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Fractionation of acids, ketones and aldehydes from alkaline lignin oxidation solution with SP700 resin

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ABSTRACT

The separation of the products from the alkaline oxidative depolymerization of lignin is currently very laborious, generally, requiring several steps of solvent extraction and precipitation. The separation of the different species was achieved by adsorption with nonpolar SP700 resin, which is able to fractionate the real solution in families of chemicals namely phenolic acids, aldehydes and ketones. The main fractions obtained during adsorption, desorption with water followed by desorption with ethanol are very distinct in composition; the first is richer in vanillic (VA) and syringic (SA) acids, the second, mostly vanillin (V) and syringaldehyde (S) and the third one concentrates acetovanillone (VO) and acetosyringone (SO).

Fractionation can be adjusted by choosing the pH of the feed mixture which was studied in the range of 9 to 12. Depending on the fixed feed pH, the recoveries of aldehydes (V + S) in the water desorption step were almost complete (> 80% at pH 10 or above) with only traces present in the fraction desorbed with ethanol. It was found that pH 12 was better for concentrating aldehydes and ketones at the same time, and that pH 10 was better at maximizing the fractionation of aldehydes and ketones since the majority of aldehydes desorb in the water phase (87%) while there is also a decrease on the amount of the ketones desorbed (from 53% to 25%). Ketones are desorbed preferably in the ethanolic phase.

1. Introduction

Lignin is a biopolymer that binds cellulose and hemicellulose in the plant cell walls granting rigidity and support. Plants can have a lignin composition up to 30% (w/w), thus making it the second most abundant biopolymer next to cellulose [1]. Side streams from the pulp and paper industry are very rich in lignin and the common routes employed for the valorization of these streams are the production of steam and electricity, making the pulp and paper industry a net seller of energy [2]. A more noble route for the valorization of lignin involves its oxidative depolymerization into highly functionalized monomers like vanillin and syringaldehyde, among other compounds [3].

One of the aspects hindering the adoption of lignin and other biomass sources as platform chemical feedstock is the difficulty on the separation of the value added compounds produced during the oxidative depolymerization without resorting to complex sequence of processes that employ harmful solvents [4–6]. Alternative approaches have been tried in the recent past, ranging from membranes, precipitations and solvent extractions or any combination of these. A useful review is available elsewhere [7].

There are real advantages to the usage of nonpolar resins including their versatility, easy regeneration and great stability at wide pH ranges. Additionally, resins have been applied to numerous studies for the recovery of other phenolic compounds, namely antioxidants from olive mill wastewater [8] and winery wastes [9], or removal of toxic phenol derivatives from wastewater [10].

The majority of the adsorption studies related to vanillin with nonpolar resins are performed with synthetic mixtures [7,11–15], and only a few of these studies were performed with real mixtures [16]. Wang et al. [16] studied the adsorption of vanillin and syringaldehyde in oxygen delignification spent liquor on the nonpolar resin D101 in the pH range from 4 to 6.5, performing the desorption steps with ethyl ether. The authors succeeded in recovering the aldehydes vanillin and syringaldehyde with high contaminations of acetovanillone and acetosyringone and trace amounts of other phenolic compounds. Purification of the compounds could be achieved by chromatographic processes or by selective crystallization. Tarabanko et al. [17] have proposed the separation of synthetic mixtures of vanillin and syringaldehyde by crystallization, based on the different solubility of the ammonium salts of these aldehydes in solutions saturated with potassium carbonate with

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Nomenclature

DAD	diode array detector
H	*p*-hydroxybenzaldehyde
HPLC	high performance liquid chromatography
MWCO	molecular weight cut-off
SLPM	standard liter per minute
Pe	Peclet number, [–]
pK_a	logarithm of the dissociation constant, [–]
V	vanillin
VA	vanillic acid
VO	acetovanillone
S	syringaldehyde
SA	syringic acid
SO	acetosyringone
TMP	transmembrane pressure, [bar]
ε	bed porosity, [–]
θ	dimensionless time, [–]
C_i	concentration of the *i*-th component in at the column outlet, [g/L]
C_{i0}	concentration of the *i*-th component in the feed reference mixture, [g/L]
C_i/C_{i0}	dimensionless concentration, [–]
V_{bed}	bed volume
Q_L	liquid volumetric flow rate, [mL min^{-1}]
$\overline{t}_r$	mean liquid residence time, [h]

recovery of 95% of vanillin and purity of 98% in just one step of crystallization.

Several authors proposed the ion exchange resins for the recovery of the phenolic compounds in oxidized spent black liquor or solutions with lignin, and although ion exchange resins have been able to adsorb monomer phenolic compounds [18–20], the resins employed were unable to fractionate the monomer phenolic compounds in families like the nonpolar resins used in this work.

In this work, an oxidation mixture containing several phenolic monomers, among other compounds, is treated by an adsorption process onto SP700 resin after ultrafiltration with a membrane with an average molecular weight cut-off of 5 kDa. This preprocessing is performed to remove some of the higher molecular weight lignin structures that were not depolymerized during oxidation. Experiments at four different pH values (9, 10, 11 and 12) were performed in order to understand the influence of the pH on the adsorption of the phenolic monomers of interest and take advantage of the presence of compounds in the mixture with different p*Ka* values [21]. The phenolic monomers quantified were *p*-hydroxybenzaldehyde (H), vanillic acid (VA), vanillin (V), syringic acid (SA), syringaldehyde (S), acetovanillone (VO) also known as apocynin and acetosyringone (SO).

The compounds are adsorbed and then desorbed using a two eluent technique, first employing deionized water and then ethanol. The desorption step with deionized water is able to recover the aldehydes and the desorption step with ethanol is able to recover the ketones along with the aldehydes that might remain. This approach is flexible and the degree of fractionation can be adjusted by using a determined pH in the feed solution.

To the best of the authors' knowledge there are no studies evaluating the influence of the pH of the feed (lignin oxidation solution) during adsorption, and at the same time, assessment of the differences in desorption phases in view of the fractionation of the acids, aldehydes and ketones in a single adsorption process.

2. Experimental methods

2.1. Production of the feed mixture

The real mixture was prepared with 60 g/L of organosolv (butanol) lignin (tobacco stalks) and 80 g/L of sodium hydroxide. The mixture was oxidized in a structured packed bubble column continuous reactor previously built in our laboratory [22]. Oxidation was performed at an average temperature of 144 °C and partial pressure of oxygen of 5 bar and total pressure of 10 bar. The liquid mixture was fed at a volumetric flow rate of 10 L/h and the gas was fed to the reactor at a rate of 2 SLPM. Afterwards, the oxidized mixture was filtered with an ultrafiltration membrane with a molecular weight cut-off (MWCO) of 5 kDa (PLEAIDE, from Orelis) in a GE Osmonics SEPA CF II filtration system. The ultrafiltration was performed in recirculation mode at a transmembrane pressure (TMP) of 20 bar and temperature of 25 °C. For each experiment, the pH of the feed mixture was adjusted to the desired value with sulfuric acid and sodium hydroxide and was then allowed to stabilize overnight. After resting overnight, the pH of the feeding solution was measured again. The mixture was then fed to the adsorption column without further treatments.

2.2. Resin activation

The nonpolar SP700 resin (resin properties in Table 1) was activated by performing several washes with acidified deionized water and methanol to remove all material adsorbed in the resin from origin as described elsewhere [12]. First the resin is placed in a beaker with excess water and after settling, the floating dry resin is removed. Then, the resin is filtered by vacuum and placed in a flask with excess water and is left to stir in the orbital shaker for up to one hour. This step is repeated once more and afterwards the resin is rinsed with methanol, filtered and placed in a flask with methanol acidified with 0.1%v/v of formic acid and left in the orbital shaker for another hour. After this the resin is filtered out, rinsed with water acidified with 0.1%v/v of formic acid, and shaken for one hour with excess acidified water. Finally, the resin is rinsed several times with deionized water and is ready to be used/transferred to the column.

2.3. Experimental installation

Experiments were carried out in a glass column (Merck–Darmstadt) with diameter of 26 mm and 446 mm of total height, packed with 151.6 g of nonpolar SP700 resin previously activated. The column cooling jacket was maintained at 25 °C by a water thermostatic bath. The pump delivering the liquid to the column is a Smartline P1000 from KNAUER. The installation has also a Smartline UV 2500 detector from KNAUER which is useful during desorption and resin cleaning/regeneration in order to monitor if there are still components being desorbed. Detector wavelength set at 280 nm. The parameters describing the column were determined by simple tracer experiments with blue dextran as described elsewhere [23]. A mean residence time of

Table 1
Physical and chemical properties of SP700 resin.

Property	Value/Designation
Resin denomination	SP700
Manufacturer	Mitsubishi Chemical Corp.
Matrix	Polystyrene-divinylbenzene(PS-DVB)
Density of wet adsorbent, (gL^{-1})	1010
Moisture content,%	60–70
Pore Volume, (mLg^{-1})	2.1
Average Porosity of Particle	81
Average Particle size, (μ m)	450
Specific surface area, (m^{2}g^{-1})	1200
Average pore radius, (nm)	9