# 58. Valorisation of *Kraft* Lignin by producing vanillin and lignin-based polyurethanes: Use of the biorefinery concept

*E. A. Borges da Silva[1], M. Zabkova[1], J. D. Araújo[1], C.A. Cateto[2,3], F. Barreiro[2], M. N. Belgacem[3], A.E. Rodrigues[1]*

[1]*Associate Laboratory LSRE/LCM, Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*
[2]*Associate Laboratory LSRE/LCM, Bragança Polytechnic Institute, Campus de Santa Apolónia, Apartado 1134, 5301-857 Bragança, Portugal*
[3]*Matériaux Polymères, École Française de Papeterie et des Industries Graphiques, BP 65, 38402 St. Martin d'Hères, France*

## Abstract

In Kraft pulp mills, the capacity of the recovery boiler is very often a limiting factor to the increase of the pulp production. Until several decades ago, an upgrade to boiler system for dealing with higher quantities of black liquor was the only alternative. The possibility of lignin extraction from black liquor seems to be much more attractive, either for energy production or combustion elsewhere, or to serve as feedstock for chemicals production. Since the beginning of the 90's, Associate Laboratory LSRE/LCM has been focused on overcoming expansion limitations in pulp industries and, in this work, we show an alternative to this industry segment for the utilization of lignin and producing high added value chemicals from renewable biomass materials. Based on biorefinery concepts, an integrated process for producing vanillin from *Kraft* lignin oxidation has been proposed and each of the needed unit operations has been investigated to provide a deeper scientific understanding on this subject.

## Introduction

Nowadays, there is an intensive effort towards the replacement of fossil carbon source by a renewable biomass. Biorefineries integrates processes and technologies for an efficient biomass conversion into base chemicals, platform chemicals, fuels and energy [1]. Sustainable development, zero-waste industries and environmentally friendly processes are feasible goals if the concept of biorefinery is well applied technologically. The so-called lignocellulose feedstock (LCF) biorefinery is particularly favoured by the sustainability and cost of biomass supply.

The main source of lignin is the pulp and paper industry. The lignin-containing raw materials can be obtained from acid sulfite pulping (lignosulfonates) and from sulfate pulping (Kraft lignin). Since Kraft pulping prevails with around 80% of the world chemical pulp production, it is important to consider this by-product as raw material. In a conventional process, the *black liquor* stream is burned to provide energy for mill operations, and to facilitate the recovery of cooking chemicals, NaOH and $Na_2S$ [2]. Nowadays, this destructive way can not be considered a satisfactory solution anymore. Moreover, it is worth mentioning that an expansion in the production of pulp implies a revamp in the burners and also increased on the capacity of the recovery boiler. This is a significant bottleneck in pulp and paper industries[3].

An alternative to the referred bottleneck is the utilization of the increased amount of black liquor in the production of high-added value products. When black liquor is burned, many organics compounds are vanished, especially lignin, from which valuable substances or materials can be produced. In this work, the focus is on an integrated process of production of vanillin from lignin obtained from sulfate pulping liquors.

According the Figure 1 a portion of the by-product stream is processed to extract lignin (traditional acidification/precipitation or LignoBoost method). After obtaining purified lignin, the subsequent process is based on three main steps: alkaline lignin oxidation, ultra-filtration and ion exchange process. Afterwards, there is a crystallization step. The degraded lignin resulting from membrane process can be considered for obtaining lignin-based polyurethanes materials[4] (or as biofuel). 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 on the area of vanillin chemical production from *Kraft* lignin oxidation [3; 5-12], as well as, polyurethane synthesis from lignin-based raw materials [4; 13-15].
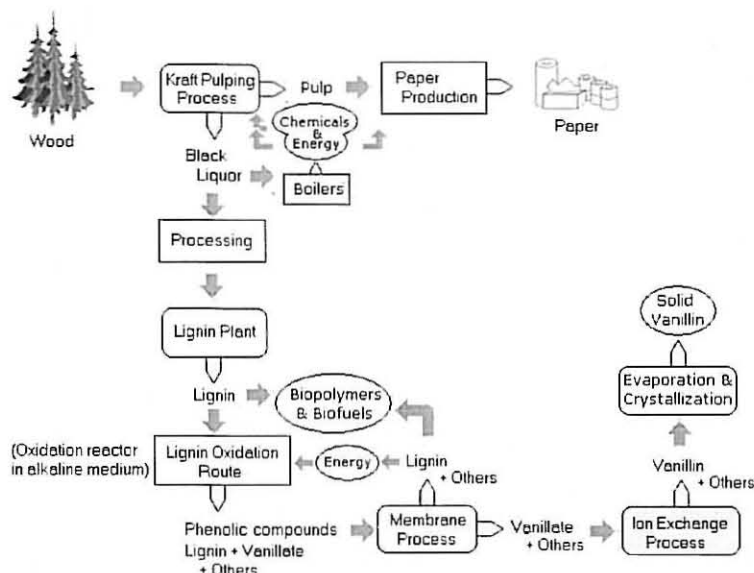


**Figure 1.** *Flow sheet of the integrated process to produce vanillin and lignin-based polyurethanes from lignin-containing raw materials*

## Description of the Integrated Process: a Biorefinery Concept

### Chemical oxidation of lignin – Batch and Continuous

The vanillin production from chemical oxidation of *Kraft* lignin has been investigated in order to analyze the effect of operating process parameters on the yield of the process. 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 [5-7].

There is a maximum obtainable vanillin yield from a specific type of lignin. The formation of phenolic compounds like vanillin is strictly related to the available percentage of its precursor in the lignin structure. Lignin from softwoods is predominantly based on structural units derived from the guaiacyl units, which are the precursors for vanillin yield [16; 17]. Mathias and Rodrigues [7] have reported that a 60g/L solution of *Kraft* lignin from Pinus Spp. can provide a maximum vanillin yield of 13% (w/w); value based on nitrobenzene oxidation (7h of reaction, 147°C, 2 N NaOH and 0.84 ml of nitrobenzene per gram of initial lignin).

Some results of lignin oxidation experiments performed at LSRE are summarized in Table 1. One can observe yields in the range of 3-10% for the *Kraft* lignin oxidation with $O_2$ using similar operating conditions. The higher vanillin yield value corresponds to a vanillin recovery of almost 80% for *Kraft* lignin (*Pinus spp.*). Araujo [9] has shown a lower vanillin yield under equal operating conditions using the *Kraft* lignin Indulin AT. 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.

An experimental pilot set-up was built to promote the concerned gas-liquid reaction in a continuous operating mode. The structured packed bubble column reactor (SPBCR) is made in 316L stainless steel with 8 liters capacity. Its main cylindrical body is the section where the gas-liquid reactions take place. It has an internal diameter of 10 cm and 70 cm height, and is filled with three modules of Mellapak 750.Y structured packing (Sulzer Chemtech, Switzerland). A 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.

In a typical run, the liquid mixture (60 g/L lignin + 80 g/L NaOH) was pumped to the reactor by a piston pump (operation range 2.12-0.99L/h). The temperature was regulated to 403 K. At the beginning of the reaction, nitrogen was admitted to the reactor to pressurize the system (10 bar). Once the operating temperature, pressure and flow rates stabilized, lignin oxidation could be initiated. The $N_2$ and $O_2$ flow rates (both $1L_{NTP}$/min; NTP: 273 K and 1atm) were controlled with mass flow controllers. These continuous experiments were performed with *Kraft* lignin Indulin AT supplied by Westvaco Co. Vanillin concentration in the SPBCR exit stream reached a steady state value of around 0.73 g/L and 0.89 g/L for two experimental runs. Considering the batch experiment, these results are about 33-40% of the maximum level of vanillin concentration obtained in the batch reactor. 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 could provide important technological advances for the application of this alternative procedure.

***Table 1.** Experimental conditions in batch experiments of Kraft lignin oxidation and the respective vanillin yields.* ([1] Initial values; $C_{NaOH}$ = 80 g/L)

| Reference | $T^1$ (°C) | $P_{O2}{}^1$ (bar) | $P^1$ (bar) | $C_{Lignin}$ (g/l) | $t_{max}$ (min) | Vanillin yield (%) | Lignin type |
|---|---|---|---|---|---|---|---|
| Mathias (1993) | 121 | 4.1 | 9.3 | 60 | 43.4 | 7.3 | *Pinus spp.* |
| | 120 | 3.7 | 9.7 | 60 | 76.5 | 8.2 | *Pinus spp* |
| | 141 | 3.8 | 10.0 | 60 | 64.4 | 10.5 | *Pinus spp* |
| | 122 | 3.8 | 9.6 | 30 | 61.4 | 10.3 | *Pinus spp* |
| | 127 | 3.5 | 9.1 | 82.5 | 92.9 | 4.1 | *Pinus pinaster* |
| | 140 | 3.8 | 9.3 | 82.5 | 46.4 | 2.8 | *Pinus pinaster* |
| | 119 | 3.5 | 9.1 | 50 | 77.5 | 8.0 | *Black liquor* |
| Fargues et al. (1996a) | 130 | 1.2 | 9.7 | 60 | 70.0 | 8.3 | *Pinus spp* |
| | 133 | 2.8 | 9.7 | 60 | 35.0 | 10.8 | *Pinus spp* |
| | 128 | 3.0 | 9.7 | 30 | 40.0 | 6.7 | *Pinus spp* |
| | 125 | 4.0 | 9.7 | 30 | 45.0 | 9.0 | *Pinus spp* |
| Araujo (2008) | 123 | 4.0 | 9.0 | 60 | 75.0 | 3.7 | Indulin AT |
| | 123 | 6.5 | 9.5 | 60 | 35.0 | 3.4 | Indulin AT |

**Membrane Processing**

In the process of *Kraft* lignin oxidation to produce vanillin, the reaction media contains degraded molecules of lignin and sodium salt of vanillin. In our proposal, the first step towards recovering the vanillin from *Kraft* lignin oxidation is the ultrafiltration (UF) process[11]. 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, 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 retentante 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 15 kDa supplied by Orelis (France) and Filtanium type with molecular weight cut-off of 1 kDa and 5 kDa supplied by Tami Industries (France). A detailed description of the lab-scale membrane set-up is shown in Zabkova et al. [11]. Considering the composition of 60g/L lignin and 6g/L vanillin (yield of around 10% from oxidation process), Table 2 shows 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. 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 1100min for the case of 1kDa cut-off membrane (Run 4), 20% in 780min for 5kDa cut-off membrane and 22% in 570min for 15kDa 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. It seems that there is no occurrence of pore internal fouling, 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.

Since membranes with bigger cut-off might combine higher flux with acceptable rejection values, a scheme of staging ultrafiltration membranes starting from larger cut-off is proposed in this step of the integrated process. In order to increase the volume reduction, higher transmembrane pressures and, also, higher temperatures of feed mixture could be applied. 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 (0.1-0.2M 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.

**Ion exchange Operation**

The vanillin leaving the oxidation reactor and the membrane separation step is in the salt form due to the used excess of sodium hydroxide required in the oxidation reaction. The resulting oxidized mixture can be acidified and/or vanillin extracted with suitable solvents. 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. [19; 20]. An alternative method to recover vanillin consists on using cationic ion-exchange resin [21; 5]. 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. According to Forss [21], 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.

**Table 2.** *Experimental conditions* [a] *and measured values* [b] *in ultrafiltration of the lignin/vanillin mixture using tubular ceramic membranes ($Q_f$, feed flow rate; $C^o_f$, feed concentration; VR, volume reduction; $V_o$, initial feed volume; $R_{obs}$, observed rejection; $R_m$, membrane hydraulic resistance).*

| $Q_f$ [a] ($L\ h^{-1}$) | $C^o_f(g\ L^{-1})$ [a] | | $pH$ [a] | $V_o(L)$ [a] | $VR$ [b] | $R_{obs}$ (Lignin) [b] | $J \times 10^{-3}$ ($L\ m^{-2}\ h^{-1}$) [b] | $R_m \times 10^{13}$ ($m^{-1}$) [b] |
|---|---|---|---|---|---|---|---|---|
| | Lignin | Vanillin | | | | | | |
| **15 kDa cut-off** | | | | | | | | |
| 101 | 60 | 6 | 8.5 | 5 | 0.313 | 0.943 | 28.12 | 0.2806 |
| 101 | 60 | 6 | 12.5 | | 0.340 | 0.865 | 16.87 | |
| **5 kDa cut-off** | | | | | | | | |
| 120 | 60 | 5 | 12.5 | 4 | 0.275 | 0.968 | 13.50 | 1.222 |
| **1 kDa cut-off** | | | | | | | | |
| 130 | 60 | 6 | 8.5 | 5 | 0.102 | 0.951 | 4.75 | |
| 120 | 60 | 6 | 12.5 | 4 | 0.103 | 0.972 | 3.75 | 2.806 |
| 120 | 2 [c] | 6 [c] | 12.5 | 4 | 0.410 [c] | 0.981 [c] | 18.00 [c] | |

(a) 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: $\eta=1.190 \times 10^{-3}\ kg\ m^{-1}\ s^{-1}$ (except to the mixture of 2g/L lignin and 6g/L vanillin)
(b) $R_{obs}$ (Vanillin) $\approx 0$ for all ultrafiltration run.
(c) Considering this filtration on the 1kDa cut-off membrane as a second stage in a staging membrane operation mode.

The use of a strong cationic resin in acid form for the vanillin isolation was studied considering the influence of both alkalinity and vanillin concentration of the treated solution by using static and dynamic approaches [10]. In the overall process of vanillin recovery from *Kraft* liquor, the ion exchange step should be designed after the membrane module. 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 further acidification or neutralization. Moreover, if the ion-exchange process is placed after the membrane, the precipitation of lignin, which could be motivated by a decrease in 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.

## Lignin-based Polyurethane

Considering the lignin potential as a raw-material for polyurethane synthesis, two lignin sources are available: (i) polymeric lignin obtained after processing the black liquor and (ii) degraded lignin (vanillin plant by-product). 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 importance of these achievements lead to the appearing of some patented results [22; 23]. 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 (i) the availability of new lignin sources, such as, sulphur free lignins and (ii) the growing interest on biorefiney processes where lignin valorisation offers impact (it represents up to 30% of biomass weight). The utilization of lignin as a macromonomer in polyurethane synthesis often follows two global approaches: (i) the direct utilization of lignin without any preliminary chemical modification, alone or in combination with other polyols [13] or, (ii) by making hydroxyl functions more readily available by chemical modification, such as esterification and etherification reactions [15].

A research has been conducted by our group in this field during the past five years. In a first approach lignin has been used directly as a co-monomer in combination with a linear polyester-polyol. In the second approach lignin has been 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 is mainly centred on developing systems where lignin is used as received and where bulk processes are favoured.

**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 has been performed by our research group using some commercially available technical lignins (Indulin AT (Meadwestvaco), Alcell (Repap), Curan 27-11P (Borregaard LignoTech) and Sarkanda (Granit SA)).

**Lignin use without chemical modification**
Within this context, our research group 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, is introduced in the formulation to impart flexibility to final products and enable polymerization in bulk. Lignin is used as received at contents of 10%, 15%, 20%, and 25% (w/w) in the polyol mixture (PCL+lignin). The obtained results, using FTIR-ATR monitoring and swelling studies, pointed out for effective lignin incorporation into final three-dimensional polyurethane networks[13].

**Lignin use after chemical modification**
We have been studying lignin oxypropylation and its subsequent incorporation into RPU foams [14]. 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 are 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. RPU foams have been prepared using a chemical system composed by lignin-

based polyol (alone or in combination with commercial polyether-polyols), glycerol (10%, w/w), surfactant (2%, w/w), water (2%, w/w) catalyst (2%, w/w of a mixture with equal amounts of DMCHA and NIAX), *n*-pentane (20%, w/w) and polymeric isocyanate. The produced lignin-based RPU foams (particularly those based on 20/80/5 polyols) exhibit slightly lower mechanical properties and density comparatively to the reference foam. Nevertheless, we must highlight some added value properties imparted by lignin, such as, improvement of moisture and flame resistance.

## Conclusion

*Kraft* lignin is a very attractive and promising raw material to produce vanillin, biopolymers and biofuels. An integrated process for producing vanillin and lignin-based polyurethanes from this biomass has been presented using the concept of biorefinery. Firstly we have performed the lignin oxidation in batch reactor and valuable information to decide the best conditions for the vanillin production has been achieved. The feasibility of continuous vanillin production was analyzed by studying the operation of a structured bubble column reactor (SBCR). The conversion from the experiments using the called Insulin AT Kraft lignin was quite low. The obtained levels of vanillin yield (1.2% of 60g/L of Kraft lignin) seem to be limited by the used raw material and by the low rates of oxygen transfer to the liquid in the reaction unit.

We have also presented one alternative route of intensive purification procedures to allow recovering vanillin from *Kraft* lignin oxidation through membrane, ion-exchange and crystallization processes. These processes have a key role on the economical competitiveness of the lignin-based process, and breakthroughs in this field will lead to major positive impacts to its expansion in the industrial scenery. A complementary approach considering the production of lignin-based polyurethanes elastomers and foams has been also explored. 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

## References

1. Kamm B, Kamm M (2004):Principles of biorefineries, *Appl. Microbiol. Biotechnol.*, 64:2, p. 137-145.
2. Wallberg O, Holmqvist A, Jonsson A S (2005):Ultrafiltration of kraft cooking liquors from a continuous cooking process, *Desalination*, 180:1-3, p. 109-118.
3. Mathias,A. L., 1993, Produção de vanilina a partir da lenhina: estudo cinético e do processo, Ph.D. Thesis, University of Porto, Porto, Portugal.
4. Cateto C A, Barreiro M F, Rodrigues A E, Brochier-Solan M C, Thielemans W, Belgacem M N (2008a):Lignins as macromonomers for polyurethane synthesis: A comparative study on hydroxyl group determination, *J. Appl. Polym. Sci.*, 109:5, p. 3008-3017.
5. Fargues C, Mathias A, Rodrigues A (1996a):Kinetics of vanillin production from Kraft lignin oxidation, *Ind. Eng. Chem. Res.*, 35:1, p. 28-36.

6.  Mathias A L, Lopretti M I, Rodrigues A E (1995):Chemical and Biological Oxidation of Pinus-Pinaster Lignin for the Production of Vanillin, *J. Chem. Tech. Biotechnol.*, 64:3, p. 225-234.
7.  Mathias A L, Rodrigues A E (1995):Production of Vanillin by Oxidation of Pine Kraft Lignins with Oxygen, *Holzforschung*, 49:3, p. 273-278.
8.  Fargues C, Mathias A, Silva J, Rodrigues A (1996b):Kinetics of vanillin oxidation, *Chem. Eng. Technol.*, 19:2, p. 127-136.
9.  Araujo,J.D.P., 2008, Processo de Produção de Vanilina a Partir do Licor Negro das Indústrias da Pasta de Papel, PhD Thesis, University of Porto, Porto, Portugal.
10. Zabkova M, da Silva E A B, Rodrigues A E (2007b):Recovery of vanillin from Kraft lignin oxidation by ion-exchange with neutralization, *Sep. Purif. Technol.*, 55:1, p. 56-68.
11. Zabkova M, da Silva E A B, Rodrigues A E (2007a):Recovery of vanillin from lignin/vanillin mixture by using tubular ceramic ultrafiltration membranes, *J. Memb. Sci.*, 301:1-2, p. 221-237.
12. Zabkova M, Otero M, Minceva M, Zabka M, Rodrigues A E (2006):Separation of synthetic vanillin at different pH onto polymeric adsorbent Sephabeads SP206, *Chem. Eng. Prog.*, 45:7, p. 598-607.
13. Cateto C A, Barreiro M F, Rodrigues A E (2008c):Monitoring of lignin-based polyurethane synthesis by FTIR-ATR, *Ind. Crops Prod.*, 27:2, p. 168-174.
14. Cateto,C.A., Barreiro,M.F., Rodrigues,A.E.,and Belgacem,M.N., 2007, Oxypropylation of lignins and characterization of the ensuing polyols, in Proceedings of the 8th ILI Forum, pp. 115-119.
15. Cateto,C.A., Barreiro,M.F., Rodrigues,A.E., Belgacem,M.N., 2008, Lignin-based polyurethane materials, in Proceedings of the 10th International Chemical and Biological Engineering Conference - CHEMPOR 2008, pp. 231-236.
16. Higuchi T, 1980, *Lignin structure and morphological distribution in plant cell wall.* , in *Lignin Biodegradation: microbiology, chemitry, and potential applications.*, Kirk, T.K., T.Higuchi, and H.M.Chang, Editors. (CRC Press: Boca Raton.), pp. 1-20.
17. Adachi S, Tanimoto M, Tanaka M, Matsuno R (1992):Kinetics of the Alkaline Nitrobenzene Oxidation of Lignin in Rice Straw, *Chem. Eng. J.*, 49:2, p. B17-B21.
18. Sridhar P, Araujo J D, Rodrigues A E. *Modeling of vanillin production in a structured bubble column reactor.* in *2nd International Conference on Structured Catalysts and Reactors (ICOSCAR-2)*. 2005. Delft, NETHERLANDS.
19. Bryan C C, Can. Patent 5,280,837., Canada, 1956.
20. Sandborn L R, Salvesen J R, Howard G C, Process of making vanillin, US Patent 2,057,117, United States, 1936.
21. Forss K G, Talka E T, Fremer K E (1986):Isolation of Vanillin from Alkaline Oxidized Spent Sulfite Liquor, *Ind. Eng. Chem. Prod. Res. Dev.*, 25:1, p. 103-108.
22. Glasser W G, Oliveira W, Kelley S S, NiehL S, U. S. Patent 5,066,790, 1991.
23. Kurple K R, U.S. Patent PCT/US96/20140, WO97/24362., 2000.