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Research paper

Catalytic production of sugars and lignin from agricultural residues using dilute sulfuric acid in γ-valerolactone

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ABSTRACT

The fractionation of sugarcane bagasse, plantain peel and brewer's spent barley to glucose, xylose and lignin was studied using 0.50 and 0.05 wt% H_2SO_4 as catalyst in a mixture of 80:20 wt% GVL:H_2O. We obtained glucose and xylose cumulative yields with up to 90, 94 and 88% for sugarcane bagasse, plantain peel and brewer's spent barley, respectively. We studied the effects of the reaction conditions and physicochemical properties of the agricultural residues on the production of sugars. The production of sugars depends on the physicochemical properties of each residue. The lignin content, biomass crystallinity and ashes composition have the strongest effects on the production of sugars. The lignin can affect the accessibility to hemicellulose and cellulose during the reaction reducing the amount of sugars that can be obtained from the residue. The ashes present in the biomass may have alkaline species that can neutralize the acid catalyst reducing the rate of sugar production for a given acid concentration. The sugar production decreases as the biomass crystallinity increases.

1. Introduction

Renewable lignocellulosic biomass is a potential source to produce biofuels and platform molecules because it is abundantly generated from agricultural residues and food industry waste. Moreover, there is available technology to produce fungible biofuels that do not require changes to the combustion engines and the transportation infrastructure due to their similarity to conventional fuels. These unique characteristics of biomass-derived fuels offer advantages over other alternatives in the automotive fuel market.

Many important chemicals and platform molecules (*i.e.*, ethanol, polylactic acid, levulinic acid, levoglucosenone, *etc.*) may be produced from biomass [1–4]. Dumesic and co-workers, demonstrated that the synthesis of different intermediary molecules for the manufacture of biofuels may be produced from different biomass derived feedstocks (*i.e.*, sugars, cellulose, hemicellulose, *etc.*) [5–8]. Moreover, they demonstrated the production of soluble carbohydrates from the deconstruction of corn stover, hardwood and soft wood using sulfuric acid (H_2SO_4) in γ-valerolactone (GVL) and water mixtures [9]. Sugars like xylose and glucose are the main products in the deconstruction of these biomass sources [9]. These sugars may be converted to many platform molecules for the production of fuels and specialty chemicals (*i.e.*, 5-hydroxymethylfurfural, furfural, ethanol, lactic acid, *etc.*) using heterogeneous catalysts [6,7,9]. Dumesic and co-workers used mixtures of GVL and water because they noted that using polar aprotic solvents such as GVL enhances the catalytic activity of the protons of H_2SO_4, which promotes the hydrolysis of cellulose and hemicellulose in the presence of water [10]. Also, GVL is a renewable green solvent that can be produced from biomass derived products [11]. Motivated by those discoveries, here we will use different local available biomass residues from the agricultural and food industry such as sugarcane bagasse, plantain peel and brewer's spent barley for sugars and lignin production using H_2SO_4 in a GVL-water mixture.

The worldwide production of sugar cane reaches 1.6 billion tons per year positioning it in the top three harvests in the world [10,11]. The main uses of sugarcane are for sugar and alcohol production. Those operations generate approximately 300 million tons of biomass residues yearly, mainly composed of bagasse and leaves [10,12]. These residues are mainly burned to produce electricity or run different processes in the industry [12]. Due to the abundance and low efficiency methods to treat the residues of sugarcane production, we consider that sugar cane bagasse is an important candidate for the catalytic production of sugars from biomass deconstruction. On the other hand, plantain and banana are also some of the most important harvests in the world. The production of plantain and banana reaches approximately 144 million tons per year, plantain contributing 38 million tons and banana 106 million tons [13]. The peel represents around 35% of the fruit weight for each case and this is translated to 50.4 tons of peel residues generated per

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year [14,15]. The main uses of plantain and banana peel are as compost and for cattle feed [14,16]. The local availability and global production of plantain and banana peel make them potential biomass sources for sugars production. Additionally, the beer breweries are producing large quantities of biomass residues. These residues are mostly the spent grain that comes from the mash or sugar extraction process for beer production [17]. The main grain used for beer production is barley. The global beer industry produces around 6 million tons of dry spent grain per year that is mainly used as animal feed [17,18]. Currently, the continuous increase in production of the craft beer industry and the limited uses for the breweries spent grain also makes this residue a potential candidate for sugar production from biomass.

In this regard, we studied the catalytic conversion of sugarcane bagasse, plantain peel and brewer's spent barley to sugars and lignin. We report sugars yields up to 90, 94 and 88% for bagasse, plantain peel and brewer's spent barley, respectively. The effect of the reaction conditions and the physicochemical properties of the biomass on the production of sugars was investigated. The physicochemical properties of each biomass source are important variables that define the process conditions for sugar production.

1.1. Materials

Deionized water (DI), γ-valerolactone (GVL) (ACROS Organics, 98% purity) and denatured ethanol (ACROS Organics, HPLC grade) were used as solvents. Sulfuric acid (H_2SO_4) (Fisher Chemical, 95–98% purity) was used as solvent and as catalyst. High purity He (Praxair, 99.999% purity) was used for the reactor pressurization. The feedstocks used were sugar cane bagasse (SCB), plantain peel (PP), and spent brewer's barley (BSB). Microcrystalline cellulose with an average particle size of 50 μm (ACROS Organics) was used for comparison. Granular fused silica (Sigma-Aldrich, 4–20 mesh) was mixed with the biomass samples to decrease heat and mass transfer effects and quartz wool (Chemglass, fiber size 8–15 μm) was used to keep the packed bed in place in the reactor. Polyvinylidene fluoride (PVDF) membrane filters (Millipore Durapore GVWP01300) were used for the recovery of lignin. The agricultural residues used were obtained from local sources.

1.2. Biomass preparation

The sugarcane bagasse used in this study came from sugar cane previously pressed in a sugar cane mill. In this step, the sugar cane juice was extracted from the cane. The barley was previously treated with 1 L of distilled water per pound of grain at 340 K for 1 h. The plantain peel was not pretreated. The biomass samples were dried at 318 K for 48 h in a conventional oven. The dried biomass was milled and sieved to obtain particles with a size of approximately 1.42 mm. At this point, the biomass was ready for fractionation.

1.3. Biomass characterization

The biomass characterization was performed according to the procedures published by the National Renewable Energy Laboratory (NREL). Before all procedures, the biomass sample was dried using the convection oven drying method published by the NREL [19]. Then, the biomass was milled and sieved using 20 and 70 mesh sieves. The resulting particles have particles sizes between 0.21 and 0.84 mm. The biomass samples were placed with a maximum depth of 1 cm and weighted. Then the sample was placed in a vacuum oven at 318 K until the weight did not change, this normally happened after 12–48 h. Finally, the sample was weighted.

We used the convection oven method published by the NREL for the determination of total solids in the biomass [20]. About 0.5–2.0 g of biomass previously dried was used for the analysis. This biomass was weighed to the nearest 0.1 mg in an aluminum pan previously weighed. The pan containing the biomass was placed in the vacuum oven at 378 K for 4 h. A small piece of aluminum foil was weighted and used as a cover for the pan with the biomass when it was extracted from the vacuum oven. The pan, biomass and the cover were weighted to the nearest 0.1 mg.

The inorganic composition of the biomass was determined using the procedure established by NREL [21]. About 1.0 and 2.0 g of dried biomass were weighed in an aluminum pan previously weighed. The sample was placed in a furnace at 378 K for 12 min with a heating ramp of 8 min from room temperature. The temperature was raised to 523 K with a heating ramp of 15 min and held for 30 min. Then the temperature was raised to 848 K using a heating ramp of 16 min and held constant for 3 h. The sample was cooled to 378 K and removed for weighting. The sample remaining in the pan is the inorganic content of the biomass.

The extractives composition were determined using the procedures published by NREL [22] to determine the biomass extractives soluble in water and ethanol. The extraction was done using a Soxhlet apparatus. It consists of a condenser tube at the top, a Soxhlet tube in the middle and a boiling flask with the solvent in the bottom. About 2–5 g of biomass were weighted in an extraction thimble. The exact quantity depends on the bulk density of the biomass and the Soxhlet tube used. The height of the biomass in the extraction thimble should not exceed the height of the Soxhlet siphon tube. The extraction thimble with the biomass sample is placed in the Soxhlet tube and 190 mL of deionized water are added to a boiling flask and the Soxhlet apparatus is assembled. The Soxhlet apparatus, specifically the boiling flask, is placed in an oil bath at 423 K for 24 h. When the extraction time is completed, the Soxhlet apparatus is removed from the oil bath. The boiling flask containing deionized water and the extractives is changed with one containing 190 mL of ethanol. The apparatus is placed again in the oil bath but this time at 383 K for 24 h. When the extraction time is completed, the Soxhlet apparatus is removed from the oil bath. The Soxhlet tube is connected to a line to perform vacuum filtration overnight. Once the filtration is finished, the extraction thimble with biomass is removed from the Soxhlet tube and placed in a vacuum oven at 318 K for 24 h. After drying is completed, the thimble with the biomass is weighted. Following the removal of extractives using water and ethanol, the biomass is used for the determination of cellulose, hemicellulose and lignin using the method proposed by the NREL [23]. For this procedure, we used 300 ± 10 mg of the corresponding biomass. The sample is placed in a vial with 3.00 mL of 72% sulfuric acid and stirred for 1 min. The closed vial is placed in a water bath at 303 K for 1 h under stirring. After this process is completed, the sample is transferred to a PTFE autoclave and 84 mL of deionized water are added. This reactor is placed in a conventional oven at 394 K for 1 h. Then, the reactor is removed from the oven and allowed to cool at room temperature. The sample is vacuum filtered, washed with at least 25 mL of distilled water and vacuum filtered for 24 h. After that the sample is removed and placed in a vacuum oven at 318 K for 24 h. The dried sample is weighted to the nearest 0.1 mg and placed in a furnace at 378 K for 12 min with a heating ramp of 8 min. The temperature is raised to 523 K with a heating ramp of 15 min and held constant for 30 min. Then the temperature is raised to 848 K using a heating ramp for 16 min and held constant for 3 h. At this point the organic material in the biomass sample is calcined and the remains correspond to inorganic material present in the biomass, which is not soluble in water and/or ethanol. The soluble inorganic material present in the biomass is subtracted from the extractives. The soluble inorganic material is calculated by subtracting the amount of non-soluble inorganic materials determined after the recovery of the extractives from the total inorganic material determined above. The remains are cooled to 378 K and the sample is removed for weighting. Finally, the absorbance at 240 nm of the liquid remaining is determined using a UV–Visible spectrophotometer (Thermo Scientific) to determine the amount of acid-soluble lignin in the biomass sample. The total amount of lignin is determined by summing the acid-soluble lignin and non-acid-soluble

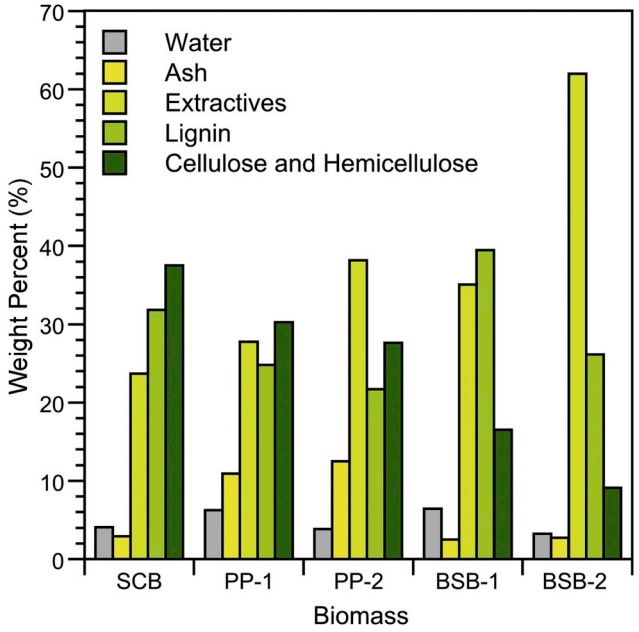

Fig. 1. Biomass composition results obtained using NREL guidelines.

lignin, which is determined by calculating the difference in mass of the sample before and after calcination. The amount of cellulose and hemicellulose is determined by the difference in mass of the dried biomass and the sum of the extractives, lignin and inorganic material.

The biomass and cellulose X-ray diffraction patterns were obtained using a Siemens Diffraktometer D5000 X-ray diffractometer equipped with cross beam optics and a Cu K_α target operating at 40 kV and 44 mA. Standard powder diffraction patterns were gathered for 2θ angles ranging from 15 to 75° at a scanning speed of 2°/min and a step size of 0.1°. The biomass crystallinity index (CrI) was calculated as follows [24]:

$$CrI = \frac{I_{002} - I_{AM}}{I_{002}}$$

were I_{002} is the intensity of the peak corresponding to the crystalline portion of biomass that in our case is at a diffraction angle of around 22°. The I_{AM} is the peak intensity for the amorphous portion of biomass, which in our case appears at a diffraction angle of around 17°.

1.4. Catalytic conversion of biomass

The reaction system consists of a 316 stainless steel (SS) tubular reactor 12.7 mm of external diameter and 254 mm of height, a 150 mm variable area flow meter with a 316 SS valve (Cole-Palmer EW-03269-18), and a backpressure regulator (Tescom 44–2200), that controls the pressure of the system. The reactor was heated using a cylindrical aluminum oven equipped with four heating rods (Omega CSH-10320). The liquid was fed using an HPLC pump (Hurst model A-30-SW). The reactor was packed vertically with 2.5 g of dry biomass, previously mixed with 5 g of silicone dioxide fused particles, between two plugs of quartz wool and silicone dioxide particles (SiO_2). The reactor was packed with SiO_2 particles to reduce the mass and heat transfer limitations during the reaction. The SiO_2 particles were larger than the biomass particles and fixed between two plugs to avoid changes in the reactor volume and residence time. The biomass sample was heated to 430 K with a linear ramp for 20 min in flowing He at atmospheric pressure to remove the remaining moisture. The temperature was equilibrated for 5 min before the reactor was pressurized to 21 bar. Then, a mixture of 80 wt% GVL, 20 wt% H_2O and 0.05 or 0.5 wt% H_2SO_4 was fed to the reactor with a flow of 1 mL/min using an HPLC pump, while the reactor was heated from 430 K to 490 K using a heating rate of 0.5–1.0 K/min. We drained the resulting accumulated liquid from the liquid collector every 10 min. Each sample was filtered using a 0.2 μm PVDF membrane filter to remove insoluble solids. Afterwards, the samples were diluted with 20 times its weight in DI water to precipitate lignin, centrifuged at 10,000 rpm, washed with DI water, filtered using a 0.2 μm PVDF hydrophilic membrane filter to recover the precipitated lignin that was dried at 358 K. Finally, the diluted liquid samples were analyzed using an HPLC and the filtered solids were dried and weighted.

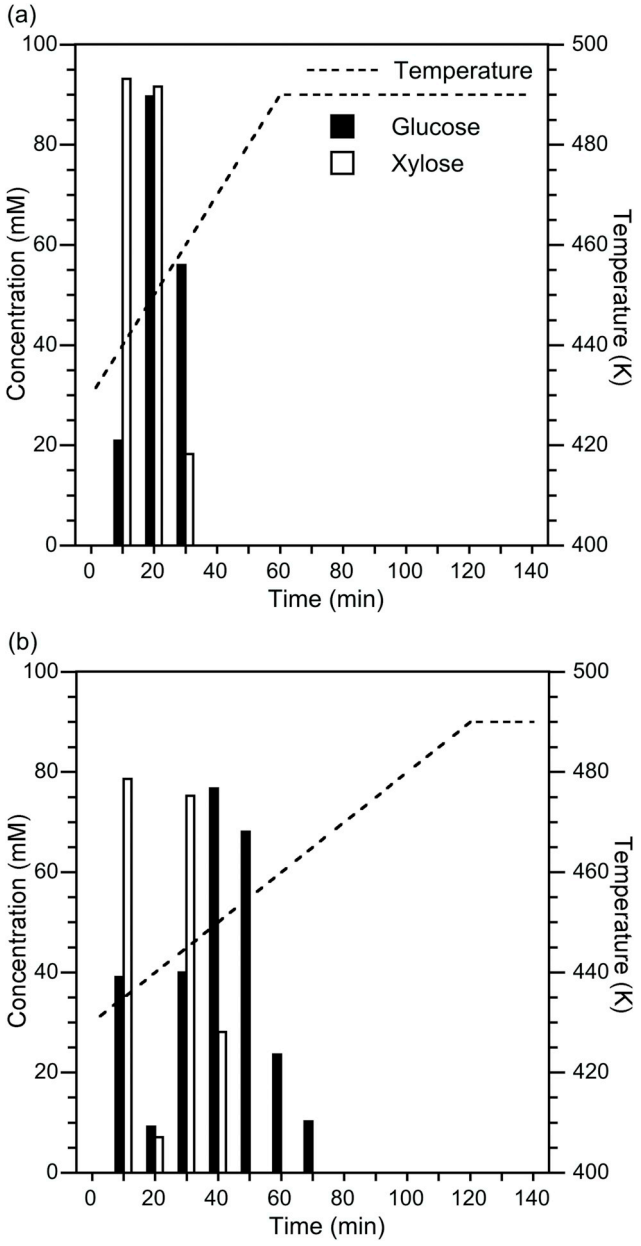

Fig. 2. Production of glucose and xylose from sugar cane bagasse using 5 mM H_2SO_4 in an 80 wt% GVL and 20 wt% H_2O mixture feed with a flow of 1 mL/min at 21 bar He and a heating rate of (a) 1.0 K/min and (b) 0.5 K/min.

1.5. Analytical methods

The samples taken during the reaction were analyzed using a high performance liquid chromatograph (Waters Alliance 2690) equipped with a refractive index detector (Waters 2410) used for sugar analysis. The separation of the reaction products was achieved using a Bio-Rad Aminex HPX-87H column. The mobile phase was an aqueous solution

Table 1
Products yields for the catalytic conversion of agricultural residues using H_2SO_4 in an 80:20 GVL:H_2O solution.

Biomass	Heating rate (K/min)	H_2SO_4 (wt%)	Y_{Sum}[a] (%)	$Y_{Glucose}$[b] (%)	Y_{Xylose}[c] (%)	Y_{Lignin}[d] (%)
SCB	1.0	0.50	59	29	30	–
SCB	0.5	0.50	62	37	25	–
SCB	0.5	0.05	90	41	49	53
PP-1	0.5	0.50	94	66	28	–
PP-1	0.5	0.05	75	34	41	–
PP-2	0.5	0.05	31	18	13	38
BSB-1	0.5	0.50	88	80	8	–
BSB-1	0.5	0.05	84	60	24	–
BSB-2	0.5	0.05	105[e]	67	38	54
Cellulose	0.5	0.05	45	39	6	0

[a] Accumulative total glucose and xylose yield determined in a carbon mole basis considering the total initial carbon contribution from cellulose and hemicellulose.
[b] Accumulative total glucose yield determined in a carbon mole basis considering the total initial carbon contribution from cellulose and hemicellulose.
[c] Accumulative total glucose yield determined in a carbon mole basis considering the total initial carbon contribution from cellulose and hemicellulose.
[d] Accumulative lignin yield determined as the ratio of the recovered lignin and solids mass and the initial lignin mass present in the biomass waste.
[e] This yield is over 100% due to the presence of sugars in the extractives that are not removed for the reaction.

of 5 mM H_2SO_4 with a flow rate of 0.3 mL/min. The column temperature was held at 353 K. The sample injection volume was 10 μL. The sugar yields were determined as the ratio of the accumulated sugar's carbon moles obtained during the reaction and the sum of cellulose and hemicellulose carbon moles present initially in each biomass sample.

Galactose and mannose may be obtained from hemicellulose fractionation [25–31]. The amount of these sugars produced is commonly low compared to xylose [25–31]. The galactose and mannose molar percent obtained from hemicellulose were around 3%, 15% and 11% for SCB, PP and BSB, respectively [27–31]. The HPLC column used for product analysis in the present study is not able to separate xylose, galactose and mannose. However, the amount of galactose and mannose that may be produced during the fractionation of biomass in this study is expected to be low. Hence, we assume that the contribution of galactose and mannose to the peak area corresponding to xylose is low; and, the amount of galactose and mannose that may be produced is lumped with xylose and reported as xylose.

2. Results and discussion

2.1. Biomass characterization

Sugar cane bagasse, plantain peel and brewer's spent barley were used to produce sugars and lignin. Each residue has a different composition depending on its species, type and origin. Hence, the residual biomass samples used for this study were previously characterized following the NREL guidelines. Fig. 1 shows the composition results on a mass basis for SCB, PP and BSB. Two different samples of BSB and PP were used. The samples were named as BSB-1 and BSB-2 for brewer's spent barley and PP-1 and PP-2 for plantain peel samples. BSB-1 and BSB-2 are two different samples of a similar mixture of barley from two different suppliers used to produce two different batches of beer. The most abundant components in the biomass studied are cellulose, hemicellulose, lignin and extractives. BSB's samples have the less content of cellulose and hemicellulose compared to SCB and PP. The barley was previously treated with water at 340 K for 1 h to produce fermentable sugars for beer production. At this temperature, the alpha and beta amylase present in barley are active and convert polysaccharides to dextrin and fermentable sugars that are soluble in water [32–34]. This treatment causes the partial conversion of a certain amount of cellulose and hemicellulose to sugars reducing its content in the barley. On the other hand, the composition of extractives in the BSB samples is higher compared with sugar cane bagasse and plantain peel. The low content of cellulose and hemicellulose and the higher extractive content in BSB samples may be attributed to the conversion of cellulose and hemicellulose to sugars after the hydrothermal treatment at 340 K for beer production. The lignin, cellulose and hemicellulose compositions are higher in sugar cane bagasse. This may be attributed to the fact that sugarcane belongs to the genus of the grass family [35]. The grasses have high cellulose, hemicellulose and lignin contents similar to hard and softwood biomass [36,37]. The ash content in PP samples is higher than that observed for SCB and BSB. It is well known that fruits like banana and plantain are rich in minerals such as potassium, calcium, sodium, among others [38–40]. These inorganic species are easily oxidized to form ashes after biomass calcination.

2.2. Catalytic conversion of biomass to sugars and lignin

2.2.1. Effect of the heating rate on sugar production

We evaluated the conversion of sugar cane bagasse to sugars using 0.5 wt% H_2SO_4 in a mixture 80:20 GVL:H_2O using two heating rates to reach 490 K from 430 K, as shown in Fig. 2. Using a heating rate of 1 K/min the bagasse was completely fractionated after 30 min of heating. On the other hand, using a heating rate of 0.5 K/min the bagasse was completely consumed after 70 min of heating. Despite that the time to complete the conversion of bagasse changes by changing the heating rate, the temperature at which the maximum production of glucose was obtained was 450 K in both scenarios. This suggests that 450 K is the optimal temperature to promote the conversion of most of the cellulose to glucose under these reaction conditions.

The glucose and xylose cumulative yields obtained for the conversion of bagasse using 1.0 K/min and 0.5 K/min heating ramps are shown in Table 1. The glucose yield increases from 29 to 37% when the heating is decreased to 0.5 K/min while the xylose yield decreases from 30 to 25%. This suggests that the heating rate has an influence on the conversion of the produced sugars to degradation products such as humins. Apparently, the degradation of glucose is higher using a heating rate of 1.0 K/min instead 0.5 K/min. The decrease in xylose yield may be attributed to a decrease in the hemicellulose depolimerization rate at lower heating rates and that its stability during thermal treatments is lower compared to that for cellulose [41]. Hence, if the hemicellulose depolimerization rate decreases, the time that the hemicellulose will be in the reactor exposed to heating will be higher causing a higher conversion to degradation products of the hemicellulose before it can be converted to xylose at these reaction conditions. Moreover, the difference in the sugars yields may be due to two main reasons: the time exposed to a certain range of temperature and how is the biomass structured. We believe that the hemicellulose and lignin are covering the cellulose. At high heating rates the hemicellulose is consumed rapidly giving access to the cellulose early compared to the reaction using a low heating rate. Hence, at low heating rates the acid interacts with the hemicellulose for a longer time promoting its degradation or xylose degradation and the interaction with the cellulose is restricted, reducing its degradation or glucose

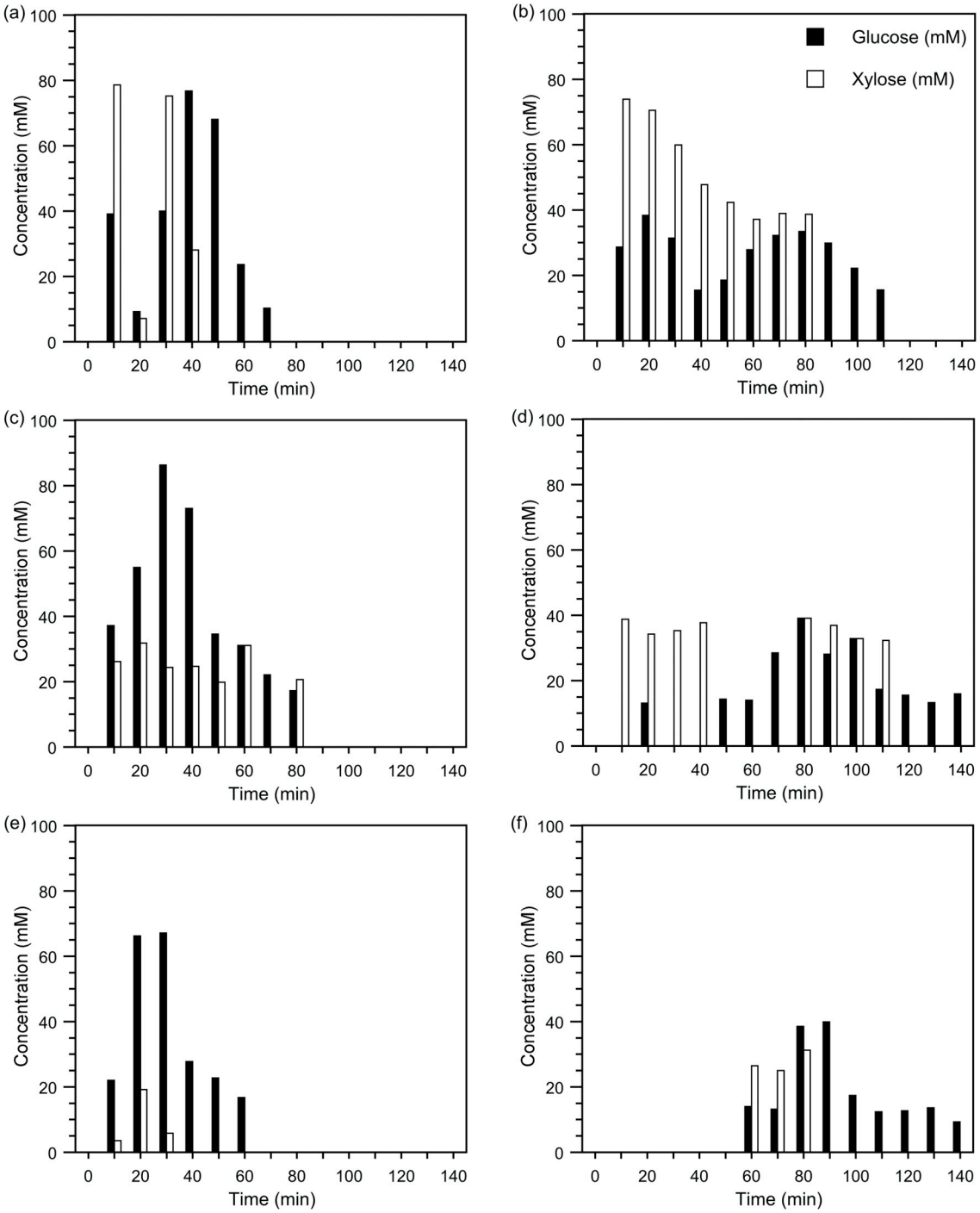

Fig. 3. Production of glucose and xylose from agricultural residues using H_2SO_4 in an 80 wt% GVL and 20 wt% H_2O mixture feed with a flow of 1 mL/min and 21 bar He and heated at 0.5 K/min. Results for (a) sugar cane bagasse using 0.5 wt% H_2SO_4, (b) sugar cane bagasse using 0.05 wt% H_2SO_4, (c) plantain peel using 0.5 wt% H_2SO_4, (d) plantain peel using 0.05 wt% H_2SO_4, (e) brewer's spent barley using 0.5 wt% H_2SO_4, and (f) brewer's spent barley using 0.05 wt% H_2SO_4.

degradation due to a limitation in the access of the acid to the covered cellulose. A more detailed study is required to test this hypothesis.

2.2.2. *Effect of the H_2SO_4 concentration on sugars production*

The catalytic fractionation of SCB, PP and BSB using two H_2SO_4 concentrations (0.50 and 0.05 wt%) was evaluated using 1 mL/min 80:20 wt% GVL:H_2O and a heating rate of 0.5 K/min. Fig. 3 shows the resultant glucose and xylose concentrations obtained after biomass fractionation as a function of reaction time. From this figure, we can compare the effect of sulfuric acid concentration on biomass fractionation with a heating rate of 0.5 K/min. Fig. 3a, c and e show the results obtained for biomass fractionation using 0.5 wt% H_2SO_4. While Fig. 3b, d and f show the results obtained using 0.05 wt%. The fractionation of 2.5 g of each residue was faster with a high concentration of sulfuric acid. The reaction time is reduced by almost half of the time required to convert the biomass to sugars using 0.05 wt% H_2SO_4. The product distributions over time are different for each residue and acid concentration. From Fig. 3 we can observe that the xylose and glucose concentrations reach a maximum at different times. Moreover, the highest concentration obtained for glucose occurs after the highest concentration for xylose as expected. Also, the concentration of xylose tends to zero before that of glucose. As expected, cellulose is hydrolyzed

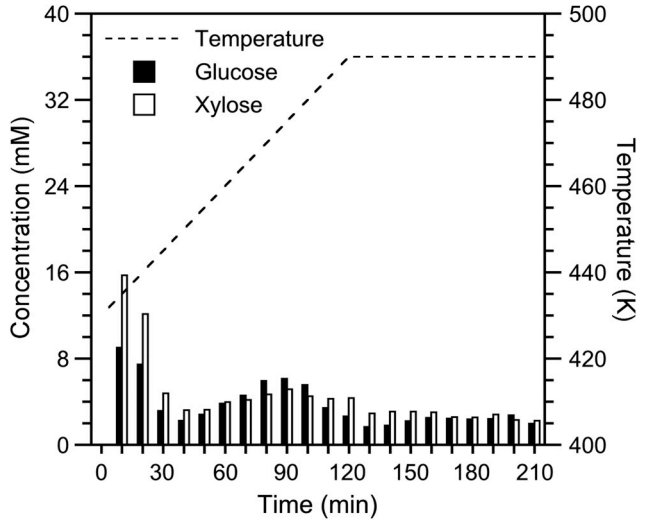

Fig. 4. Production of glucose and xylose from plantain peel using 0.05 wt% H_2SO_4 in an 80 wt% GVL and 20 wt% H_2O mixture feed with a flow of 1 mL/min and 21 bar He, heated from 430 to 490 K at 5 K/min and kept at 490 K for an additional 90 min.

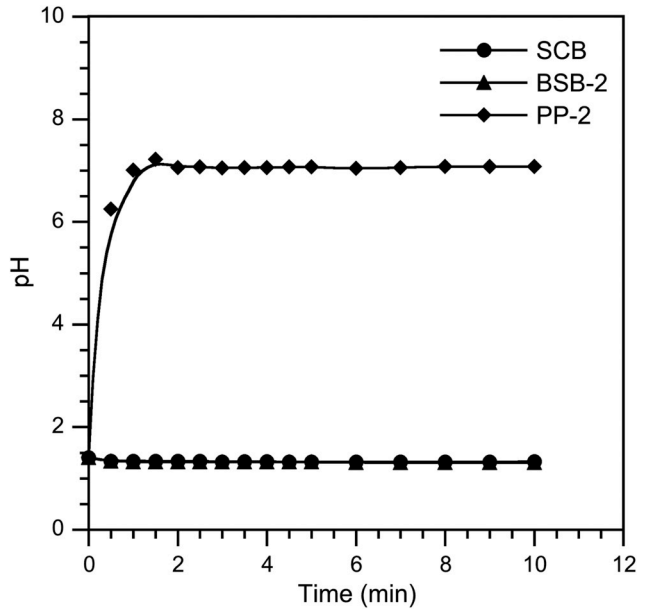

Fig. 5. Change in pH by exposing a solution of 0.05 wt% H_2SO_4 in 80 wt% GVL and 20 wt% H_2O to biomass ashes at room temperature.

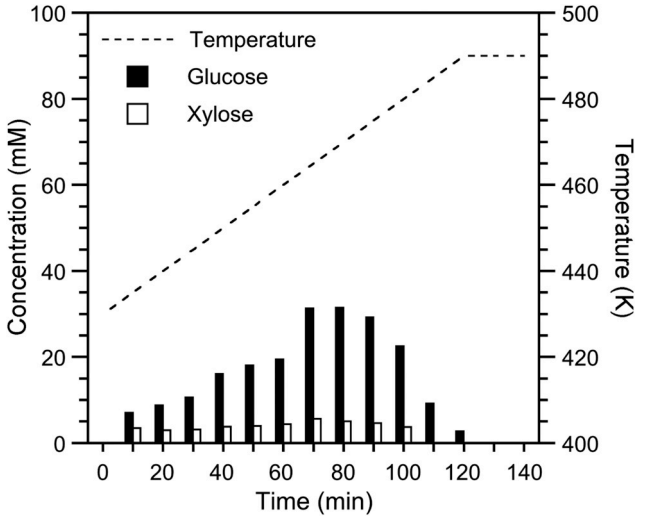

Fig. 6. Production of glucose and xylose from microcrystalline cellulose using 0.05 wt% H_2SO_4 in an 80 wt% GVL and 20 wt% H_2O mixture feed with a flow of 1 mL/min and 21 bar He while heated at 5 K/min.

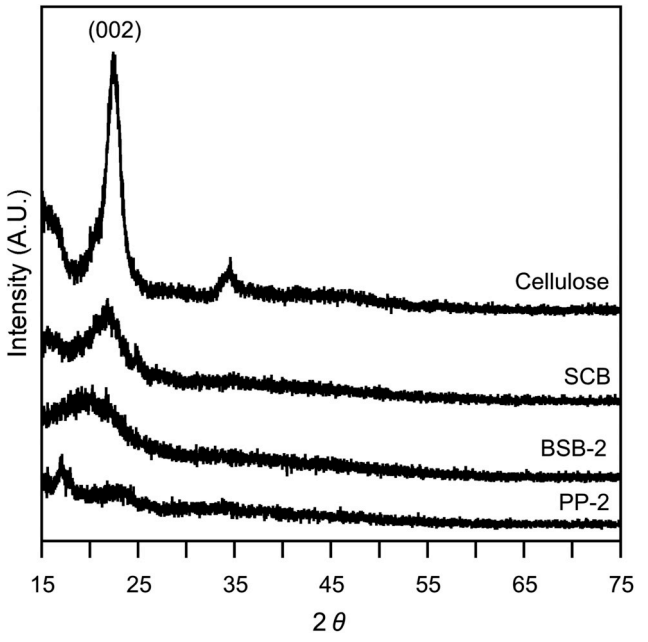

Fig. 7. XRD diffraction patterns for dried agricultural residues and microcrystalline cellulose.

at a higher temperature than hemicellulose. This is because the energy required to break the glucan bonds to produce glucose is higher than the energy needed to break the xylan bonds to produce xylose. The acid concentration and the temperature have a strong impact on the different reaction rates, altering the product distributions [42].

From Fig. 3b, d and f we can observe that when using 0.05 wt% H_2SO_4 the concentration distributions for glucose and xylose reach two maxima for SCB and PP. This behavior may be attributed to the presence of different xylan and glucan types in each sample. The glucan and xylan may be classified in two fractions, easy-to-hydrolyze and hard-to-hydrolyze [42–45]. The easy-to-hydrolyze fractions need a lower energy or temperature to hydrolyze than the hard-to-hydrolyze. The sugars concentrations obtained for reactions times of 60 min and lower are higher for bagasse followed by plantain peel. This suggests that the content of easy-to-hydrolyze xylan and glucan present in bagasse is higher compared to plantain peel and BSB.

Table 1 shows the sugars yields obtained for each residue after reaction using 0.05 and 0.50 wt% H_2SO_4. The xylose yields for all the samples studied decrease when the concentration of H_2SO_4 is high (0.50 wt%). The reduction in the xylose yields may be attributed to the decomposition of xylose into furfural and furan resins in the presence of sulfuric acid [42,46–48]. However, we did not detect furfural in the fractionation products. Hence, the furfural that may be formed during the reaction is at concentrations so low that cannot be detected with our analytical method or the furfural produced is converted to degradation products such as humins during the reaction. The yield obtained for glucose (37%) after the fractionation of sugar cane bagasse is lower using 0.50 wt% H_2SO_4 compared to that obtained using 0.05 wt% (41%). On the other hand, the glucose yield obtained from BSB-1 is lower when a low concentration of H_2SO_4 was used while the xylose yield is higher. Moreover, for BSB-1 no sugars production was observed during the first 50 min of reaction using 0.05 wt% H_2SO_4. A possible

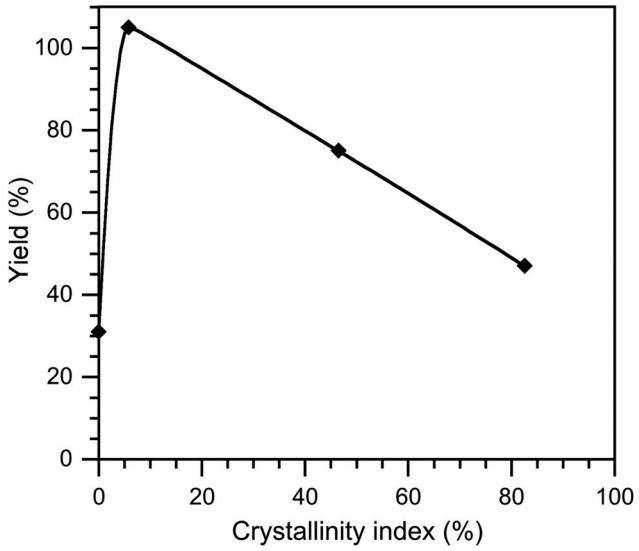

Fig. 8. Effect of the crystallinity index on the sugars yield obtained for agricultural residues and cellulose fractionation using 0.05 wt% H_2SO_4 in an 80:20 wt% GVL:H_2O mixture and a heating ramp of 0.5 K/min.

explanation for these observations is that depending on the type of residue studied the structural properties of the cell wall and lignin arrangement can affect the production of sugars from cellulose and hemicellulose. The lignin composition in BSB-1 is higher than in SCB. Lignin is a polymer that serves as support in plants and its part of the plant cell wall in which the cellulose and hemicellulose are contained [49]. The hemicellulose is normally covering the cellulose, while lignin covers or is between hemicellulose and cellulose channels. The lignin may be also cross linked with hemicellulose in the cell wall retarding the hemicellulose fractionation [50]. Hence, we speculate that at 0.05 wt% H_2SO_4 the removal of lignin and the fractionation of hemicellulose in BSB-1 occurs with lower rates and cellulose is exposed to heat for longer times promoting its degradation. Using a high concentration of H_2SO_4 (0.50 wt%) promotes a quick release of the lignin and conversion of hemicellulose and cellulose. Hence, the yields obtained for glucose are higher at these conditions, but this affects the xylose production that is sensitive to acid concentration and temperature [42,46].

The sugars yield obtained for PP-1 decreases by reducing the H_2SO_4 concentration from 0.50 to 0.05 wt%, as shown in Table 1. Fig. 3d shows the glucose and xylose concentration obtained as a function of time during the conversion of PP-1 using 0.05 wt% H_2SO_4. For 140 min of reaction the biomass was not completely fractionated. Hence, the catalytic fractionation of plantain peel was repeated increasing the reaction time to 210 min using a new batch of peel (PP-2), as shown in Fig. 4. The heating protocol was the same for the other samples, using a heating ramp of 0.5 K/min, but the time that the sample was maintained at 490 K was extended. We observed that there is production of sugars at 210 min of reaction and apparently, the PP-2 was not completely consumed by increasing the reaction to that time. Both plantain and banana peels are rich in minerals such as potassium and sodium [51]. The potassium composition in plantain peels is around 37 g per kg [40]. The content of ashes in plantain peel is higher than in SCB and BSB, as shown in Fig. 1. We believe that the potassium and sodium in the plantain peel are oxidized into basic metal oxides that can neutralize the acid catalyst. To test our theory we did an experiment in which the ashes of the biomass were exposed to the same solution used during the deconstruction, 0.05 wt% H_2SO_4 80:20 wt% GVL:H_2O, at room temperature under stirring. Fig. 5 shows the pH of the reaction mixture as a function of time during the exposure of the biomass ashes to the solution. The pH for the suspension containing the bagasse and

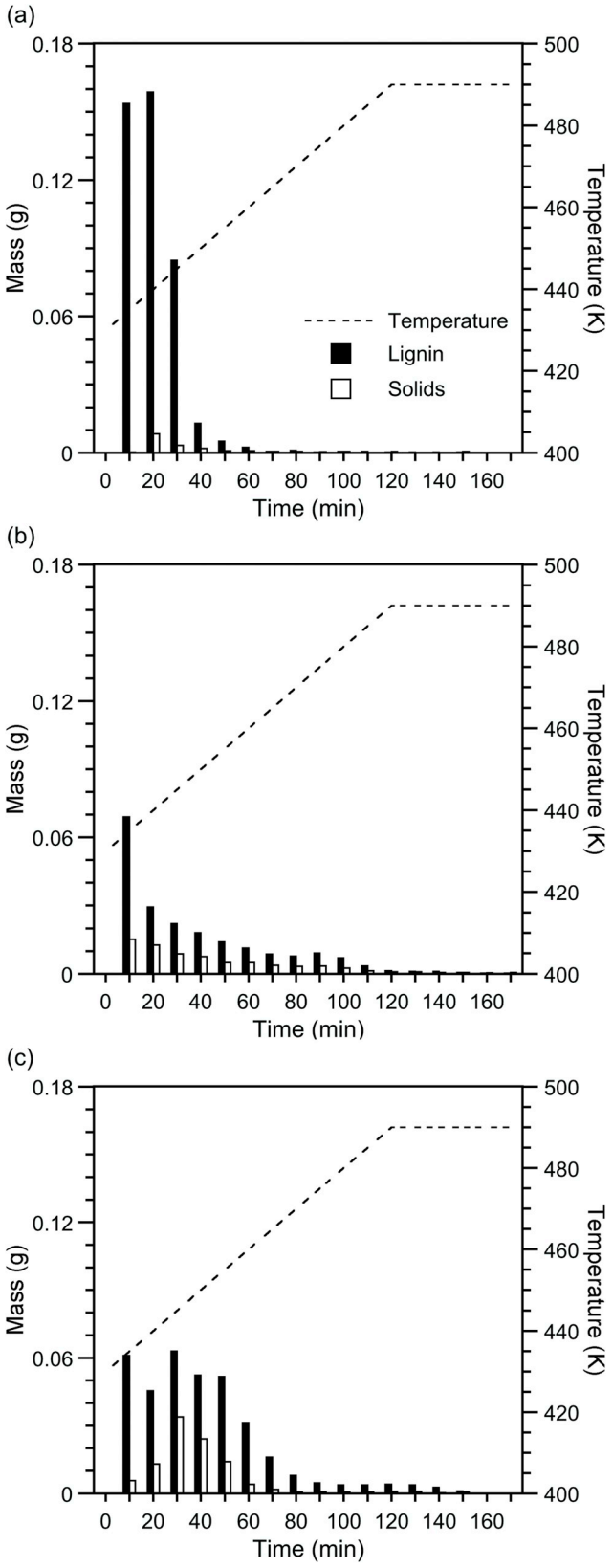

Fig. 9. Lignin recovery from residues fractionation for (a) SCB, (b) PP-2 and (c) BSB-2 using 0.05 wt% H_2SO_4 in an 80 wt% GVL and 20 wt% H_2O mixture feed with a flow of 1 mL/min and 21 bar He. The samples were heated from 430 to 490 K with a ramp of 5 K/min and kept at 490 K for an additional 90 min.

BSB-2 ashes remains almost constant after 10 min while the pH for the plantain peel increases to 7.0 after 1 min, neutralizing the acid. These results show that the ashes present in the plantain peel neutralize the acid during the reaction causing a reduction in the acid proton availability and reducing the rate of sugars production. However, using 0.5 wt% H_2SO_4 the sugars yield was 94% mitigating the effect of the ashes in the production of sugars. These results demonstrated that the inorganic content affects the biomass fractionation by neutralizing part of the acid catalysts but increasing the acid catalyst concentration reduces this effect.

2.2.3. Effect of biomass crystallinity on the production of sugars

The effect of the biomass crystallinity on the sugars production was evaluated by comparing the cumulative sugars yield obtained from each residue fractionation using 0.05 wt% H_2SO_4. The biomass crystallinity is mainly attributed to the cellulose crystallinity [50]. Hence, we also compared the fractionation of commercial microcrystalline cellulose under the same experimental conditions. Fig. 6 shows the glucose and xylose production from microcrystalline cellulose. The production of xylose during the conversion of microcrystalline cellulose indicates that this cellulose has a small amount of hemicellulose that was converted to xylose. The maximum production of glucose was observed around 70 min of reaction at a temperature of 465 K, like the time at which the maximum production of glucose was obtained for the agricultural residues studied here. The cumulative yield towards glucose was 39%and 6% for xylose. We believe that the low sugar production is mainly attributed to the high cellulose crystallinity.

Fig. 7 shows the XRD patterns for bagasse, BSB-2, PP-2, and microcrystalline cellulose. The crystallinity of the samples is significantly different. The most crystalline agricultural residue is bagasse, which has a crystallinity index of 46%. The less crystalline residue is PP-2 that is essentially amorphous with a crystallinity index of 0%. Microcrystalline cellulose and BSB-2 have crystallinity indexes of 83% and 6%, respectively. Fig. 8 shows the cumulative sugar yield as a function of the biomass crystallinity index. It is observed that as the crystallinity index increases the cumulative sugars yield decreases except for the crystallinity index of 0% that corresponds to PP-2. The PP-2 sample has high ashes content with a strong alkaline character that neutralizes the acid catalyst, reducing the sugars production. That effect causes the apparent different trend for PP-2 and does not contradict the theory that the crystallinity of the biomass affects the sugars production. Hence, from these results it is demonstrated that increasing the biomass crystallinity results in a decrease in sugars yield. A recommendation of our work is that decreasing the residue's crystallinity should increase the production of sugars. This can be achieved using physical or chemical treatments such as, for example, milling or acid treatment with phosphoric acid.

2.2.4. Lignin production from biomass fractionation

The insoluble lignin and other solids present in the agricultural residues were recovered by filtration of the resulting product fractions. The amount of these solids recovered is higher than the amount of ashes present in the biomass samples. Hence, we believe that these filtered solids include insoluble lignin, humins and ashes present in biomass. The soluble lignin was recovered by adding water to the reaction mixture to precipitate the lignin that was recovered by centrifugation and filtration. Fig. 9 shows the mass of solids and lignin recovered after the fractionation of SCB, PP-2 and BSB-2. The distribution with time of the lignin recovered during the reaction is different for each residue. The solids and lignin mass recovered from SCB passes through a maximum at 30 min of reaction, as shown in Fig. 9a. This behavior was also observed for BSB-2 but at a reaction time of 20 min, as shown in Fig. 9c. The solids and lignin mass recovered from PP-2 decreases from the beginning of the reaction, as shown in Fig. 9b. Most of the lignin recovered for PP-2 and bagasse were obtained during the first 30 min of reaction. For BSB-2 the time to recover most of the solids and lignin is around 60 min. This observation supports our theory that the lignin present in BSB is more difficult to remove compared to that present in the other samples and this has a significant effect on the fractionation of cellulose and hemicellulose, as explained above. Table 1 shows the cumulative lignin yields obtained for all samples studied. The lignin yield is less than 60% of the theoretical yield. For the recovery of lignin, we used 0.2 μm filters. It has been reported that the lignin particle size can range from less than 0.03 μm to over 3.5 μm [52]. Hence, we believe that our filtration method limits the lignin amount that can be recovered.

3. Conclusions

The fractionation of sugarcane bagasse, plantain peel and brewer's spent barley to glucose, xylose and lignin was studied using H_2SO_4 as catalyst in a mixture of GVL and water. The reaction conditions such as heating rate and acid catalyst concentration affect the yield and products distribution. The use of high heating rates reduces the time needed to convert the biomass to sugars, but promotes the degradation of sugars during the reaction reducing its yield. The temperature at which the maximum sugar production was observed is independent of the heating rate, but depends on the acid catalyst concentration. Using a high concentration of H_2SO_4 (0.50 wt%) reduces the time needed to fractionate the biomass but as observed for the heating rate, it also promotes the degradation of the sugars. The production of glucose and xylose from biomass is affected by the physicochemical properties of the biomass such as composition and structure. We found that alkaline species present in the ashes promote the neutralization of acid catalyst reducing the rate of sugar production. The content of lignin affects the biomass fractionation by reducing the accessibility to the hemicellulose and cellulose during the reaction. Limiting the access to cellulose and hemicellulose results in its thermal degradation affecting its conversion to sugars. The sugars yield is affected by the biomass crystallinity, an increase in the biomass crystallinity results in a reduction in the sugars yield obtained. We demonstrated that the physicochemical properties of the agricultural residue have an important role in its conversion to sugars.

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