr>
<tr>
<td></td>
<td>133</td>
<td>2.8</td>
<td>9.7</td>
<td>60</td>
<td>35.0</td>
<td>10.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>1.2</td>
<td>9.7</td>
<td>60</td>
<td>70.0</td>
<td>8.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>135</td>
<td>5.0</td>
<td>9.7</td>
<td>60</td>
<td>20.0</td>
<td>8.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>128</td>
<td>3.0</td>
<td>9.7</td>
<td>30</td>
<td>40.0</td>
<td>6.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>4.0</td>
<td>9.7</td>
<td>30</td>
<td>45.0</td>
<td>9.0</td>
<td></td>
</tr>
<tr>
<td>Indulin AT Westvaco</td>
<td>123</td>
<td>4.0</td>
<td>9.0</td>
<td>60</td>
<td>75.0</td>
<td>3.7</td>
<td>Araujo (2008)</td>
</tr>
<tr>
<td></td>
<td>123</td>
<td>6.5</td>
<td>9.5</td>
<td>60</td>
<td>35.0</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>Pinus pinaster Portucel</td>
<td>127</td>
<td>3.5</td>
<td>9.1</td>
<td>82.5</td>
<td>92.9</td>
<td>4.1</td>
<td>Mathias (1993)</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>3.8</td>
<td>9.3</td>
<td>82.5</td>
<td>46.4</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>Black liquor Portucel</td>
<td>119</td>
<td>3.5</td>
<td>9.1</td>
<td>50</td>
<td>77.5</td>
<td>8.0</td>
<td></td>
</tr>
</tbody>
</table>

In all experimental runs: C<sub>NaOH</sub> = 80 g/L (pH<sub>initial</sub> ≈ 14).

* Initial values except for Fargues et al. (1996a) where the values presented result from average conditions.

(defined as the ratio: mass of produced vanillin/mass of initial lignin) for batch oxidations. This value corresponds to a vanillin recovery of almost 80% for Kraft lignin (Pinus spp.). Vanillin recovery is defined as the ratio between the obtained vanillin yield and the maximum vanillin yield based on nitrobenzene oxidation. However, results from Araujo (2008) have shown a lower vanillin yield under equal operating conditions. Here, it is important to notice that two different Kraft lignins were used as raw material. Both the Kraft lignin Indulin AT and the Kraft lignin from the Pinus spp. have been supplied by Westvaco Co., but the first seems to have a reduced capacity for vanillin production. Tarabanko et al. (1995a,b) have presented a study where the influence of lignin origin, conditions of production and type of pre-treatment on the obtained yields of vanillin and syringaldehyde was inspected by lignin oxidation. The results have indicated a competition between lignin fragments condensation (syringil fragments and guaiacyl fragments) and lignin oxidation into aldehydes.

The degradation of the produced vanillin is an extremely important point from a techno-economic approach. To avoid losses of vanillin by oxidation, two operational parameters should be taken into account: oxygen partial pressure (P<sub>O<sub>2</sub></sub>) and reaction time. There is a conflicting effect on these two parameters, i.e., a high value of P<sub>O<sub>2</sub></sub> can reduce reaction time but leads to vanillin degradation; on contrary, a low P<sub>O<sub>2</sub></sub> increases reaction time but it hinders vanillin oxidation. Moreover, during the Kraft lignin oxidation, formation of acid compounds can occur, lowering the pH of the medium. At lower pH values (<11–12) vanillin losses by oxidation become more significant. Fig. 2 shows the vanillin concentration and pH as a function of reaction time for two batch experiments described in Table 1. One can verify that during the lignin oxidation a maximum amount of vanillin is reached from where pH value begins to decrease and, as consequence, the vanillin yield decreases considerably. It is known that at higher alkali concentration (pH > 12) the rate of vanillin degradation is lower. At lower pH (pH < 12) the vanillin oxidation rate is second order with respect to the vanillin concentration (Fargues et al., 1996a,b).

With regard to the influence of the operating conditions on the Kraft lignin oxidation process, these works reported in Table 1 contain information to decide the best conditions for the production of vanillin. In the case of Pinus spp. lignin, an optimal production was found for an oxygen partial pressure of 2.8 bar, under a temperature of 133 °C for a lignin concentration of 60 g/L, dissolved in 2N NaOH.

4.2. The continuous process of lignin oxidation

From an industrial point of view, the continuous process of lignin oxidation will be a priori more attractive than the batch process.
In a typical run, the liquid mixture (60 g/L lignin + 80 g/L sodium hydroxide) was pumped to the reactor by a piston pump (work range 1.3–13 L/h). The temperature inside the reactor was regulated to 403 K. At the beginning of the reaction, nitrogen was admitted to the reactor to pressurize the system. Once the operating temperature, pressure and flow rates stabilized, lignin oxidation could be initiated. The desired N2 and O2 flow rates were controlled with two mass flow controllers. With the purpose of determining the reactor performance for lignin oxidation in terms of vanillin formation, the experiments of Kraft lignin oxidation were performed in two different reactor configurations: structured packed bubble column reactor (SPBCR) and bubble column reactor (i.e., with no internals; BCR). The operating conditions used in these experiments are summarized in Table 2.

These continuous experiments were performed with Kraft lignin Indulin AT supplied by Westvaco Co. The steady state was reached at approximately 6 h of operation for both types of reactor configuration. Vanillin concentration in the BCR exit stream reached a steady state value of around 0.56 and 0.67 g/L for the run BCR1 and BCR2, respectively. The vanillin yield had a slight improvement in experiment BCR2 due to an increase in gas flow rate (higher mass transfer coefficients) and also a higher pO2 for the oxygen solubility in the liquid phase. Considering the batch experiment, these results are about 25–30% of the maximum level of vanillin concentration obtained in the batch reactor.

In the second configuration, the hydrodynamics environment (i.e., dispersion coefficient, phase hold-up or even heat transfer coefficients) for the structured packed bubble col-

alternative, mainly due to the huge Kraft liquor volumes to be treated in a pulp industry. Also, continuous processes are easier to control and to attain constant product characteristics as well as their overall investments and operating costs are usually lower (Lebo et al., 2001; Rase, 1977). An experimental pilot set-up was built to promote the concerned gas–liquid reaction in a continuous operating mode. A schematic diagram of the operational pilot installation at LSRE is shown in Fig. 3. The bubble column reactor is made in 316L stainless steel with 8 L capacity. The main cylindrical body of the reactor is the section where the gas–liquid reactions take place. It has an internal diameter of 10 and 70 cm height, and is filled with three modules of Mellapak 750.Y structured packing (Sulzer Chemtech, Switzerland). The goal was to enhance the overall mass transfer performance of the system. Each of the modules is rotated 90° with respect to the adjacent one to promote radial mixing of the fluids in the transition between packing elements. In Fig. 3c a picture of a Mellapak 750.Y packing element is shown. This type of packing is characterized by a geometric specific area of 750 m2/m3 and a void fraction of 0.95 (Siminiceanu et al., 2007). The corrugated metal sheets that make up these packings are inclined by an angle of 45° with respect to the vertical axis. The separation head at the top of the reactor works to separate the gas and liquid streams, obtaining a final liquid stream with no dispersed gas, taking advantage of the impulsion forces on the gas bubbles. More details on the reactor set-up can be found elsewhere (Sridhar et al., 2005).

In a typical run, the liquid mixture (60 g/L lignin + 80 g/L sodium hydroxide) was pumped to the reactor by a piston pump (work range 1.3–13 L/h). The temperature inside the reactor was regulated to 403 K. At the beginning of the reaction, nitrogen was admitted to the reactor to pressurize the system. Once the operating temperature, pressure and flow rates stabilized, lignin oxidation could be initiated. The desired N2 and O2 flow rates were controlled with two mass flow controllers.

With the purpose of determining the reactor performance for lignin oxidation in terms of vanillin formation, the experiments of Kraft lignin oxidation were performed in two different reactor configurations: structured packed bubble column reactor (SPBCR) and bubble column reactor (i.e., with no internals; BCR). The operating conditions used in these experiments are summarized in Table 2.

These continuous experiments were performed with Kraft lignin Indulin AT supplied by Westvaco Co. The steady state was reached at approximately 6 h of operation for both types of reactor configuration. Vanillin concentration in the BCR exit stream reached a steady state value of around 0.56 and 0.67 g/L for the run BCR1 and BCR2, respectively. The vanillin yield had a slight improvement in experiment BCR2 due to an increase in gas flow rate (higher mass transfer coefficients) and also a higher pO2 for the oxygen solubility in the liquid phase. Considering the batch experiment, these results are about 25–30% of the maximum level of vanillin concentration obtained in the batch reactor.

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In the second configuration, the hydrodynamics environment (i.e., dispersion coefficient, phase hold-up or even heat transfer coefficients) for the structured packed bubble col-
umn reactor is quite different from the bubble column reactor, because of the structured packing (Mellapak 750.Y) above the gas distributor. At steady state, the concentration of vanillin obtained from the SPBCR configuration was 0.73 and 0.89 g/L for runs 3 and 4, respectively (i.e., corresponding to 33–40% vanillin yield from batch oxidation of Indulin AT Kraft lignin). One can expect that the improvement on the vanillin content because of the structured packing (Mellapak 750.Y) above the gas distributor. At steady state, the concentration of vanillin obtained in the batch reactor. Araujo (2008) has shown that the mass transfer coefficient was 8.1 × 10⁻⁴ s⁻¹ using packing against 6.0 × 10⁻⁴ s⁻¹ without packing (that means a 1.35-fold increase). However, in both cases, the lignin mass conversion was substantially lower than that obtained for the batch operation. The main reason of this difference is the poor mass transfer of oxygen from the gas phase to the liquid phase.

To improve the performance of the continuous reactor and reach the production levels obtained in batch mode, the influence of some operating conditions was studied using a model developed by Araujo (2008). Since the oxygen mass transfer was the limiting step to vanillin formation, the limiting situation of pure oxygen in the gas feed was considered. Of course, the liquid residence time should be decreased as the oxygen mass transfer rate increases in order to avoid excessive vanillin oxidation. From the structured reactor operating at steady state, it was possible to achieve a value of the vanillin concentration in the exit stream of approximately 1.8 g/L, which is 85% of the maximum levels of vanillin concentration obtained in the batch reactor.

It should be noticed that vanillin yield obtained in batch experiments with Insulin AT Kraft lignin was quite low, limiting strongly the operation of the continuous reactor. These levels of vanillin yield seem to be limited by the used raw material and by the low rates of oxygen transfer to the liquid in the reaction unit. These two points are crucial for improving the vanillin formation from Kraft lignin.

Despite the technical details to be solved or improved in envisaging the industrial vanillin production from Kraft lignin, an optimistic sight might be considered in view of the available Kraft lignin resources, reflecting on its low cost and its supply sustainability; crucial aspects that could make the economic application of this technology commercially feasible. One should also keep in mind that the profitability of the lignin extraction from the black liquor must be taken into account (Olsson et al., 2006).

The commercial practicability of this process might be attained if special attention is directed to the proper biomass (Kraft lignin) to be used. Improving the pre-treatment methods in order to preserve the essential fragments needed for vanillin and improving the knowledge on biomass, and how to produce more homogeneous lignin raw materials (for example, using membrane processes before the reaction step), could provide important technological advances for the application of this alternative procedure. Anyway, it corresponds to a considerable progress towards solving the mentioned bottleneck in pulp and paper industries.

In this process, the energy requirements for the conversion of lignin into vanillin can be provided by the exceeding Kraft liquor from the pulp industry or even from the by-products of lignin oxidation process (degraded lignin), according the current biorefinery concept. We must remark that surplus energy obtained from burning lignin is, nowadays, sold as electricity in current Kraft pulp mills; thus, the cost of producing energy for vanillin production instead of electricity should be added to the final product.

In conclusion, considering the mentioned factors and the achievable yields of Kraft lignin oxidation process, a favourable balance could be obtained. The success of this process will largely depend on the nature and composition of this complex raw material.

### 4.3. Membrane separation

In the process of Kraft lignin oxidation to produce vanillin, the reaction media contains degraded molecules of lignin and sodium salt of vanillin as well as other species. Some other oxidation products can be acetovanillone, dehydrodivanillin, guaiacol, p-hydroxybenzaldehyde, and aromatic acids (Pearl, 1942). Mathias and Rodrigues (1995) have shown, using HPLC and GC analyses, that after chemical oxidation of pine Kraft lignin with molecular oxygen the lignin molecule is degraded producing vanillin and, in some cases, acetovanillone (only under strong oxidation conditions). The isolation of vanillate from the oxidized solution is an important stage in the vanillin production. Industrial companies as Monsanto (U.S.A.), Salvo Chemical Co. (U.S.A.), and Ontario Paper Co. (Canada) produce vanillin from the air oxidation of sulphite lignin and carry out the extraction of vanillin from the reactant medium by using liquid–liquid extraction with suitable solvents (benzene or toluene) after acidification of the medium. The acidification step is to precipitate the compounds of high molecular weight (MW) and a large amount of acidic solution is required. Furthermore, it is possible that vanillin is lost during this process, since vanillin may be co-precipitated during the acidification.
step of the lignin (Craig and Logan, 1962; Fargues et al., 1996a; Zabkova et al., 2006). Accordingly, the traditional precipitation procedure, either by using toxic chemicals or by the waste generation, is an option to be changed by more satisfactory solutions.

In our proposal, the first step towards recovering the vanillin from Kraft lignin oxidation is the ultrafiltration (UF) process. In a simple approach, vanillin goes to the permeate stream because of its low molecular weight, whilst the lignin as a macromolecule is retained by the membrane during the ultrafiltration. Membrane processes have all the requirements needed to act as key separation units in biorefineries due their excellent fractionation capability, low chemical consumption and low energy requisites (Jonsson et al., 2008). The energy requirement is directly related to the volumetric flux of the process. The cost of filtration processes can be reduced if optimal operating conditions are defined for this operation. Since 1960s the pulp and paper industry has paid attention to membrane processes focused on the fractionation and concentration of sulphite liquor (to reduce the discharge of bleach plant effluent or to use as biofuel) and also on the re-use of water from purification of mill process effluents. The treatability of spent sulphate liquor has also been considered in a commercial-sized membrane plant (Jonsson et al., 2008) and many researches have been focused on the filtration of Kraft black liquor (Keyoumu et al., 2004; Liu et al., 2004a,b; Wallberg et al., 2006).

The application of membrane technology on black liquor has been largely limited due to its high temperature, high pH value and high suspension solids concentration. Nowadays, there is a high effort towards lignin extraction by ultrafiltration of the Kraft black liquor (Barnier et al., 1987; Kirkman et al., 1988; Tanistra and Bodzek, 1998; Wallberg et al., 2006; Woerner and McCarthy, 1984). The cost of this operation is related to the flux, cleaning frequency, membrane life-time and energy requirement.

A number of works dealt with the use of UF and other filtration techniques in view of the fractionation of chemical compounds obtained from spent liquor (Afonso and Pinho, 1991; Bhattacharya et al., 2005; Drouin and Desroches, 1988; Tsapiuk et al., 1989). The UF technique has been evaluated at LSRE to recover vanillin from Kraft lignin oxidation (Zabkova et al., 2007a). As seen, the temperatures of the solution at the exit stream of the oxidation reactor are above 100 °C and the pH values are around 9–12. Since ceramic membranes can withstand hard conditions of temperature, pH and alkalinity, they are appropriate for this application. Therefore, tubular ceramic membranes with different molecular weight cut-offs were tested for the continuous fractionation of well-defined high and low molecular weight fractions from lignin and vanillate mixtures.

The experiments were carried out in the batch mode, in which the retentate was recirculated to the feed tank and the permeate was withdrawn to a separated reservoir. The membranes were Kerasep type with molecular weight cut-off of 15kDa supplied by Orelis (France) and Filtanium type with molecular weight cut-off of 1 and 5kDa supplied by Tami Industries (France). Kerasep membranes are made of Al2O3–TiO2 active layer on the ceramic support (working transmembrane pressure (AP): 0–4 bars; total membrane area: 0.008 m²; 400 mm length; 6 and 10 mm inside (øi) and outside (øe) diameter, respectively). Filtanium membranes are made of TiO2 active layer on the ceramic support (working AP: 0–10 bars; membrane surface: 0.011 m²; 400 mm length; øi = 6 mm and øe = 10 mm). Although the mixtures of vanillin, lignin and sodium hydroxide used on the experiments have been prepared (i.e., they did not come from the exit stream of the oxidation step), these experiments allow understanding the involved phenomena, performances and expected problems related to this operation. A detailed description of the lab-scale membrane set-up is shown in Zabkova et al. (2007a).

Considering the composition of 60 g/l lignin and 6 g/L vanillin (a mixture artificially prepared assuming a vanillin yield of around 10% from oxidation process), Tables 3a and 3b show the experimental conditions together with the measured values (permeate flow, rejection, volume reduction (permeate volume withdrawn/initial volume of the feed tank)) in UF of the lignin/vanillate mixture using tubular ceramic membranes. Vanillin and lignin concentration were measured by UV–vis spectrophotometer after pre-treatment of the samples (Zabkova et al., 2007a,b). The value of the permeate flux refers to the first measurement of the flux in which, at this case, concentration polarization layer was already formed. This is due to the fact that the feed solution was circulated through the system without opening the permeate valve in order to fill the membrane system and to adjust the feed flow rate. Afterwards, the permeate valve was opened and the first measurement of the flux was performed. During the batch UF experiments, the permeate flow rate, the retentate flow rate and transmembrane pressure were measured. For the case of pH 12.5, the percentage of reduction of the permeate flux during the UF experimental run was 24% in 1100 min for the case of 1kDa cut-off membrane (Run 4), 20% in 780 min for 5 kDa cut-off membrane and 22% in 570 min for 15 kDa cut-off membrane.

Lignin is mostly rejected and predominantly responsible for the surface fouling, when a progressive growth of a deposited layer at the surface membrane takes place during the ultrafiltration operation. The smaller molecules of vanillin (152 Da MW) can diffuse entirely through the pore. Once the vanillin transport across the membrane is facilitated, no vanillin rejection has been observed. It seems that there is no occurrence of pore internal fouling (completely or partially pore clogging), since there was no changing in membrane rejection characteristics. It should be mentioned that if a real stream was employed as feed, some other oxidation products can be present. We can expect that compounds having similar molecular weight to the vanillin will be recovered in the permeate stream. In the crystallization step, the vanillin can be purified. UF experiments using mixtures resulting from the oxidation reaction must be considered in future work. In current case, the cleaning step of the membrane using alkaline solution has restored the original membrane permeability.

As one can see from Table 3b, the optimal membrane cut-off used to recover vanillin from lignin/vanillin mixture is not obvious since there are two important parameters involved that should be taken into account: the purity of vanillin in the permeate and the optimal permeate flux. The highest lignin rejection value was obtained with a membrane of 1 kDa cut-off (RL = 0.972), but, due to the small cut-off, a significant decrease of permeate flux was observed comparatively to other membranes with bigger cut-off.

Since membranes with bigger cut-off might combine higher flux with acceptable rejection values (as a comparison between the results obtained from the 1 and 5kDa cut-off), a scheme of staging ultrafiltration membranes starting from larger cut-off is proposed in this step of the integrated process. In fact, the permeate of a first membrane might be taken as the
feed of the second membrane of smaller cut-off, which means a lower concentration of degraded lignin on the feed mixture and, consequently, a higher permeate flux. From Table 3b, the permeate flux with 1 kDa cut-off in staging mode was almost 5-fold larger in comparison to that when high concentration was filtrated (Run 6). Considering the low concentration of lignin in the solution, the flux decline does not represent significant limitation in the process and this could be a way to optimize the recovery of vanillin from Kraft lignin oxidation media using ultrafiltration. In order to increase the volume reduction, higher transmembrane pressures and, also, higher temperatures of feed mixture could be applied. It is worth mentioning that if an acidification step is used to precipitate the compounds of high molecular weight (MW) from the retentate in order to recover its vanillin content, a reduced amount of acidic solution will be required.

Despite the limitation of permeate flux caused by the surface fouling attributed to concentration polarization and gel formation, a very high cleaning efficiency can be obtained using a simple alkali cleaning medium (0.1–0.2 M NaOH). This fact, in addition to membrane cleaning frequency and the membrane lifetime, will be determinant parameters to decide on the feasibility of this process.

### 4.4. Ion-exchange process purification

The mixture leaving the oxidation reactor and the membrane separation step will contain vanillin and other vanillin related low molecular weight phenolates. The vanillin is in the salt form due to the used excess of sodium hydroxide required in the oxidation reaction.

According to a patent of Hibbert and Tomlinson (1937), the mixture can be acidified and vanillin extracted with suitable solvents such as benzene or toluene. A drawback of this technique is related to the large amount of acid needed to neutralize the mixture with high alkalinity leading to lignin precipitation that further complicates the extraction and causes vanillin losses. The precipitation can be avoided by direct extraction of sodium vanillate with n-butyl alcohol or isopropyl alcohol (Bryan, 1956; Sandborn et al., 1936). The disadvantage of this process is also related to the high alkalinity since sodium vanillate presents limited solubility in such organic solvents.

An alternative method to recover vanillin without needing acidification of the oxidized liquor consists on using cationic ion-exchange resin as suggested by Forss et al. (1986) and Fargues et al. (1996a). It was found out that eluting the strongly alkaline effluent with water through a cationic ion-exchange resin in the sodium form provides good separation of vanillin, and other oxidation products, from lignin, which elutes first. Moreover, more than 60% of the sodium contained in the effluent is eluted together with lignin and could be reused without any neutralization, a step always performed prior to chemical recovery in pulp mills.

According to Forss et al. (1986), in vanillin production, the treatment involving ion exchange in sodium form should be carried out between the oxidation and extraction steps. This method has some advantages such as separation of 80% of dry matter, lignin and sodium from the vanillin reactor effluent and the quantity of acid needed to neutralize the vanillin fraction is small. Moreover, the ion-exchange resin does not require a regeneration step and the lignin can be returned to the chemical recovery of the pulp mill.

In 1971, Craig and Logan (1971) have reported the use of a weak-ion-exchange resin in acid form for the vanillin isolation. The same procedure is mentioned by Logan (1965) as one of the steps in a cyclic process for the recovery of vanillin. The exchange capacity strongly depends on the effluent pH.

### Table 3a – Experimental conditions in ultrafiltration of the lignin/vanillin mixture using tubular ceramic membranes ($v_{C-flow}$, cross-flow velocity; $C_i^0$, feed concentration; $V_0$, initial feed volume).

<table>
<thead>
<tr>
<th>Run</th>
<th>Cut-off membrane (kDa)</th>
<th>$v_{C-flow}$ (m s$^{-1}$)</th>
<th>$C_i^0$ (g L$^{-1}$)</th>
<th>pH</th>
<th>$V_0$ (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Lignin</td>
<td>Vanillin</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>15</td>
<td>0.992</td>
<td>60</td>
<td>6</td>
<td>8.5</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>0.992</td>
<td>60</td>
<td>6</td>
<td>12.5</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>1.179</td>
<td>60</td>
<td>5</td>
<td>12.5</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>1.277</td>
<td>60</td>
<td>6</td>
<td>8.5</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>1.179</td>
<td>60</td>
<td>6</td>
<td>12.5</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>1.179</td>
<td>2</td>
<td>6</td>
<td>12.5</td>
</tr>
</tbody>
</table>

Transmembrane pressure: $\Delta P$ (1 and 5 kDa cut-off) = 1.55 bar; $\Delta P$ (15 kDa cut-off) = 1.30 bar. Viscosity of solution: $\eta = 1.190 \times 10^{-3}$ Pa s (except to the mixture of 2 g/L lignin and 6 g/L vanillin). The ultrafiltration experiments have run at ambient temperature.

### Table 3b – Measured values in ultrafiltration of the lignin/vanillin mixture using tubular ceramic membranes (VR, volume reduction; $J$, permeate flux; $R_{obs}$, observed rejection; $R_m$, membrane hydraulic resistance).

<table>
<thead>
<tr>
<th>Run</th>
<th>Cut-off membrane (kDa)</th>
<th>VR</th>
<th>$R_{obs}$ (lignin)$^a$</th>
<th>$J \times 10^{-3}$ (L m$^{-2}$ h$^{-1}$)</th>
<th>$R_m \times 10^{13}$ (m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>0.313</td>
<td>0.943</td>
<td>28.12</td>
<td>0.2806</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>0.340</td>
<td>0.865</td>
<td>16.87</td>
<td>1.222</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>0.275</td>
<td>0.968</td>
<td>13.50</td>
<td>1.222</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>0.102</td>
<td>0.951</td>
<td>4.75</td>
<td>2.806</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>0.103</td>
<td>0.972</td>
<td>3.75</td>
<td>2.806</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>0.410$^b$</td>
<td>0.981$^b$</td>
<td>18.00$^b$</td>
<td>2.806</td>
</tr>
</tbody>
</table>

$^a$ $R_{obs}$ (Vanillin) $\approx$ 0 for all ultrafiltration run.

$^b$ Considering this filtration on the 1 kDa cut-off membrane as a second stage in a staging membrane operation mode.
high enough), the H\(^+\) ion from the resin exchanges for Na\(^+\) ion and vanillin in solution (or only vanillate if the pH value is during the ion-exchange process.

The pH profile depends on the buffer vanillate/vanillin formed the vanillin appears in the outlet of the column. The behaviour of pH in the opposite case, can be avoided. The main advantages of the integrated process include: (1) no need of acid to neutralize the vanillin fraction (is only needed to regenerate the resin bed); (2) no lignin precipitation during the ion-exchange process; (3) no need of high cost equipment neither equipment working under high pressure is needed; and (4) ion-exchange resin regeneration easy to perform.

When the solution contains only a base (NaOH), the H\(^+\) ion from the resin is exchanged with the Na\(^+\) ion from the solution and converted into water due the irreversible reaction with the OH\(^-\) co-ion in solution. When the solution contains vanillate and vanillin in solution (or only vanillate if the pH value is high enough), the H\(^+\) ion from the resin exchanges for Na\(^+\) ion from the solution and vanillin is produced. Fig. 4 shows the typical ion-exchange profiles of the Na\(^+\) ions, vanillate (VNa), vanillin (VH) and pH for a feed solution of vanillate and vanillin with pH 11.9 using a fixed bed (resin: Amberlite IR120H; 293 K; 19 mL min\(^{-1}\)). The resin will be converted to sodium form and sodium vanillate can be directly introduced to the column filled with a strong cation ion-exchange resin in H\(^+\) form.

This particular method, where a strong cationic resin in H\(^+\) form is applied, was studied considering the influence of both alkalinity and vanillin concentration of the treated solution by using static and dynamic approaches (Zabkova et al., 2007b).

In the overall process of vanillin recovery from Kraft liquor, the ion-exchange step should be designed after the membrane module where the high molecular weight compounds and dry matter are safely removed. Therefore, the application of an appropriate membrane cut-off, temperature and high alkalinity resistance materials are essential. The permeate stream containing low molecular weight phenolates and sodium vanillate can be directly introduced to the column filled with a strong cation ion-exchange resin in H\(^+\) form. Since the eluent which is collected in the outlet of the column contain all compounds in phenolic form there is no need for cooling the media before it enters the ion-exchange column.

4.5. Vanillin crystallization—process description

The vanillin obtained by the Kraft liquor oxidation and later recovered at a certain yield using a combination of membrane and ion-exchange processes can still contain small amounts of impurities. The final purification step of vanillin represents a difficult task and multistage crystallization is needed to obtain a high purity product (Makin, 1984).

The main impurities of vanillin consist of low molecular weight substances, e.g., o-vanillin, 5-formyl vanillin, vanillin acid, acetovanillone, etc. The number of crystallization steps should be always based on further vanillin applications but it also depends on impurity contents and type. It is well established that the needed vanillin purity for technical applications is over 97%, while the vanillin grade suitable for foodstuffs applications should be higher than 99.8%.

Schoeffel (1962) reported that vanillin can be purified using multiple crystallization steps from water–methanol solutions. The vanillin obtained from lignin oxidation is dissolved in a solvent mixture of water and methanol with a composition preferably of 40% of the methanol (w/w). In the beginning of the crystallization process the solution is stirred and rapidly cooled to reach a temperature between 23 and 25 °C. The first indicator that crystallization begins is the slight increase in temperature which must be measured inside the reactor.

As already mentioned, the main target in batch crystallization is to control the supersaturation and nucleation especially during the initial stage. This can be performed by seeding using purified crystalline vanillin to obtain a better crystallization performance. The temperature is maintained, for approximately one hour, within a range of ±2 °C of the initial crystallization temperature. Afterwards, the reactor with the vanillin solution is continuously stirred and the content slowly cooled during about three hours to reach a temperature around 5 °C. The crystallization is completed following a stirring period of about 2 h of the reactor mixture maintaining a temperature of 5 °C.

The following step in vanillin purification includes filtration of the crystallized mixture. The solids filter cake must be washed with successive amounts of cold water (under 5 °C) and thereafter carefully dried. The vanillin crystals obtained in first crystallization step should be analyzed for the mentioned impurities and methanol content in order to plan the needed multiple crystallization steps.

In the case that the vanillin was not obtained with the desired purity, the recrystallization can be performed using a similar procedure but with a solvent mixture containing methanol at 50% (w/w). The vanillin in the crystalline form is first diluted at higher temperature (40–50 °C) and later rapidly cooled to 35 °C under continuous stirring. The content of the reactor is again seeded using finished pure vanillin and the crystallization is carried on at 30–34 °C under continuous stirring during a time period of 1 h. Afterwards, the reactor is cooled slowly during 2 h to reach a temperature of 13 °C. Finally, the crystals are filtered and dried using the previously described procedure. The filtrates containing methanol obtained from multiple crystallization steps, and from the performed washings, can be lately reused. The methanol content could be easily distilled and recycled to the crystallization.

Apart from multiple water–methanol crystallization process, the purified vanillin can be also obtained by one or more crystallizations from water, using charcoal to adsorb the remaining impurities traces (Major and Nicolle, 1977; Schoeffel, 1962). First, the vanillin solution is prepared by dis-
solving vanillin in hot water at around 90 °C. The solution is thereafter cooled till the crystallization begins (at around 50 °C). The crystallization continues for a time period of 2 h at 45 °C. Afterwards, the temperature is slowly decreased to reach 13 °C during 3 h. Finally, the crystallization is completed after an additional period of 1 h maintaining the same conditions. Finally, the obtained product is carefully washed and dried.

4.6. Lignin-based polyurethane synthesis

This section discusses lignin potential as a raw material for polyurethane synthesis having in view the valorisation of a co-product generated during the biorefinery process. In this context, two lignin sources are available: (1) polymeric lignin obtained after processing the black liquor generated during the papermaking process (lignin plant product) and (2) degraded lignin obtained as a by-product of the vanillin synthesis process (vanillin plant by-product).

Polyurethanes are considered as one of the most versatile polymeric materials offering a wide range of products with various applications in diverse sectors. Rigid polyurethane (RPU) foams and elastomers belong to this class of products. The interest to explore lignin as a raw material for polyurethane synthesis has lead, in the past few decades, to some research works where various types of materials (rigid foams, elastomers, sealants) have been produced using a wide range of chemical systems. The exhibited properties were found promising and, in some cases, similar to those of conventional polyurethanes. The importance of these achievements leads to the appearing of some patented results (Glasser et al., 1991; Kuprle, 2000; Yoshida et al., 1986). It is worth to mention that the interest for developing lignin-based applications, including lignin-based materials, became more notorious during the last few years. Two major factors are related to this situation, namely (1) the availability of new lignin sources, such as, sulphur-free lignins and (2) the growing interest on biorefinery processes where lignin valorisation offers impact (it represents up to 30% of biomass weight).

The utilization of lignin in polyurethane synthesis often follows two global approaches: (1) the direct utilization of lignin without any preliminary chemical modification, alone or in combination with other polyols (Cateto et al., 2008c; Evtuguin et al., 1998; Vanderlaan and Thring, 1998; Yoshida et al., 1990) or, (2) by making hydroxyl functions more readily available by chemical modification, such as esterification and etherification reactions (Cateto et al., 2008b; Gandini et al., 2002; Glasser, 1989; Hatakeyama, 2002; Nadji et al., 2005). A summary of possible synthetic routes is shown schematically in Fig. 5. Path (1) shows lignin direct use as macromonomer, path (2) followed by path (3) illustrates lignin liquefaction by chemical modification and its subsequent use in rigid polyurethane foams preparation, path (2) followed by path (4) illustrates the preparation of an intermediate lignin-based polyol and its subsequent incorporation into polyurethane elastomers, and path (5) corresponds to the direct use of lignin as a reactive filler in polyurethane foam chemical systems.

Table 4 shows a summary of some representative research works putting in evidence synthesis details and the used approach according to the synthetic routes defined in Fig. 5.

Within this work we report the research conducted by LSRE in cooperation with LGP2 in this field during the past five years. Briefly, in the first approach lignin was used directly as a co-monomer in combination with a linear polyester-polyol. In the second approach lignin was oxypropylated and the resulting liquid polyols incorporated into RPU foams, alone or in combination with other commercial polyether-polyols. In order to develop a competitive green process, our objective was mainly centred on developing systems where lignin is used as received and where bulk processes are favoured.

4.6.1. Lignin characterization

For polyurethane synthesis, the knowledge of lignin hydroxyl content is needed to establish a formulation. Typical analytical procedures used for that purpose are based on spectroscopic techniques (NMR, UV, FTIR), or on wet chemical methods (acetylation, permanganate oxidation, aminolysis, etc.), or in a combination of both. A review on lignin hydroxyl groups determination was reported in previous work using some commercially available technical lignins (Indulin AT (Meadwestvaco), Alcell (Repap), Curan 27-11P (Borregaard LignoTech) and Sarkanda (Granit SA)) (Cateto et al., 2008a). The hydroxyl contents were determined using NMR techniques, namely: H, C and P NMR and a titration procedure based on a standard method (ISO 14900:2001 (E) method). The combination of the used analytical techniques allowed for a complete hydroxyl characterization: type and content. Table 5 shows total and phenolic hydroxyl contents determined by C NMR using acetylated samples according to the procedure ISO 14900:2001(E). Acid content was determined by P NMR, and ash content gravimetrically after subject lignin samples to a muffle furnace at 525 °C during 5 h.

4.6.2. Lignin use without chemical modification

Lignin can be directly incorporated into polyurethane formulations. It contains, within its structure, both aliphatic and aromatic hydroxyl groups which can potentially act as reactive sites for isocyanate groups (formation of urethane linkages). This strategy has a main drawback: the produced materials are, most often, rigid and brittle. Lignin molecules are relatively stiff polyhydroxy macromolecules thus gener-
Table 4 – Summary of some representative works in the field of lignin-based polyurethane synthesis.

<table>
<thead>
<tr>
<th>Work</th>
<th>Lignin type</th>
<th>Synthesis details</th>
</tr>
</thead>
</table>

Polyols: polybutadiene glycol (PBD), poly(ethylene glycol) (PEG), hydroxyl-terminated polybutadiene (HTPB), polycaprolactone (PCL). Isocyanates: Toluene diisocyanate (TDI), methylene diphenyl diisocyanate (MDI), octadecyl isocyanate (ODI). Catalysts: Stannous octoate (SnOct), dibutyltin dilaurate (DBTDL), Triethylamine (TEA), NIAAX and DMCHA are amine based catalysts. Solvents: Tetrahydrofuran (THF), dimethylformamide (DMF).

...ating highly branched three-dimensional polyurethanes, in which the lignin residues act as crosslinking sites. To overcome this restriction and generate more attractive materials, like elastomers, it is a current practice to incorporate a linear polyol, such as PEG, in the original formulation. However, the efficiency of this approach strongly depends on lignin type, molecular weight and content, and polyol type and molecular weight.

Within this context, we have conducted some studies using a three-component system, namely lignin (Indulin AT),...
4,4-methylene-diphenylene isocyanate (MDI) and a linear polycaprolactone (PCL) of three different average-molecular weights (1000, 750 and 400). PCL, a biodegradable polyester, was introduced in the formulation to impart flexibility to final products and enable polymerization in bulk. Lignin was used as received at contents of 10%, 15%, 20%, and 25% (w/w) in the polyol mixture (PCL + lignin). Preparation details can be found elsewhere (Cateto et al., 2008b,c). Samples were characterized by Dynamic Mechanical Analysis (DMA) using an RSA3-TA instrument working in tensile modulus.

The obtained results, using FTIR-ATR monitoring and swelling studies, pointed out for effective lignin incorporation into final three-dimensional polyurethane networks (Cateto et al., 2008c). For Indulin AT, our results support the conclusion that the use of PCL400 favours lignin incorporation but, in terms of mechanical properties, it showed to be too short to impart flexibility into final products. The produced materials were brittle and consequently, not useful, even for structural applications. For longer PCL chains, like PCL1000, a decrease in lignin incorporation efficiency was observed, mainly justified as a result of the increasing dilution factor of hydroxyl groups with increasing PCL molecular weight. It is also expected that for too short PCL segments, and depending on lignin type and molecular weight, the PCL segments attached to a lignin become difficult to react with isocyanates appended to other lignin molecules, thus hindered the formation of a three-dimensional network (Thring et al., 2004). For the used PCL molecular weight range, 400, 750 and 1000, the effect was not noticed for Indulin AT based systems but clearly appeared for systems based on Alcell lignin. Comparatively to Indulin AT, Alcell lignin, an organosolv lignin, has lower molecular weight and lower hydroxyl content. These results pointed out that, lower molecular weight lignins like degraded lignins obtained as by-products of the vanillin process, will need higher molecular weight PCL to produce useful materials. In this situation we may assume that lignin has a main role of chain extender.

Fig. 6 shows the effect of Indulin AT content on the storage modulus ($E'$) and loss tangent ($\tan \delta$) with temperature. As can be observed, the maximum of $\tan \delta$ shifts towards higher temperatures and the peak becomes broader as the lignin content increased. Thus, glass transition temperature ($T_g$) increases with the increase of lignin content reflecting an increasing of lignin incorporation. For the rubbery region the $E'$ value increases with lignin content until a maximum of 20%. $E'$ value for the sample prepared with 25% has shown no variation comparatively to the sample with 20% lignin content.

### 4.6.3. Lignin use after chemical modification

Within this approach we have studied lignin oxypropylation and its subsequent incorporation into RPU foams (Cateto et al., 2007). Oxypropylation has been recognized as a viable and promising approach to overcome the technical limitations and constrains imposed by the polymeric nature of lignin when directly used as a macromonomer for synthesis purposes. By means of oxypropylation, the hydroxyl groups, in particular the phenolic ones entrapped inside the molecule and of difficult access, are liberated from steric and/or electronic constrains and, at the same time, the solid lignin becomes a liquid polyol, thanks to the introduction of multiple ether moieties.

The optimal oxypropylation conditions were fixed on the basis of the requirements which a given polyol should fill when used in rigid polyurethane foam formulations, i.e., a hydroxyl index between 300 and 800 and a viscosity below 300 Pa s. Table 6 shows the technical properties of the produced Indulin AT based polyols using lignin/propylene-oxide/catalyst (L/PO/C, w/v/(%), w/w) formulations of 20/80/5 and 30/70/2, where the catalyst content is based on lignin weight. The oxypropylation reaction was carried out in bulk using a 450 mL Parr reactor. The desired amount of lignin, propylene oxide and the catalyst (KOH) were placed in the reactor that was thereafter closed and heated under stirring till 160 °C. After reaching a maximum, the pressure decreased almost instantaneously (1–3 min) reflecting the propylene oxide consumption. When the relative pressure reached zero, the reactor was cooled under stirring and the ensuing polyols recovered.

Oxypropylation is always accompanied by homopolymerization of propylene oxide arising from transfer reactions during the anionic grafting mechanism. The produced polyols are in fact a mixture of oxypropylated lignin and some low molecular weight products, polypropylene oxide oligomers. These oligomers are normally left in the final mixture since they constitute a very useful bifunctional co-monomer, decreasing viscosity and the glass transition temperature. The prepared lignin-based polyols were introduced into RPU foam formulations without performing any type of purification in which regards homopolymer and catalyst (KOH) presence. A typical RPU foam formulation included a polyol prepared with the lignin-based polyol (alone or mixed with 25–75%...
Table 6 – Technical properties of the produced Indulin AT based polyols.

<table>
<thead>
<tr>
<th>Lignin-based polyol (L/PO/C, w/v/(%, w/w))</th>
<th>Viscosity (Pa s)</th>
<th>IOH (mg KOH/g)</th>
<th>Homopolymer content (% w/w)</th>
<th>Mn (g/mol)</th>
<th>Mw (g/mol)</th>
<th>PI</th>
</tr>
</thead>
<tbody>
<tr>
<td>20/80/5</td>
<td>4.34</td>
<td>326.2</td>
<td>36.7</td>
<td>1224</td>
<td>3829</td>
<td>3.1</td>
</tr>
<tr>
<td>30/70/2</td>
<td>66.5</td>
<td>348.8</td>
<td>24.2</td>
<td>1453</td>
<td>5331</td>
<td>37</td>
</tr>
</tbody>
</table>

Molecular weight data (Mn, Mw and polydispersity index [PI]) based on PS standards.

Table 7 – Density, thermal conductivity and compressive modulus of Indulin AT based RPU foams.

<table>
<thead>
<tr>
<th>Lignin-based polyol (L/PO/C, w/v/(%, w/w))</th>
<th>Lignin-based polyol content (% w/w)</th>
<th>Density (kg/m³)</th>
<th>Conductivity (mW/mK)</th>
<th>Compressive modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20/80/5</td>
<td>100</td>
<td>19.2</td>
<td>26.8</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>22.4</td>
<td>32.9</td>
<td>2.4</td>
</tr>
<tr>
<td>30/70/2</td>
<td>100</td>
<td>23.1</td>
<td>27.4</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>23.7</td>
<td>29.1</td>
<td>3.6</td>
</tr>
<tr>
<td>Reference foam (100% commercial polyol)</td>
<td></td>
<td>31.1</td>
<td>30.3</td>
<td>4.6</td>
</tr>
</tbody>
</table>

5. Conclusions

Sustainable growth involves safe raw materials resources for the industrial production of goods. In this context, Kraft lignin, as a large available biomass resource (by-product stream of pulp mills), is a very attractive and promising raw material to produce vanillin, biopolymers and biofuels to be used in process unit operation. This idea concept was explored by designing an integrated process for producing vanillin and lignin-based polyurethanes.

Vanillin is produced using Kraft lignin oxidation under alkaline medium generating a stream containing degraded lignin and salt of vanillin. For the separation of these two fractions, and due to the presence of other contaminants, the use of intensive purification procedures is required. We have discussed one alternative route to allow vanillin recovering using consecutive membrane, ion-exchange and crystallization processes. These processes have a key role on the economical competitiveness of lignin-based process, and breakthroughs in this field will lead to major positive impacts towards its expansion in the industrial scenery.

A complementary approach considering the production of lignin-based polyurethanes elastomers and foams has been also explored. The incorporation of lignin into materials is in fact an attractive approach since it can take advantage of macromolecular properties. Both approaches of using lignin (as such or after chemical modification) yielded materials with quite promising properties. A reliable economic evaluation could be noteworthy in this context, but is difficult to achieve at this stage of development. In a first approach it needs to be based on existing technology (that sometimes is not suitable) and on the knowledge of market product acceptance. Furthermore, assessment of the degree of difficulty for developing new technology must also be needed. In any case, some lignin-based polyurethanes with quite interesting properties, in some cases quite similar to those prepared with conventional counterparts, have been produced, which corroborate the interest and viability of this approach both as a primary or secondary product.

Acknowledgments


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