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Study of thermal treatment combined with radiation on the decomposition of polysaccharides in sugarcane bagasse

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ABSTRACT

Sugarcane bagasse pretreatment is a physical and chemical process that reduces the crystalline structure and disrupts the hydrogen bonding of cellulose to improve the accessibility to hydrolytic depolymerization reactions. The combination of pretreatment technologies intends to decrease the severity of the processes and to avoid excessive sugar degradation and formation of toxic by-products. An effective pretreatment preserves the pentose fractions and limits the formation of degradation products that inhibits the growth of fermentative microorganisms. This study presents the evaluation of the cleavage of polysaccharides from sugarcane bagasse using ionizing radiation combined with thermal and diluted acid treatment to further enzymatic or chemical hydrolysis of cellulose. Samples of sugarcane bagasse were irradiated using a Radiation Dynamics electron beam accelerator with 1.5 MeV and 37 kW, with different absorbed doses, and then were submitted to thermal and acid (0.1% sulfuric acid, m/m) hydrolysis for 10, 20 and 40 min at 180 °C. Taking into account the sugars and by-products liberated in these treatments the conversion rates of cellulose and hemicelluloses were calculated.

1. Introduction

The process to convert the sugarcane bagasse to ethanol biofuel consists of three well known steps. The delignification step, which is the liberation of cellulose and hemicelluloses from lignin, is named as pretreatment. The depolymerization of the carbohydrate polymer (hydrolysis) and the fermentation step of mixed hexose and pentose sugars to produce ethanol (Brenner et al., 1979; Mosier et al., 2005).

The main obstacle to produce ethanol bio-fuel from cellulose is how to accelerate the hydrolysis reaction that breaks it down into starches and sugars, suitable for fermentation. The major cellulose hydrolysis processes, as chemical or enzymatic reactions, are so harsh that toxic degradation products are produced, and can interfere with fermentation. The commercial success of this task depends mainly on the improvement of pretreatment processes, optimization of enzymatic or acid hydrolyzes reactions and the development of more efficient enzymatic complexes with lower costs (Mosier et al., 2005; Yu et al., 2008).

Pretreatment such as steam explosion, lime ammonia, and hydrothermal and dilute acid have potential as cost-effective methods (Mosier et al., 2005). Lignocellulosic biomass hydrothermal treatment consists of submitting a sample to high temperatures (150–230 °C) and pressures in the presence of water to separate the hydrolysates composed essentially of hemicelluloses derivatives and solid pulp composed of cellulose and lignin residue (Van Walsum et al., 1996). The major reactions in hydrothermal and acid pretreatment at low oxygen pressures (827–1655 kPa) and temperatures (120–170 °C), involve acid catalyzed hydrolysis of the lignin and hemicelluloses into low-molecular-weight water-soluble products. At higher temperatures (170–220 °C) and pressures (1655–3310 kPa) the major products are carboxylic acids (mainly acetic and formic acid), formed by oxidation and fragmentation of the polysaccharides (cellulose and hemicelluloses) (Kadam et al., 2004; McGinnis et al., 1984; Yu et al., 2008).

When pretreatment severity is increased, by increasing the temperature or catalyst concentration, or time of reaction, areas of biomass readily exposed to catalyst undergo excessive treatment leading to sugar degradation and formation of toxic by-products. The combination of pretreatment technologies intends to decrease the severity of the processes and to avoid excessive sugar degradation and formation of toxic by-products as aliphatic acids, e.g. acetic, formic and levulinic acid; furan derivatives, e.g. furfural and 5-hydroxyl-methyl-furfural (HMF); and phenol compounds that are formed during the saccharification of lignocelluloses. These compounds might seriously inhibit the enzyme, decreasing the hydrolyzis yield. Furfural is the main compound formed by the oxidation of arabinose and xylose, and its degradation produce formic acid (Brenner et al., 1979; McGinnis et al., 1984; Palmqvist and Hagerdal, 2000).

The free radicals produced by interaction of high-energy radiation in water react with the polysaccharides decreasing the degree of polymerization and increasing the carbonyl content due

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to the chain scission reaction within the cellulose and hemicelluloses molecules (Folddary et al., 2003; Han et al., 1983; Khan et al., 2006).

This study reports the effects of ionizing radiation combined with hydrothermal and dilute acid treatment on the cleavage of polysaccharides from sugarcane bagasse, with the objective of decreasing the formation of by-products to make enzymatic hydrolysis easier and more economical.

2. Experimental

Sugarcane bagasse was obtained from sugar and ethanol factory in Piracicaba, SP. Sample were collected just after the milling, and presented 42.4% of moisture content.

2.1. Radiation processing

The electron beam irradiation was carried out with 1.5 MeV of electrons energy, provided by the IPEN's Electron Beam Facility (Dynamitron type from Radiation Dynamics Inc., USA). The irradiation parameters were 112 cm (94.1%) scan and 6.72 m/min conveyor stream velocity. All the irradiations were performed in a batch system and the delivered irradiation absorbed doses were 10 kGy, 20 kGy, 30 kGy, 50 kGy, 70 kGy, 100 kGy, and 150 kGy.

2.2. Dosimeter system

This electron beam is calibrated routinely with the Fricke dosimeter to determine the absorbed dose rate. The thicknesses of samples for each assay to obtain the desirable dose were calculated according to the bagasse densities, and calibrated using cellulose triacetate, CTA, dosimeter. Ten dosimeters were distributed over and below the sugarcane bagasse, on the corners and on the center of the Pyrex. The coefficients of variation range are from 9.3% for 10 kGy to 12.5% for 100 kGy.

2.3. Thermal and dilute acid hydrolysis

The thermal and dilute acid hydrolysis of the irradiated sugarcane bagasse was carried out using a stainless steel batch reactor which was 10.2 cm in diameter, 12.0 cm in height and had a volume of 230 mL. The temperature was controlled by a digital system and an intermediary temperature was chosen, considering the temperature normally used for steam explosion pretreatment. In the present study, 2.0 g of irradiated and dried sugarcane bagasse was used with 50 mL of distilled water and the system was heated at 180 °C for 10, 20 and 40 min (TH). In a second step the thermal process was conducted under the same operational conditions as the hydrothermal treatment, but adding sulfuric acid to get the concentration of 0.1% (m/m) (35 mg/g of dry mass), this step was called acid hydrolysis (AH). Considering the samples of sugarcane bagasse irradiated in triplicate, 56 samples were obtained in this way.

2.4. Chemical analysis

Total solubility rate was determined using 2.0 g of sample added to 100 mL of distilled water and the mixture was refluxed for 3 h at 100 °C. The sample was filtered and the precipitate was dried for 24 h. The filtered samples were analyzed to determine the presence of sugars and by-products.

2.4.1. Sugar analysis

Characterization and quantification of the sugars were made by HPLC with the Evaporative Light Scattering Detector (ELSD), model 17A from Shimadzu Co. The column temperature was 80 °C; pump pressure was 22 kg cm^{-3}; mobile flow of 0.8 mL min.$^{-1}$; detector temperature 50 °C; detector gain 10, and detector pressure 350 kPa. The calibration curve of the sugars were obtained using standard analytical grade of D-glucose (99.5%), D-xylose (> 99%), D-galactose (99%), L-arabinose (99%), D-mannose (99.9%) and celobiose (98%) from Sigma Aldrich Brazil Ltda. The curves regression coefficient was 0.999, and the obtained experimental variability ($N=10$), expressed as standard deviation, was about 10% for all sugars.

2.4.2. By-products analysis

The by-products formed after irradiations were analyzed by GC–MS, Shimadzu, model GC-MS QP-5000 with a DB5 fused capillary columns (30 m × 0.25 mm I.D.) with low polar bonded phase. The column temperature was adjusted to 50 °C for 0 min, then to 150 °C at 10 °C/min and hold 0 min., then to 300 °C at 15 °C/min and hold 5 min. The injector temperature was 200 °C. The mass detector operation was in electron impact mode (EI), using 1.50 kV of ionizing voltage and a temperature of 250 °C, operated in continuous mode (SCAN). The solvent extractors used were acetonitrile 1:1 v/v and hexane/dichloromethane 1:1 v/v.

3. Results and discussion

After the hot extraction of sugarcane bagasse, the solubility rates were calculated considering only irradiation in different doses (EBI), irradiation combined with thermal hydrolysis (TH) and irradiation combined with acid hydrolysis (AH) for 10, 20 and 40 min, and the results are presented in Table 1. The increase in

Table 1
Solubility rate of sugarcane bagasse after electron beam irradiation (EBI) in various absorbed doses and after thermal (I+TH) and diluted acid hydrolysis (I+AH) for 10, 20, and 40 min.

Absorbed dose (kGy)	Solubility rate (%)						
	EBI	I+TH 10 min	I+TH 20 min	I+TH 40 min	I+AH 10 min	I+AH 20 min	I+AH 40 min
0	6.3 ± 0.3	29.0 ± 1.5	33.4 ± 1.7	41.4 ± 2.1	48.5 ± 2.4	47.8 ± 2.4	52.0 ± 2.6
5	7.9 ± 0.4	34.2 ± 1.7	34.8 ± 1.7	40.2 ± 2.1	46.4 ± 2.3	46.5 ± 2.3	51.3 ± 2.6
10	8.1 ± 0.4	32.1 ± 1.6	38.8 ± 1.9	42.0 ± 2.1	44.6 ± 2.2	47.8 ± 2.4	52.6 ± 2.7
15	8.1 ± 0.4	32.9 ± 1.7	37.0 ± 1.4	40.6 ± 2.1	48.2 ± 2.4	46.6 ± 2.3	50.2 ± 2.5
20	8.8 ± 0.4	32.6 ± 1.7	37.4 ± 1.4	42.9 ± 2.2	47.7 ± 2.4	49.6 ± 2.5	52.1 ± 2.6
30	9.1 ± 0.5	29.2 ± 1.5	39.7 ± 2.0	44.4 ± 2.2	47.7 ± 2.4	52.1 ± 2.6	51.8 ± 2.6
50	9.4 ± 0.5	31.3 ± 1.6	37.7 ± 1.9	40.1 ± 2.0	46.4 ± 2.3	50.0 ± 2.5	52.6 ± 2.7
70	9.9 ± 0.5	37.4 ± 1.8	42.2 ± 2.1	45.2 ± 2.3	46.9 ± 2.3	48.8 ± 2.4	52.1 ± 2.6
100	11.4 ± 0.6	34.1 ± 1.7	38.8 ± 1.9	44.5 ± 2.3	50.2 ± 2.5	49.8 ± 2.5	57.7 ± 2.9
150	16.3 ± 0.8	41.7 ± 2.1	44.4 ± 2.2	44.1 ± 2.2	49.4 ± 2.5	51.2 ± 2.6	57.4 ± 2.9

solubility was proportional to the radiation dose and hydrolysis time. Considering only irradiation there was an increase of 16% in solubility, applying 150 kGy. Taking into account only the thermal hydrolysis for 10 min an increasing 22.7% can be observed, and with the addition of dilute acid, the solubility rate increased to 42.2%. However, radiation processing was more important when the samples were thermally hydrolyzed rather than acid hydrolyzed. Considering the solubility of samples non irradiated and irradiated at 150 kGy, the acid hydrolysis presented an increase of 1%, 3% and 6% for 10, 20 and 30 min, respectively, while thermal hydrolysis shows 13%, 11% and 3% for 10, 20 and 40 min, respectively.

3.1. *Characterization of free sugar after thermal and acid hydrolysis of irradiated sugarcane bagasse*

In Fig. 1 is shown the main sugars and the oligosaccharides after 10, 20, and 40 min of thermal hydrolysis as a function of the absorbed dose. The decomposition of these oligosaccharides, identified as 'A' and 'B,' was proportional to the duration of thermal treatment and absorbed dose. The total decomposition of oligosaccharides and the maximum concentration of xylose were reached when the bagasse were irradiated with 30 kGy and thermally processed for 40 min. For absorbed doses higher than 40 kGy a decrease of xylose can be observed, because radiodegradation of this sugar may have occurred. Glucose was not identified in the slurry of these thermal processed samples.

The addition of dilute acid changes this picture, and after 10 min a total decomposition of oligosaccharides was achieved, as can be seen in Fig. 2. These figures show the chromatograms of dilute acid hydrolysis for 10, 20, and 40 min. The xylose liberation reached a maximum when sugarcane bagasse was irradiated at 20 kGy and thermally processed with dilute acid for 10 min,

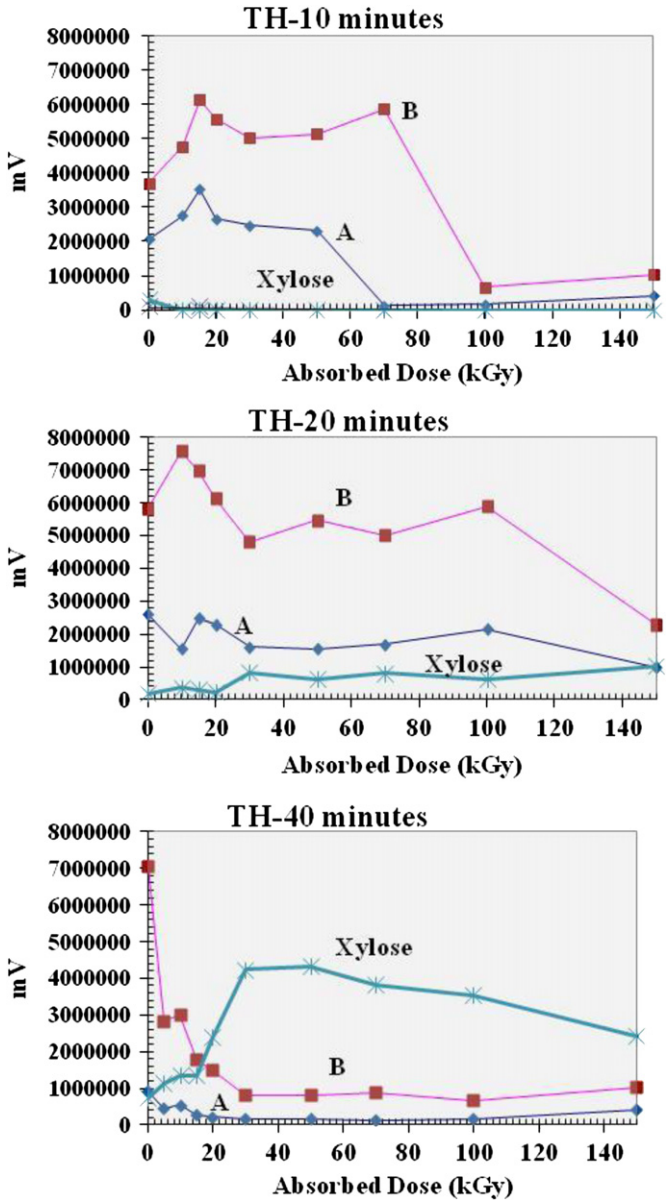

Fig. 1. Main sugar and oligosaccharides (a, b) in sugarcane as a function of absorbed doses after thermal hydrolysis (th) for 10, 20, and 40 minutes.

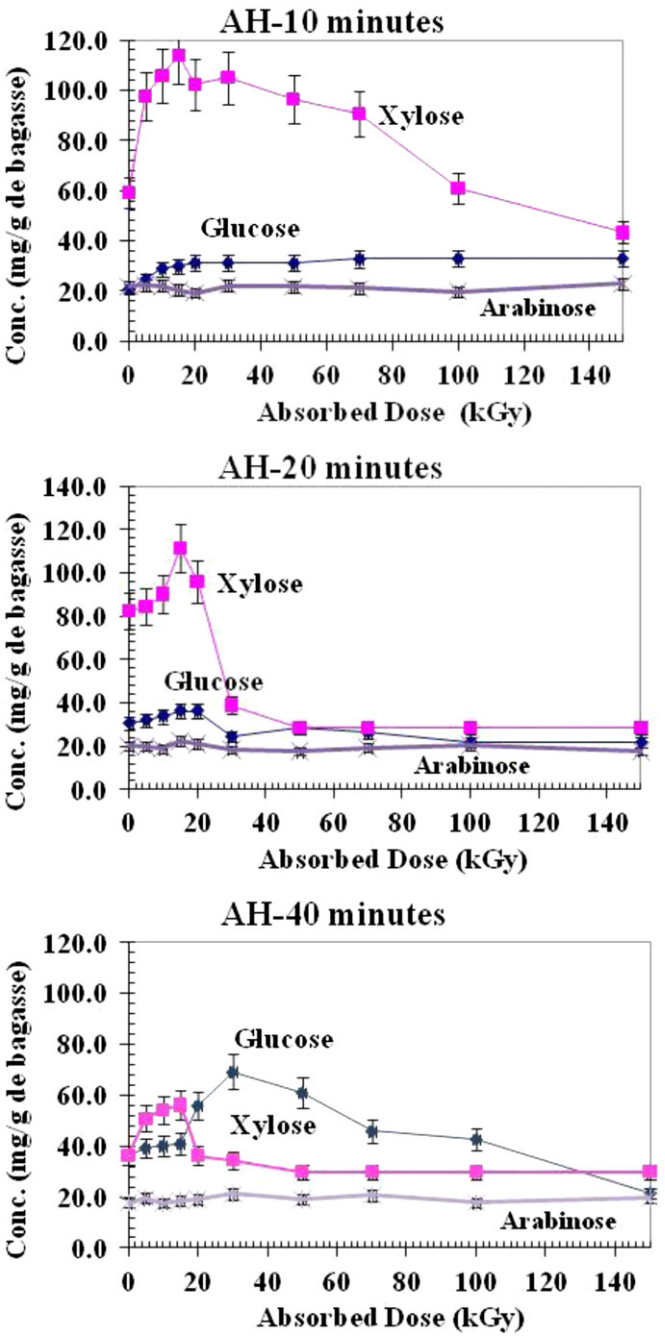

Fig. 2. Concentration of the main sugars in sugarcane bagasse, as a function of absorbed doses after dilute acid hydrolysis (AH) for 10, 20, and 40 minutes.

Table 2
Formic acid concentration after thermal (TH) and diluted acid (AH) hydrolysis of sugarcane bagasse (10, 20, and 40 min), in various absorbed doses.

Absorbed dose (kGy)	Formic acid (mg/g of bagasse)					
	I+TH 10 min	I+TH 20 min	I+TH 40 min	I+AH 10 min	I+AH 20 min	I+AH 40 min
0	22 ± 2	25 ± 2	45 ± 4	114 ± 11	260 ± 26	125 ± 12
10	221 ± 22	371 ± 37	475 ± 47	225 ± 22	315 ± 31	126 ± 12
30	186 ± 18	430 ± 43	535 ± 53	302 ± 30	719 ± 71	224 ± 22
70	272 ± 27	426 ± 42	464 ± 46	456 ± 45	893 ± 89	114 ± 11
100	288 ± 28	409 ± 40	436 ± 43	732 ± 73	732 ± 74	121 ± 12
150	398 ± 39	359 ± 35	229 ± 22	311 ± 31	368 ± 36	113 ± 11

Table 3
Furfural concentration after thermal (TH) and diluted acid (AH) hydrolysis of sugarcane bagasse (10, 20, and 40 min), in various absorbed doses.

Absorbed dose (kGy)	Furfural (mg/g of bagasse)					
	I+TH 10 min	I+TH 20 min	I+TH 40 min	I+AH 10 min	I+AH 20 min	I+AH 40 min
0	29.1 ± 2.9	33.5 ± 3.3	41.5 ± 4.1	35.4 ± 1.5	70.7 ± 7.1	80.2 ± 8.0
10	32.1 ± 3.2	37.1 ± 3.7	42.0 ± 4.2	44.0 ± 3.4	82.0 ± 8.2	91.9 ± 9.2
30	32.7 ± 3.2	38.8 ± 3.9	43.0 ± 4.3	46.0 ± 3.6	107.6 ± 9.9	93.6 ± 9.3
70	37.5 ± 3.7	42.3 ± 4.3	45.2 ± 4.5	88.6 ± 8.8	101.7 ± 9.9	79.2 ± 7.09
100	34.1 ± 3.4	38.8 ± 3.9	44.5 ± 4.4	101.7 ± 9.9	86.9 ± 8.7	60.5 ± 6.0
150	41.7 ± 4.1	44.4 ± 4.4	44.1 ± 4.4	77.3 ± 7.7	74.9 ± 7.4	58.0 ± 5.8

following which degradation of xylose should occur. The liberation of glucose increased with the hydrolysis time reaching the maximum at 30 kGy and 40 min. The results in the present study suggest a decomposition of glucose and xylose proportional to dose and time processing by radiation and thermal hydrolysis processing. The identification of by-products is important to demonstrate this statement.

3.2. By-products

The main by-product identified after irradiation was acetic acid, however after thermal hydrolysis of irradiated bagasse this acid was absent, but formic acid had formed at a higher concentration, followed by furfural, propionic acid, and benzofuran. Some phenolic compounds were identified at very low concentrations, which could have resulted from a small break in the lignin structure. In Tables 2 and 3 the concentrations of formic acid and furfural in different absorbed dose after thermal and dilute acid processing are presented. The presence of formic acid and furfural indicates a degradation of xylose and arabinose, because they are formed by oxidation of the terminal group on the carbohydrate. This degradation was observed even after 10 min of thermal processing, and it increased with the radiation absorbed dose. The most likely mechanism for this reaction involves the formation of hydroperoxy radicals which interact with the carbohydrates. In the thermally treated samples, the formic acid was formed in higher concentration than furfural. When diluted acid was added the xylose increased, but some amount was degraded, forming furfural.

3.3. Conversion

Using the conversion factors (Rodrigues et al., 2010; Gouveia et al., 2009) of hemicelluloses (0.88 × xylose mass, 0.88 × arabinose mass, 0.72 × acid acetic mass and 1.37 × furfural mass), and cellulose (0.90 × glucose mass, 3.09 × formic acid mass), the total conversion of these polysaccharides were obtained and the results are shown in Fig. 3. Radiation processing of sugarcane bagasse at 15 kGy converts about 0.5% of cellulose to glucose. These conversions did not increase after thermal treatment at studied time and temperature, however when dilute sulfuric acid was added, an increase in the cellulose conversion was observed, reaching 14.8% at 30 kGy and 40 min of thermal treatment (Fig. 3).

The conversion of hemicelluloses reached about 1.9% (represented by arabinose liberation) in irradiated sugarcane bagasse at 100 kGy of absorbed dose (Fig. 3). However after thermal treatment for 40 min this conversion reached about 38.2% at 50 kGy. After the addition of sulfuric acid, the conversion rate increased to 48.2%, the absorbed dose decreased to 10 kGy, and the time of thermal treatment reduced to 10 min (Fig. 3).

These results are comparable to some studies of xylose yield in the literature, but in present case under less severe conditions. Boussarsar et al. (2009) obtained 55% after 4 h at 170 °C of hemicellulose to xylose conversion, but in 2 h the yield was 48.8%. The highest value of xylose yield obtained by Rodrigues et al. (2010) was 73.4% at 130 °C for 20 min and 100 mg acid/g of dry bagasse.

4. Conclusion

Hydrothermal hydrolysis for 40 min at 180 °C after irradiation at 50 kGy showed a total reduction of oligosaccharides, which are formed by the partial decomposition of cellulose and hemicelluloses, liberating mainly xylose. However, the presence of formic acid and furfural, even for 10 min of thermal treatment, means that xylose and glucose are being decomposed just after liberation from hemicelluloses and cellulose. With the addition of dilute acid the same amount of xylose was liberated, in this case the time was reduced from 40 to 10 min, and the absorbed dose was reduced from 50 to 10 kGy. The best yield in the present study

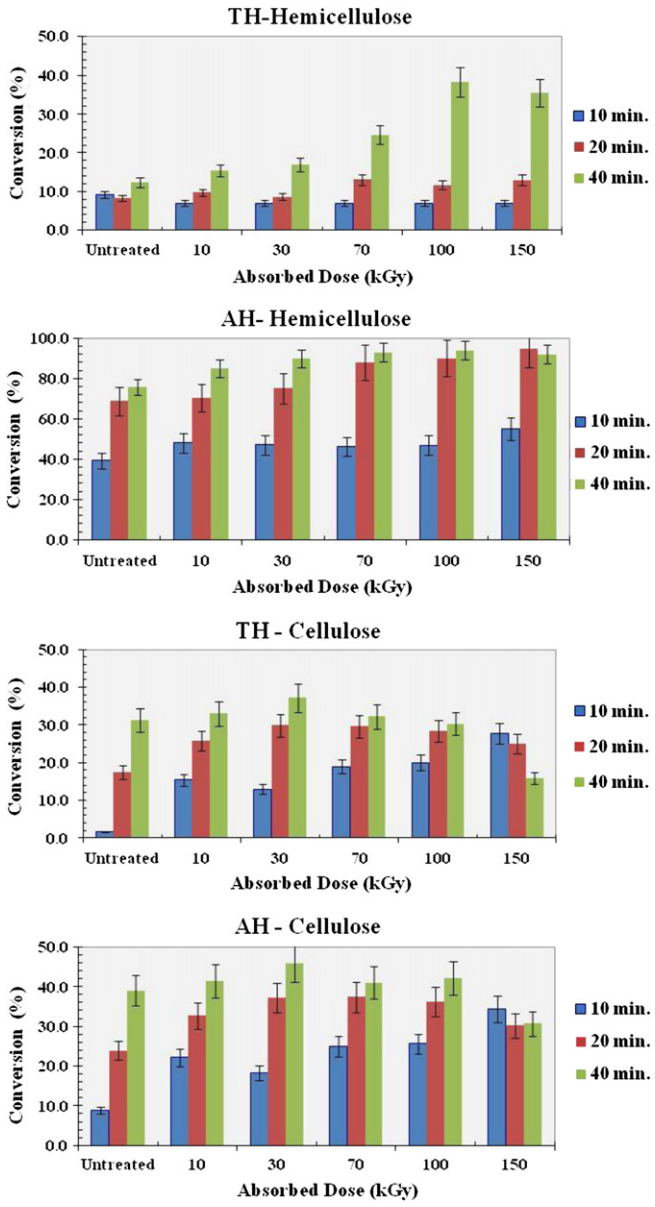

Fig. 3. Conversion of cellulose and hemicelluloses after irradiation and irradiation combined with thermal (TH) and dilute acid (AH) hydrolysis of sugarcane bagasse (10, 20, and 40 minutes), as a function of absorbed dose.

was obtained by processing the samples irradiated at 20 kGy with diluted acid (35 mg/g of dry bagasse) by 10 min of thermal hydrolysis at 180 °C.

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