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Non-thermal gas-phase pulsed corona discharge for lignin modification

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ABSTRACT

Lignin has the potential to become a significant resource of renewable aromatics for the chemical industry. The current work studies pulsed corona discharge (PCD) as an alternative method for lignin modification. The effect of initial lignin concentration and gas phase composition on aldehydes formation was studied experimentally. Kraft lignin was used as a test compound. It was concluded in the work, that treatment in low oxygen content atmosphere and high initial lignin concentration leads to higher lignin conversion to aldehydes. Despite the proven aldehydes formation, the precise nature of the changes in the lignin structure during oxidation with PCD remained unclear. To address this question, a number of advanced analytical techniques were implemented: NMR, GPC, HSQC, HPSEC, and GCMS. The effect of PCD treatment on lignin structure was studied for two types of lignin: kraft lignin, purchased from Sigma Aldrich, and birch lignin acquired from a pressurized hot water extraction and soda pulped biorefinery process (BLN lignin). Changes in solubility, molecular weight and proportion of phenolic and aliphatic OH groups, as well as lignin repolymerization were detected. The findings are of value to efforts to make lignin modification tunable to the production of desired products.

1. Introduction

Lignin is a potential raw material for the production of various products including phenolic substances and aromatic aldehydes. The pulp and paper industry is currently the main source of lignin. For annual production of 130 million tons of chemical pulps, approximately 60 million tons of kraft lignin and 4 million tons of lignosulfonates are produced. It has been estimated that only 1–2% of the lignin is isolated from pulping liquors and used for chemical and material applications; the major part of industrial lignin is used as fuel for the production of process steam and energy [1].

Lignin decomposes very slowly and generates very high amounts of solid residue compared to other lignocellulose components. Thus, most biorefinery processes focus on utilization of more easily convertible fractions, and lignin has attracted much less attention [2]. However, lignin is a complex chemical compound and potentially a good source of valuable chemicals. One of the main challenges to its utilization is the irregular structure of lignin arising from the uncertain order of the phenylpropane unit linkages. Moreover, the structure of isolated lignin differs from that of native lignin, and composition, structure, types of monolignols and their combinations depend on the origin of the lignin, the pulping method, and the lignin isolation method [3–5]. The proportions of the structural elements derived from the three phenylpropanoid units (trans-coniferyl, *trans*-sinapyl, and *trans*-p-coumaryl alcohols) can vary significantly [6,7].

In spite of the difficulties, the subject of lignin chemical modification and its conversion to more value-added products has attracted researchers' attention since the beginning of the twentieth century. Currently, products obtained from lignin are mostly phenolic products. The reported yields for production of vanillin and syring aldehydes range from 8 to 15% depending on the lignin type [8]. However, drawbacks of existing methods include severe toxicological problems with nitrocompounds. Furthermore, current methods are only effectively applicable to lignosulfonates and are not well-suited to kraft and hydrolysis lignins. Since only lignosulphonates are used as a raw material, the production of phenolic products, especially vanillin, exists as a supplementary operation in pulp mills with sulphite cooking. Other lignin types give much smaller yield [9–11].

The pulp and paper industry generates a significant amount of wastewater containing high concentrations of lignin, which cause increased COD and brown-colored effluents. The problem of high lignin concentration in wastewaters is more acute with thermomechanical and mechanical pulping processes than chemical pulping [12]. Lignin is difficult to degrade by microorganisms, and the lifetime of lignin in aqueous media in nature is counted in months. Consequently, conventional biological wastewater treatment is insufficient from the lignin

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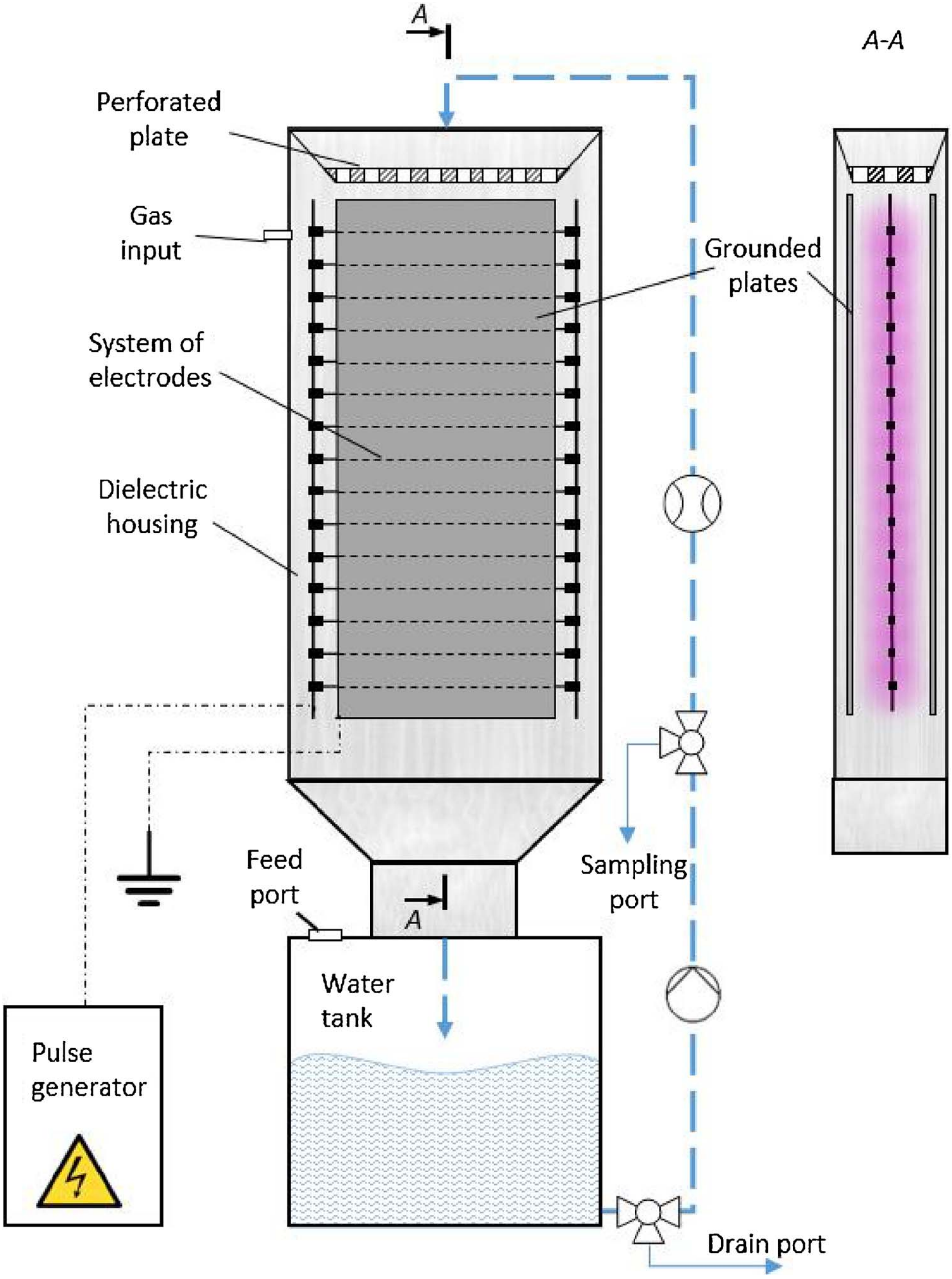

Fig. 1. Experimental setup.

removal point of view [13].

Pulsed corona discharge (PCD) can be applied as a treatment process not only for lignin removal from water but also for lignin modification to transform the lignin into a high value feedstock. The method has hydroxyl-radicals and ozone as the main oxidation species and is effective in oxidation of many organic molecules. The application of this electric discharge technique has previously been investigated by [14–17]. These studies showed a concentration of gas-phase discharges in close vicinity of the gas-liquid border.

The commercial application of electric discharge systems for such treatments is still in its infancy, and they are the subject of much study. The various systems and phenomena studied include: pulsed streamer discharges in liquid and gas-bubbled reactors with pulses at microsecond diapason [18,19], gas-phase dielectric barrier discharge (DBD) of various configurations [16,20,21], spark discharge (SD) in gas bubbles [22], pulsed corona discharge (PCD) over the water surface [23,24], plasmotrons utilizing gliding arc discharge (GAD) for bombardment of treated surfaces with ionized gas [25–27], and PCD in water aerosol [28].

PCD generates plasma in the gas-phase atmosphere. While some research has been presented investigating how plasma affects lignin, very little work has specifically considered effect of plasma on lignin structure modification. Zhou et al. [29] studied the effect of oxygen plasma treatment on the glass transition temperature of enzymatic hydrolysis lignin. However, the lignin structure after treatment was not reported. Chirila et al. [30] and Nistor et al. [31] investigated modification of organosolv lignin powder with different carboxylic acids such as oleic, lactic and butyric acids and butyrolactone under cold plasma discharge. Although these papers studied the influence of carboxylic acids and butyrolactone, the plasma effect was not considered. In general, most work on lignin and plasma discharge effects presents information about changes in solubility, decrease in particle size, reduction in conductivity of the aqueous solutions and decrease in homogeneity, whereas consideration of changes in phenolic and