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## PRETREATMENT OF SUGARCANE BAGASSE TO ACID OR ENZYMATIC HYDROLYSIS APPLYING THE ADVANCED OXIDATION PROCESS BY IONIZING RADIATION TO ETHANOL BIOFUEL PRODUCTION

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Figure 1. Sugarcane bagasse irradiation in batch system at the Electron Beam Accelerator from Radiation Dynamics Inc., USA, with 1.5 MeV, and 37 kW

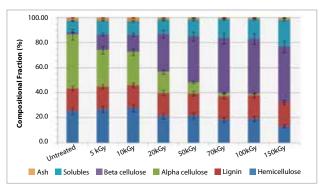


Figure 2. Compositional fraction of sugarcane bagasse untreated and irradiated in different absorbed doses

The main objective of the project is to study the cleavage of lignocellulosic material from sugarcane bagasse using ionizing radiation from an industrial electron beam accelerator, in order to make easier the cellulose hydrolysis and the fermentation of their sugars to ethanol biofuel production. The major drawback of pretreatments technologies is the formation of byproducts as carboxylic acids, furfural, and hydroxymethylfurfural formed by the dehydration reaction of xylose. Because of this fact, it is very important to keep a compromise between the severity and yield of the hydrolysis in order to get a maximum of glucose and celobiose liberation with the minimum byproducts formation.

Chemical modification of cellulose reactions by the free hydroxyl groups is one method for the production of value-added products, resulting in the production of cellulose derivatives. The reactive species generated by the interaction of ionizing radiation with water (oxidant OH radical, reductants e-ag, and H radical) reveal to be a very efficient method for the organic compounds oxidation in simple molecules and can modiify the structure of biomass making cellulose more accessible to the enzymes that convert the carbohydrate polymers into fermentable sugars. The main challenge of electron beam treatment is to obtain the desirable effects applying doses as low as necessary to get some break in the polysaccharides, and at the same time to avoid the loosing of sugars due to uncontrolled degradation of cellulose and hemicelluloses.

This project evaluated the effect of irradiation on the structure and composition of sugarcane bagasse, and on the combination with enzymatic hydrolysis, and hydrothermal treatment. The combination of technologies is meant to decrease the severity of the process avoiding sugar degradation and the formation of toxic byproducts.



### SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

#### 1. Radiation effect on structure and composition of sugarcane bagasse

The radiation processing promotes an increase in the soluble portion that is related to hemicellulose and cellulose cleavage. The cellulose with high molecular weight (alpha) presented a total reduction with absorbed dose of 50 kGy. The changes observed in the cellulose suggest some effects on the lignin structure (Fig. 1). The main sugars identified in the soluble fraction are glucose and arabinose, and it is also detected the water-soluble cello-oligosaccharides of glucanases and xylanases. The obtained results show that radiation interacts initially on the surface of hemicelluloses liberating the arabinose, and then act on the xylose polymers. The main byproduct liberated is acetic acid originated from the deacetilation of hemicelluloses; the removal of this acetyl group enhances the accessibility of the enzyme to the cellulose and can increase the enzymatic hydrolysis. This sequence of radiation interaction probably happens due to the location of xylose in the backbone of arabinoxylan, while arabinose is located in the branches of the macromolecules where the glycosidic bonds are easier to hydrolyze.

#### 2. Radiation effect on enzymatic hydrolysis of cellulose

The enzymatic hydrolysis were done in the Sugarcane Technology Center, using a commercial Trichoderma reesei cellulase preparation (Celluclast 1.5 L), kindly supplied by Novozymes (Bagsvaerd, Denmark), with 5 FPU/g of cellulase and Beta-glycosidase 0.5% (p/p). The enzymatic conversion yield of cellulose to glucose increased from 8% to 14%, and from 6% to 18% in the Sample 1 and 2, respectively with 20 kGy of absorbed dose and 48 h of incubation. In an additional experiment applying absorbed doses up to 500 kGy, the conversion yield of cellulose to glucose did not increase for doses higher than 50 kGy. One reason for these results is the degradation of glucose by radiation and the inhibitory products formation.

#### 3. Radiation combined with hydrothermal treatment

The hydrothermal hydrolysis of sugarcane bagasse at 180°C after irradiation with 50 kGy show a total reduction in oligosaccharides, liberating mainly xylose. However, the presence of formic acid and furfural, after 40 minutes of thermal treatment, mean that xylose and glucose are decomposed just after their liberation from hemicelluloses and cellulose. With the addition of diluted acid, the same amount of xylose is liberated as before, reducing the time from 40-10 minutes and the absorbed dose 50-10 kGy. In *Fig. 3* is showed the increase in solubility that is proportional to the radiation dose and hydrolysis time; otherwise, radiation processing is more important when the samples were treated with thermal rather than acid hydrolysis.

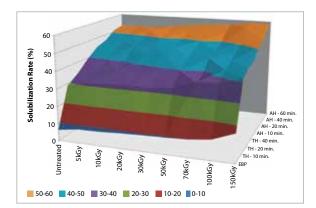


Figure 3. Sugarcane Bagasse Solubilization after Electron Beam Processing (EBP) followed by Thermal (TH) and Acid Treatment (AH)

# 4. Radiation combined with hydrothermal treatment and enzymatic hydrolysis

The conversion of hemicelluloses reached 42% after thermal treatment by 40 minutes for sugarcane bagasse irradiated with 50 kGy. After the addition of diluted sulfuric acid (0.1% v/v), almost the totality of hemicellulose is converted in xylose and byproducts, mainly furfural. The enzymatic conversion yield of cellulose reached 72% in samples irradiated with 50 kGy and 60 min. of thermal treatment. When dilute sulfuric acid was added, it was observed an increase in the cellulose conversion, however the time was reduced, and the higher value (74%) was reached in 40 minutes of diluted acid treatment and 24 h of enzymatic hydrolysis.

The structural and chemical modifications produced by ionizing radiation in the sugarcane bagasse are very important matter to be included in the second generation energy production and it depends on the combination of pretreatment technologies to transform these modifications into bioethanol production growth. The industrial application of electron beam accelerator on the second generation process is a challenging task and very feasible since the equipment could take part in the first generation installation.

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