Ozone Measurements by Absorption Spectroscopy Applying Dieletric Barrier Discharges at Atmospheric Pressure for Sugarcane Bagasse Treatment

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Ozone was generated using dielectric barrier discharges at atmospheric pressure to treat sugarcane bagasse for bioethanol production. It was shown that interaction of ozone molecules with pretreatment reactor wall (stainless steel) need to be considered during bagasse oxidation in order to evaluate the pretreatment efficiency. The results have indicated that ozone decomposition has occurred more efficiently on the biomass material than on the reactor wall.

Renewable energy sources are the focus of many research groups in our time. The cellulosic ethanol could be an attractive route to be followed. Several chemical, biological and physical processes are able to release sugar from lignocellulosic materials in order to obtain ethanol as a final product. The so-called atmospheric pressure plasmas have been employed to treat different biomasses to modify their surface and structure properties for some applications [1,2,3]. These plasmas are able to produce reactive specimens, such as ozone when air or pure oxygen is used as feed gas. Ozone is a powerful bactericide and oxidant molecule which has been applied on biomass treatment because it is important on deconstruction of lignocellulosic materials [4,5,6], mainly on lignin compounds [4-6].

Many investigations have been done to evaluate ozone decomposition on different metallic surfaces [7,8,9]. These works have emphasized the importance of ozone interaction with metallic walls, considering that ozone losses by O_2 collisions is less important than that occurred at the walls [7,9,10]. Moreover, other studies have been proposed to investigate ozone effects on biomass [4,5]. Binder et al. [4] have verified the kinetic of ozonation processes on wheat straw. They have found two different phases for ozone destruction on the straw: the first one was strongly related to lignin compounds and the second one to the carbohydrates slightly. Mbachu and Manley [5] have determined the rate constants of ozone degradation on two types of isolated lignin (periodate and cuoxam) and on protolignin structure from wood. They concluded that their kinetics were first-order. The aim of our work was to estimate the rate constants of ozone decomposition on sugarcane bagasse, as well as on the reactor wall.

Herein an ozonizer based on atmospheric pressure dielectric barrier discharge (DBD) device has treated 20g of a milled (0.5mm) and moistened sugarcane bagasse sample (water content of 50%). This biomass amount was placed in a stainless steel reactor (Ø 10cm) for the breakdown of the lignin structure. The DBD power supply (10.0kHz and 13.0kV) was connected to coaxial electrodes separated by a ceramic tube. The system was fed by 0.9 slm of molecular oxygen (purity of 99.999%). An optical fiber was connected to the entrance slit of a monochromator (0.55 m focal length and 1800 lines/mm grating) and set perpendicular to a quartz absorption cell (Ø 0.8 cm). The detector used to record the spectra was a CCD 1024x256 pixels. Ozone concentrations were determined before and during the bagasse treatment. The experiments, lasting 6h, were carried out by monitoring the absorption of ozone molecules on Hg emission line at 253.65nm [11].

Ozone concentrations could be expressed as $N=N_0\, e^{-kt}$ [7] where N and N_0 are, respectively, the final and initial ozone concentration, t is the time of ozonization, $k = 1/\tau$ is the rate constant of ozone decomposition and τ is the ozone decay time. From figure 1a, the reaction rate of O_3 with the reactor wall presented a linear dependence during the first 25 min. After that, the ozone adsorption-desorption balance processes was achieved. In contrast, the interaction of O_3 with sugarcane bagasse has presented three different reaction rates (figure 1b). According to Binder et al. [4], the primary phase should correspond to the ozone reaction mostly with the double bounds of aromatic rings of lignin, which has occurred during the first 10 min. The other phases, with different reaction rates, probably were related to the ozone interaction with other sugarcane compounds than lignin [4]. However, in the second phase (20-60 min) some reactions with lignin and its fragments should faintly occur, but no more on the third phase (150-270 min). Further experiments should be done using isolated compounds in order to elucidate these results.

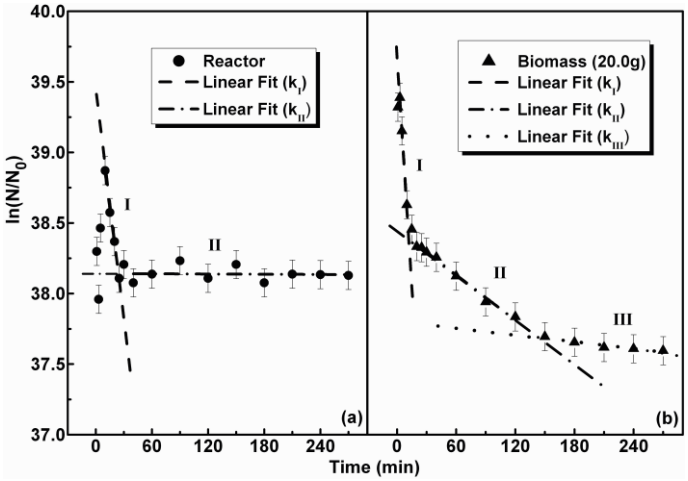

Fig. 1. Ozone decomposition as a function of time: (a) stainless steel reactor wall (circles) and (b) bagasse surface (triangles).

The stainless steel rate constant obtained from our data (8.3 ±0.4) x $10^{-4}s^{-1}$ had good agreement with that one determined by Horvath et al. (9.1 x $10^{-4}s^{-1}$) [8], as well as it was close to that one of Pontiga et al. (6.9x$10^{-4}s^{-1}$) [7]. The rate constants determined for sugarcane material were (1.8±0.1)x$10^{-3}s^{-1}$, (0.89±0.04)x$10^{-4}s^{-1}$ and (1.4±0.2)x$10^{-5}s^{-1}$ for phase I, II and III, respectively. It can be noted that the ozone decomposition on sugarcane bagasse is mostly due to interaction with lignin (phase I) and is more efficient than on the protolignin and two isolated lignin compounds from wood [5] where Mbachu and Manley [5] found 5.10x$10^{-4}s^{-1}$, 5.09x$10^{-4}s^{-1}$ and 6.96x$10^{-4}s^{-1}$, respectively. Our results have also shown the collision frequency of ozone decomposition on phase I of sugarcane bagasse was higher than that occurred on stainless steel material.

In conclusion, the ozone decomposition at the reactor wall had an important influence on the ozone adsorption-desorption balance process with rate constant of (8.3±0.4)x$10^{-4}s^{-1}$. This result has indicated high frequency of ozone destruction at the reactor wall which should not be despised and should be taken into account when treating biomass. During the ozone interaction with bagasse three rate constants (1.8 ± 0.1) x $10^{-3}s^{-1}$, (0.89 ± 0.004) x $10^{-4}s^{-1}$ and (1.4 ± 0.2) x $10^{-5}s^{-1}$ were determined. The first one was related to ozone decomposition on lignin which was more efficient than that occurred at the reactor wall.

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