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Vanillin production from lignin oxidation in a batch reactor

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ABSTRACT

Vanillin production from lignin oxidation is a biomass-based process that employs a by-product of the pulp and paper industry and air to obtain a high-added value compound. However, lignin is an organic polymer with a structure that depends strongly on the source and the conditions to obtain vanillin should be adjusted for different samples.

The objective of this work is to establish a fast and standard protocol to characterize lignin conversion to vanillin by batch oxidation. The experimental technique is coupled with a mathematical model that allows us to fit the data and determine kinetic rate constants under non-isothermal conditions. Two examples of vanillin oxidation with very different lignin sources are presented. The results revealed vanillin yields with respect to the lignin mass ranging from 3.5% to 7.6% for the high and low-molecular weight lignins, respectively.

Keywords: Vanillin; Kraft lignin; Batch reactor

1. Introduction

Vanillin (4-hydroxy-3-methoxybenzaldehyde) is the major flavour constituent of vanilla. It has a wide range of applications in food industry and in perfumery. Vanillin is also very useful in the synthesis of several pharmaceutical chemicals (Bjørsvik and Liguori, 2002; Walton et al., 2003).

Historically, the production of vanillin was its direct extraction from vanilla beans. However, to satisfy constantly increasing markets, new chemicals routes were developed. Nowadays, vanillin produced from guaiacol accounts for 85% of the world supply, with the remaining 15% being produced from lignin (Triumph Venture Capital, 2004). Synthetic vanillin obtained from guaiacol is nearly absent of by-products, simplifying its separation which is an important advantage. However, the guaiacol route is fully depending on petroleum-derived compounds. Synthesis of vanillin from renewable sources should result in a greener and more sustainable process. One possible path to produce vanillin based on biomass is through controlled oxidation of lignin.

The main source of modified lignin is the pulp and paper industry, where nowadays the Kraft pulping process prevails with approximately 80% of the world chemical pulp production (Ullmann's Encyclopedia, 2003). A by-product stream of this process, known as *black liquor*, contains typically 30–34% of lignin in dry solid weight basis. This stream is burned to provide energy for mill operations and to facilitate the recovery of pulping chemicals. Due to the complex energetic integration of the Kraft process, an expansion in the production of pulp implies a revamp in the burners. An alternative plant design to the burners revamp will be the utilization of a fraction of the *black liquor* in the production of high-added value products, eliminating the production bottleneck at the recovery boiler (Mathias, 1993; Axelsson et al., 2006).

Production of high-added value compounds from black liquor involves the transformation of a natural polymer (lignin) into much smaller molecules. Lignin is a three-dimensional amorphous macromolecule made of different amounts of phenyl propane units that arise from the copolymerization of three primary precursors: coniferyl alcohol, sinapyl alcohol and *p*-coumaryl alcohol. The lignin content and composition in wood varies greatly with species and with the environment and conditions in which the plant develops. Softwoods (gymnosperms) have a lignin content of 25–35% dry weight (Wool and Sun, 2005) while hardwoods (angiosperms) have a slightly smaller content of 18–25%.

It is recognized that the lignins from softwoods are predominantly based on structural units derived from coniferyl alcohol (guaiacyl units) in quantities usually higher than 90%, with the remainder small percentages of structural units being

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Nomenclature

A	velocity reaction constant for vanillin oxidation ($l\,mol^{-1}\,min^{-1}$)
A_{ext1}	area of the external wall of the cylindrical glass of the reaction zone (m^2)
A_0	parameter of the Antoine equation relating vapor pressure to temperature
A_1	internal area of the cylindrical glass limiting the reaction zone (m^2)
A_2	surface area of the steel plates (m^2)
B	velocity reaction constant for vanillin oxidation (l/mol)
B_0	parameter of the Antoine equation relating vapor pressure to temperature
C_L	concentration of lignin (mol/l)
C_V	concentration of vanillin (mol/l)
C_{O_2}	concentration of oxygen (mol/l)
$Const$	parameter relating oxidated lignin and acid products formed (eq/g)
Cp_{org}	heat capacity of organic species ($J\,mol^{-1}\,K^{-1}$)
Cp_{NaOH}	heat capacity of sodium hydroxide ($J\,mol^{-1}\,K^{-1}$)
Cp_{H_2O}	heat capacity of water ($J\,mol^{-1}\,K^{-1}$)
Cp_{gl}	heat capacity of internal glass wall ($J\,kg^{-1}\,K^{-1}$)
C_0	parameter of the Antoine equation relating vapor pressure to temperature
D_s	width of the stainless steel plates (m)
D_1	diameter of the external wall of the internal cylindrical glass (m)
D_2	diameter of the internal wall of the external cylindrical glass (m)
E_a	activation energy of lignin oxidation (J/mol)
f(pH)	function of C_{H+}
h_{als}	heat transfer coefficient from the external wall of the lower steel plate to the ambient ($W\,m^{-2}\,K^{-1}$)
h_{aus}	heat transfer coefficient from the external wall of the upper steel plate to the ambient ($W\,m^{-2}\,K^{-1}$)
h_{fgl}	heat transfer coefficient from the thermo fluid to the external glass walls of the reactor ($W\,m^{-2}\,K^{-1}$)
h_{gll}	heat transfer coefficient from the internal glass walls to the liquid inside the reactor ($W\,m^{-2}\,K^{-1}$)
h_{sg}	heat transfer coefficient from the gas inside the reactor to the internal wall of the upper steel plate ($W\,m^{-2}\,K^{-1}$)
h_{sl}	heat transfer coefficient from the liquid inside the reactor to the internal wall of the lower steel plate ($W\,m^{-2}\,K^{-1}$)
I	ionic strength of the liquid medium (mol/l)
k_s	thermal conductivity of stainless steel ($W\,m^{-1}\,K^{-1}$)
k_{gl}	thermal conductivity of glass ($W\,m^{-1}\,K^{-1}$)
k_1	velocity reaction constant for vanillin formation ($(l/mol)^{1.75}\,min^{-1}$)
k_2	velocity reaction constant for vanillin oxidation ($l\,mol^{-1}\,min^{-1}$)
L	height of the cylindrical glass (m)
m_{gl}	mass of the internal glass tube delimiting the reactor (kg)
m_L^i	initial mass of lignin (g)
M_{H_2O}	molecular weight of water (g/mol)
M_n	lignin mean molecular weight (g/mol)
M_V	molecular weight of vanillin (g/mol)
n_L	number of moles of lignin (mol)
P	total pressure (bar)
P_{O_2}	partial pressure of oxygen (bar)
P_{N_2}	partial pressure of nitrogen (bar)
P_{H_2O}	partial pressure of water (bar)
Q	heat received by the system from the surroundings (W)
r_{ext1}	radius of the external wall of the glass that limits the reaction zone (m)
r_{int}	radius of the internal wall of the internal cylindrical glass (m)
r_1	rate of formation of vanillin ($mol\,m^{-3}\,s^{-1}$ or $mol\,m^{-3}\,min^{-1}$)
r_2	rate of oxidation of vanillin ($mol\,m^{-3}\,s^{-1}$ or $mol\,m^{-3}\,min^{-1}$)
R	universal gas constant ($l\,atm\,mol^{-1}\,K^{-1}$)
T	reaction temperature (K)
T_{amb}	ambient temperature (K)
T_F	thermo fluid temperature inside the jacket (K)
U_1	overall heat transfer coefficient from the thermo fluid in the jacket to the liquid inside the reactor ($W\,m^{-2}\,K^{-1}$)
U_2	overall heat transfer coefficient from inside of the reactor to the ambient through the top and bottom stainless steel plates ($W\,m^{-2}\,K^{-1}$)
V_l	volume of the liquid phase inside the reactor (m^3)
V_g	volume of the gas phase inside the reactor (m^3)
X	variable that encloses all possible acid products from lignin oxidation (eq/l)

Greek letters

$\Delta H_{R,1}$	heat of reaction of lignin oxidation (J/mol)
$\Delta H_{R,2}$	heat of reaction of vanillin oxidation (J/mol)
Δt	time interval between collection of two consecutive liquid samples (s)
ΔV_l	volume of liquid taken from the system in each sample collection (m^3)
α	lignin stoichiometric coefficient on the lignin oxidation reaction
$\lambda_{vap}^{H_2O}$	heat of vaporization of water (J/mol)

attributed to the *p*-coumaryl alcohol precursor (Kirk-Othmer Encyclopedia, 2005). On the other hand, hardwood lignins are polymers that present structures with much broader chemical compositions, consisting in varying proportion ratios of guaiacyl and syringil (derived from sinapyl alcohol monomers).

The oxidation of lignin to produce vanillin was already demonstrated at very alkaline pH (almost 14), and high temperatures (403 K) and oxygen pressure higher than 3 bar (Fargues et al., 1996a,b; Mathias, 1993; Mathias et al., 1995; Mathias and Rodrigues, 1995; Villar et al., 1997; Tarabanko et al., 2000; Villar et al., 2001; Sales et al., 2004). These oxidants can be air, oxygen, nitrobenzene or metallic oxides, with or without the help of catalysts (Tarabanko et al., 1995a; Mathias, 1993). The oxidation should be controlled to avoid further oxidation of vanillin (Fargues et al., 1996b). Lignin is degraded