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Direct cost-efficient hydrothermal conversion of Amazonian lignocellulosic biomass residue

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Abstract

The transformation of non-edible lignocellulosic biomass into high-added-value chemicals and biofuels associated with lower energy process requirements is a promising strategy for meeting the actual demands of clean energy. Here, we report the study of the non-catalytic conversion of biomass wastes issued from two Amazonian abundant fruits (Cupuaçu shell and Assai stone) into liquid valuable chemicals. The parent biomass samples were first comprehensively characterized using TG, XRD and FTIR, then they were pretreated by ball milling and by chemical processing in ionic liquid, and finally they were hydrothermally treated for them to be converted into chemical products benefiting from their hemicellulose and cellulose contents. The results revealed the importance of the pretreatments in the conversion rate while the selectivity into main chemical products (such glucose, HFM, furfural, xylose) is not affected by the pretreatments neither physical nor chemical ones. The conversion of both biomasses and their products' distribution were comprehensively discussed, with the highest conversion obtained using Assai stone biomass (90%). This study could pave the way for investigating the non-catalytic route of biomass conversion, as a lesser energy process, resulting in a cost-effective conversion process.

Keywords: Biomass conversion; Amazonian fruits; Non-catalytic route; Non-pretreatment process; Cost-effective process.

1. Introduction

The competitive production of renewable chemicals and biofuels in front of fossil fuels-derived products has recently been widely accepted by society [1–5]. It is a parallel solution for energy supply aimed to reduce the dependence on petroleum feedstock that involves more sustainable and green methods to obtain fuels and chemicals [6]. The second generation of biofuels, derived from non-edible biomass, significantly contributes to avoiding disagreeable conflicts arising from the competitive social needs in food and energy (i.e., fuel) [7]. Non-edible biomass is mainly lignocellulosic biomass and consists of hemicellulose, cellulose, and lignin [8]. Recently, fruit waste biomasses have been valorized in terms of biofuel production [9, 10]. Amazonian fruits like Assai and Cupuaçu are very abundant local fruits in the northern region of South America. In Brazil, Para state, the Cupuaçu fruit is used not only as food, but also in conventional medicinal drugs and cosmetics, with an annual production of about 28 kt in 2018 [11], generating a huge quantity of the husk and seed wastes (~30% of the fruit load). The Assai palm (*Euterpe oleracea* Mart.) presents a large-scale consumption in the same region and produces a thousand tons of waste (estimations of 2018: about 220 kt of acai palm were consumed, which represents approximately 176 kt of acai seeds (80% residue from the total processed fruit in Northern Brazil)) [12, 13]. Many processes were used to upgrade it to high added-value chemicals [14, 15], i.e., pyrolysis to obtain bio-oil [16], gasification to produce syngas [17], fermentation for bio-ethanol production [18], etc. Biomass liquefaction with water is a process that can be integrated in the future, under optimized conditions, for the simultaneous production of fuel additives and valuable chemicals [19]. It is considered an advantageous process owing not only to its low cost and pollution-free, but also to its facility and recycling abilities [20, 21].

Many studies have focused on reducing costs and finding easy and beneficial ways for improving biomass conversion [22, 23]. In certain situations, non-catalytic hydrothermal processes have some advantages over catalytic processes (i.e., the non-catalytic processes are generally more cost-effective than the catalytic processes due to several reasons: the catalytic processes require the use of a catalyst material, which can be expensive to produce, maintain, and replace over time. Also, they often require more complex equipment and higher levels of expertise to operate, leading to higher labor costs.

However, the comparison of the results from non-catalytic hydrothermal conversion of biomass with catalytic ones [24, 25], and the fact that catalytic and non-catalytic procedures lead to different products have encouraged, and even forced, when a desired final product is only obtained via catalytic routes, many research groups to focus on the catalytic reactions for their biomass conversion studies [22, 26–28].

In the present work, we have investigated the conversion of two Amazonian biomasses (Assai Stone and Cupuaçu Shell) through a one-pot non-catalytic reaction to transform them into liquid carbohydrates, that in turn can be converted into biofuel products, thus associated with lower energy process requirements. The non-catalytic conversion of used biomass samples has shown promising efficiency, with low-cost processing.

2. Materials and methods

The two biomasses used in this study are the Assai stones and the Cupuaçu shell from the Brazilian part of Amazonian forests, and they will be referred to as AS and CS, respectively. The two samples were preliminarily crushed to facilitate their manipulation. Then, both samples were submitted to a ball-milling (BM) pretreatment, and also to an ionic liquid (IL) pretreatment to weaken their rigid structure and to minimize the original crystallinity for providing more accessibility and more reactivity during the reaction [29–31].

2.1. Ball milling pre-treatment

The treatment was carried out using a planetary ball mill PM 200 Restch, a weight ratio agate balls/cellulose of 3, at 500 rpm for 7 hours, with reverse rotation every 60 min. It must be mentioned that the AS biomass was difficult to mill since the resulting powders seemed to present a larger particle size than milled CS.

2.2. Ionic liquid pre-treatment

The ionic liquid (IL) pretreatment was performed over both AS and CS biomasses to make simpler and weaker the biomasses' rigid structure. The treatment mainly produces the removal of lignin from these lignocellulosic biomasses [32–36]. For this purpose, as a primary test, the samples were treated at 105 °C with 1-ethyl-3-methylimidazolium acetate (5 wt.% of the biomass sample in IL). The CS sample needed about 6 hours to be dissolved, while only 2 hours were required for the AS. Once dissolved, each sample was precipitated with water, and the regenerated biomass (solid) was collected by filtration and washed with water to eliminate the remaining IL residues. Finally, the samples were dried at 80°C for 4 hours [37]. The recovered biomass in weight percentage was 32% for CS and 42% for AS. The aspect of the IL-pretreated samples, shows the IL-treated samples having a less dense structure than the original ones.

2.3. Characterizations of studied biomasses

The biomass samples were characterized by Thermogravimetry (TG), X-ray Diffraction (XRD), Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIRS) and Scanning Electronic Microscopy (SEM). For the TG measurements about 10 mg sample of the crushed biomass were heated at 5 °C/min in N₂ flow (100 ml/min) up to 950 °C, using the thermobalance TG SDT Q600 (TA Instruments). The measured mass loss is attributed to the decomposition of the different components of the raw biomass (cellulose, hemicellulose and lignin). The dTG profile is very useful to estimate the relative proportion of these components, because they present a different rate of weight loss in different temperature ranges. Deconvolution of dTG profiles (by multi-Gaussian function (with Origin software)) was used to determine the relative percentage of cellulose, hemicellulose and lignin according to the method proposed by Cozzani et al. [38], used and proved also in other studies [39, 40]. The XRD measurements were done using the Miniflex II Rigaku equipment using a Cu K α ($\lambda=0.154056$ nm) radiation source and operated at 30 kV and 15 mA, with a scanning rate of 2°/min in the 2 θ range of 6-80° under ambient conditions. ATR-FTIRS data were obtained in a Bruker spectrometer, model TENSOR 27, in the range of 4000–600 cm⁻¹ by accumulating 32 scans at a resolution of 4 cm⁻¹. The morphology and the elemental composition were investigated by SEM-EDS using the equipment VEGA3- TESCLAN ANALYTICS, Fuveau, França, equipped with an Oxford micro-analysis

system, model AZTec Energy X-act with 129 eV resolution. The samples were coated with a thin conductive layer of gold and analyzed at 30 kV working voltage.

2.4. Biomass conversion

The hydrothermal transformation of the biomass samples was carried out in a high-pressure stainless-steel reactor with a Teflon recipient inside, in the following conditions: 500 mg biomass, 25 ml water, 190 °C, and 3h. After the reaction, the solid and liquid phases were separated by filtration. The solid was dried and weighed to calculate the biomass conversion, and the liquid phase was analyzed by high-performance liquid chromatography (HPLC 1260 Infinity) to calculate the yield.

Biomass conversion (X) is calculated as indicated in equation (1):

$$X = ((\text{weight of charged biomass} - \text{weight of unreacted biomass}) / \text{weight of charged biomass}) \times 100 \quad (1)$$

The yield of different products found in the solution has been calculated as shown in equation (2).

$$\text{Yield (A)} = ([A] / (C_{\text{cellulose}} + C_{\text{Hemicellulose}})) \times 100 \quad (2)$$

Where $[A]$ is the concentration of product A determined by HPLC, while $C_{\text{Cellulose}}$, and $C_{\text{Hemicellulose}}$ are, respectively, the concentration of cellulose and hemicellulose (in g per liter of water in the reactor) estimated from the biomass composition determined by TG analysis, as explained in section 3.1.

3. Results and discussions

3.1. TG analysis

Fig. 1 presents, respectively, the obtained TG and dTG profiles obtained for the two biomasses. The TG data show that the weight loss of both fruit waste biomasses, CS and AS, is similar and close to 75 % when the temperature reaches 900°C. The whole mass loss corresponds to the humidity and the decomposition of: i) so-called “extractives” or compounds of low-temperature volatility and degradation, like: tannins, terpenes, resins, oils, and waxes that account usually around 4-8 wt.%; ii) hemicellulose; iii) cellulose; and iv) lignin. The remaining mass corresponds to residues and ashes, as previously reported [38, 40].

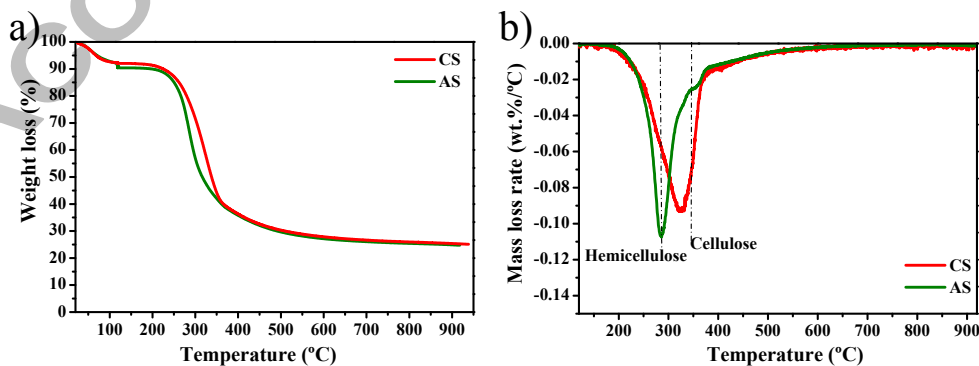


Figure 1. TG (a) and dTG (b) profiles obtained for the biomass samples.

The method proposed by Cozzani et al. [38] consists in using the dTG data obtained for samples of cellulose, lignin, and xylan (as a substitute material for hemicellulose) to fit the experimental dTG curve of certain biomass. It is a TG-weighted sum method, in which the fractions of macro-components were estimated using a mathematical method through the coefficients required to fit the experimental curve. Moreover, H. Yang et al.[39] reported independent TG and dTG curves of the three components. Taking into account the reported information by Cozzani et al. and Yang et al. [38, 39], in the present work the dTG profiles obtained for both biomasses (Fig. 1) were deconvoluted to estimate the proportion of each macrocomponent present in the samples. The deconvolution (shown in Fig. 2) has been carried out based on the temperature intervals of weight losses and the temperature at the maximum weight loss rate reported in the literature [38, 39].

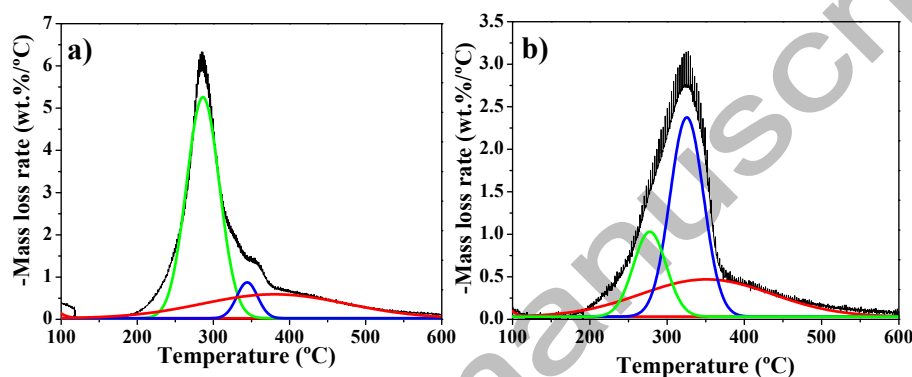


Figure 2. dTG curves and their deconvolution for a) CS and b) AS. Green-hemicellulose; Blue-cellulose and Red-lignin.

The approximated percentage of cellulose, hemicellulose and lignin in the studied biomasses has been calculated based on the deconvoluted peaks shown in Fig. 2. The obtained data values are presented in Table 1.

Table 1. Macrocomponent composition of the two studied biomasses (estimated with an error in the range of 2-3%).

Sample	Hemicellulose (%)	Cellulose (%)	Lignin
<i>Cupuaçu shell (CS)</i>	19	47	34
<i>Assai stone (AS)</i>	63	7	30

It can be observed that the composition of both wastes is quite different. In sample CS the percentage of cellulose is the highest, 47%, followed by lignin and hemicellulose. However, in AS the cellulose content is very low compared to its high hemicellulose one. The different compositions of the biomasses will be taken into consideration to explain their different reactivity and the distribution of products obtained from them in the catalytic conversion process. Besides, the calculated percentages of cellulose and hemicellulose in each biomass will also be used to determine the yield of different products based on them. A correlation between the lignin content and the conversion of biomass residues was demonstrated in several studies from the literature [41], and allows a comparative factor for biomass conversion results. Thus, the chemical composition data provided by TG and dTG could contribute well to understanding the influence of the composition properties on the conversion of biomass.

3.2. XRD characterization

3.2.1. Ball milled biomass

The studied biomass samples were pretreated physically by the ball milling (BM) process as described in section 2.1, and the raw and milled biomasses were analyzed by XRD. Fig.3 shows the obtained XRD diffractograms.

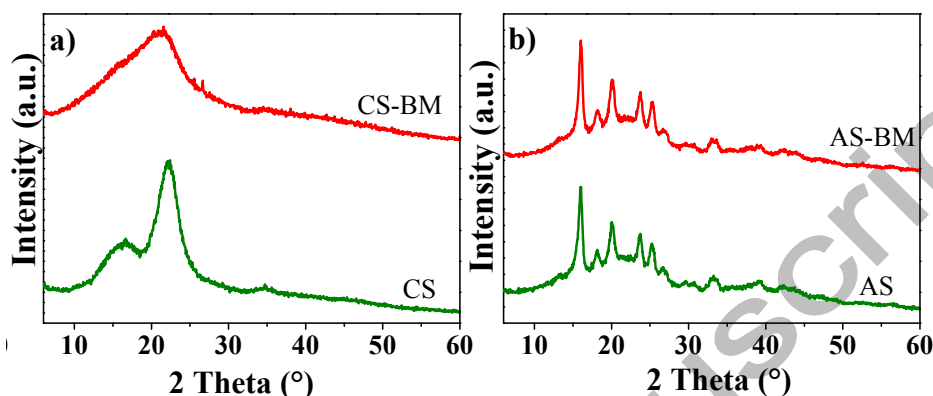


Figure 3. XRD data of the biomasses a) CS and b) AS after and before the ball milling pretreatment (BM means ball-milled sample).

The results of Fig. 3 indicate that the crystallinity of the CS biomass decreased after the ball-milling treatment. However, no remarkable change was observed in the XRD patterns of sample AS-BM compared to AS, meaning that the Assai stones have a very strong structure, difficult to be milled (even after a long-time milling process of 24 hours, no change in its structure occurs). The rigidity of the biomass is among the important factors influencing the liquefaction reaction, highlighting that the composition of each biomass can affect the dissociation of molecule's bonds in water solvent. Accordingly, those factors can significantly influence the biomass conversion rate.

3.2.2. Ionic liquid treated biomass

Since the rigid structure of the AS biomass was maintained even after the hardball milling pretreatment, it was necessary to assay another type of treatment to degrade it. Thus, both CS and AS biomasses were treated with ionic liquid (IL), as indicated in section 2.2. Fig. 4 shows the X-ray diffraction profiles of the IL-treated AS and CS samples, comparing the results obtained with those of the ball-milled and untreated samples

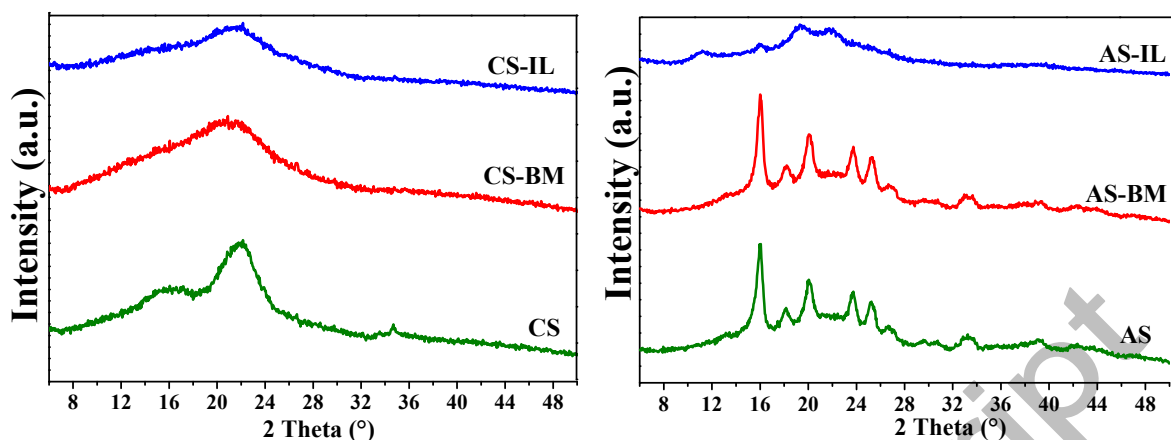


Figure 4. XRD profiles for a) CS and b) AS biomasses, IL pretreated, ball milled and in raw form.

The obtained results show that the crystallinity of CS decreased by the IL pretreatment, similar to ball milling. In contrast, IL pretreatment over AS biomass was efficient to decrease its crystallinity. Thus, although there are also some challenges associated with ionic liquid pretreatment, including the high cost of the ionic liquids and their potential toxicity and/or environmental impacts, the IL pretreatment can be a suitable pre-treatment for achieving a high biomass conversion.

3.3. FTIR analysis

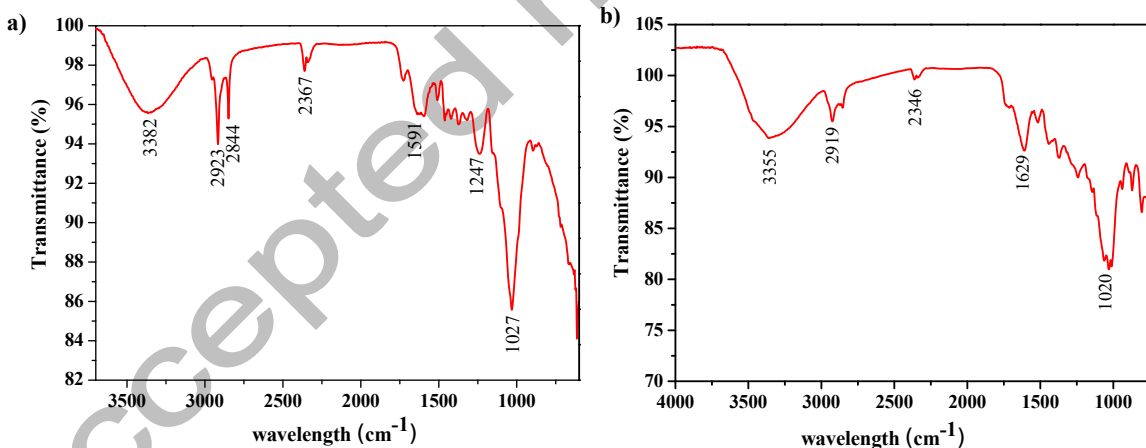


Figure 5. FTIR spectrum for row biomass; a) CS and b) AS

The molecular structure and chemical bond interactions of CS and AS have been investigated using infrared spectroscopy. The FTIR spectra for these samples are presented in Figs. 5a and b, and showed an increase in the intensity at 3400 cm^{-1} , a typical absorption band of (OH). Bands located in the region of 2924 cm^{-1} and 2853 cm^{-1} were attributed to the C-H stretches and to its aromatic ring vibration in the lignin structure. The absorption bands at 1591 and 1629 cm^{-1} correspond to the C=C stretching of aromatic skeletal compounds in lignin and extractives. The peak around 1247 cm^{-1} corresponds to C-O and O-H stretching in polysaccharides. Bands at 1020 cm^{-1} can be related to the C-H deformation in cellulose and C-O stretching in polysaccharides [42, 43]. The presence of several

functional groups and their acidity favor the solubility of biomass extracts in water and biomass wettability. In line with TG analysis (Table 1), the spectrum of CS in Fig. 5a showed high absorption peaks 1027, 1247 and 1591 cm^{-1} (related to cellulose) [44] compared with AS in Fig.5b. Similarly, peaks associated to hemicellulose, those located at 1629 and 1700 cm^{-1} [45, 46], confirm the higher hemicellulose content in the AS sample (see TG results in Table 1). This information is very useful for a good knowledge on the physico-chemical properties of the CS and AS biomasses and would be helpful to better understand their behavior in the hydrolysis process.

3.4. SEM analysis

The studied row biomasses were analyzed using the microscopy technique of SEM. A well-ordered and flat structure, with a well-defined cell wall, is observed for the CS biomass (Figs.6 (a-c)).

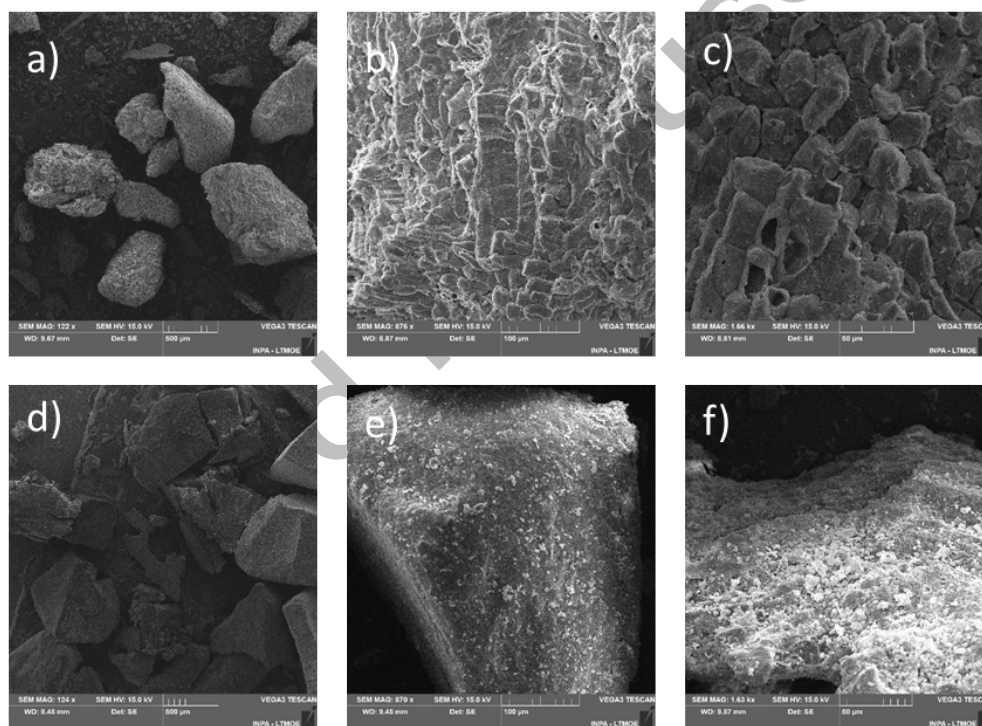


Figure 6. SEM images of CS sample (a-c), and AS sample (d-f).

Fig. 6d with image magnification of 124x shows the cross-sectional image of the endocarp (AS), containing microfibrils in concentric polygonal shapes. With a higher image resolution of 870x (Fig.6e) it is noticeable that the endocarp has a porous texture. Fig.6f represents the fiber compactly covering the kernel, and it should be recalled that most of the fruit stone is formed by endocarp [47]. Thus, the presence of a porous structure will likely help the good accessibility of the solvent to the biomass surface and facilitate its degradation.

3.5. Hydrothermal reactions

The hydrothermal treatment was carried out in the original, ball-milled and IL-treated biomass samples. Figure 7 illustrates the achieved biomass conversion and yield of C₆ (ethylene glycol and polyethylene glycol), C₅ (pentose, xylose, xylitol and furfural) and C₂ (ethylene glycol and polyethylene glycol) products determined for each studied substrate. The obtained results show that although the AS biomass is harder to mill, its conversion under reaction conditions is higher than that of CS samples. The obtained yields of the identified products were calculated based on the amount of cellulose and hemicellulose. Here, it can be noted that the product distribution from both biomasses is different, with furfural, glucose and HMF being the main identified products. The formation of the main products can be explained as follows: glucose is produced from cellulose hydrolysis [48], xylose from the hemicellulose degradation [49], furfural generally results from xylose [50], and HMF can be produced from both sugars [51]. Also, several unidentified oligosaccharide products were detected. The detailed yield results of each compound are illustrated in Table S1 (see SM).

As shown in Fig. 6, obtained C₆ mainly corresponds to hexoses including sorbitol, mannitol, glucose and hydroxymethylfurfural. C₅ includes pentose, xylose, xylitol and furfural. C₂ is the representative of ethylene glycol and polyethylene glycol molecules.

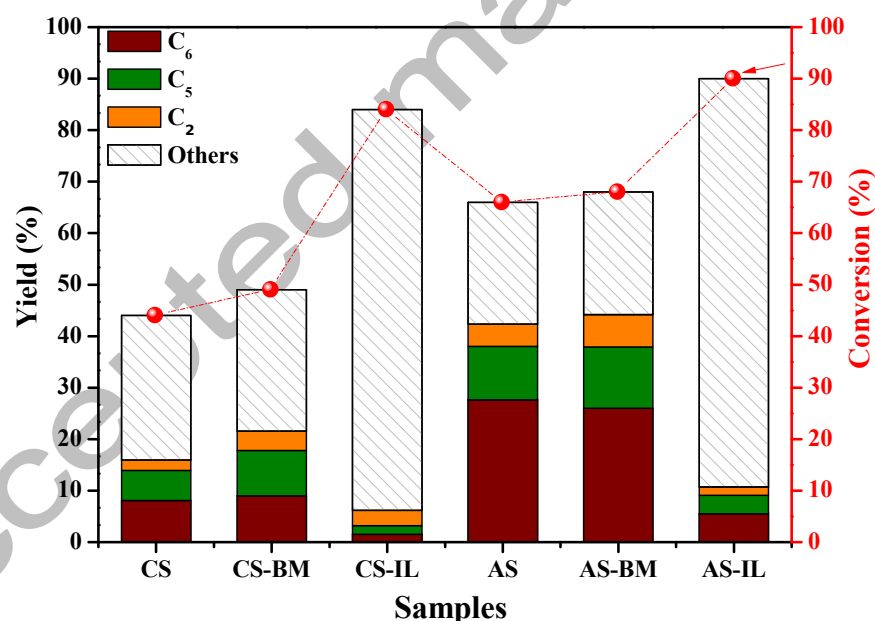


Figure 7. Yield and conversion results of biomass samples before and after pretreatments

Fig. 7 indicates that the pristine biomass conversion results into CS conversion of 44% and AS conversion of 66%. Regarding the effect of the pretreatments, data in Fig. 7 show that ball-milling produces a slight increase in biomass conversion comparing to the pristine biomass (up to 50% in CS and 68% in AS), but no significant modification in terms of the products' distribution was detected for both biomasses. Comparing both biomass, pristine and BM-treated AS give higher yield values than their counterparts CS samples, especially toward C₆ products, about 27%,

and higher conversion values of 68%, compared to 9% and 49%, respectively. Furthermore, the pretreatment with IL over CS and AS samples leads to a significant increase in conversion (up to 90% and 84%, respectively), which corresponds to the important crystallinity reduction, as revealed by the XRD data (Fig.4). However, the yield of identified products is much lower than in the case of the pristine and ball-milled samples, and a large number of unidentified oligomers products are formed.

In general, the pretreatment of the biomass samples improved their reactivity. After the ball milling treatment, the conversion of biomasses slightly increased because of a reduction of the cellulose crystallinity (as shown by the XRD profiles) and the partial removal of lignin. The conversion was even higher after the ionic liquid pretreatment, which makes the rigid lignocellulosic structure easy to degrade during the reaction (the biomass structure was quite amorphous according to XRD results). Here, it is worth mentioning that a direct established relation was found between the crystallinity of the biomasses and their conversion.

The high reactivity of AS compared to the CS samples, in both raw (pristine biomass) and pretreated biomass cases, was linked to the important quantities of hemicellulose revealed by DTG curves, confirmed by the FTIR high-intensity absorption peak at 1630 cm^{-1} (spectrum Fig.5b) [46, 52]. On another hand, the poor stability of hemicellulose in biomass samples was also reported by Yao et al. [53] in their tracked in-situ studies of lignocellulosic biomasses pyrolysis, which may equally explain in our study case the high conversion for raw biomass and also after ball-milling treatment.

In addition, regarding the detailed results obtained for each specified product yield (see Table S1 from supplementary material) we reveal that assai stone in both forms AS and AS-BM about 26 and 25 % of HMF were obtained which makes this biomass waste feedstock promising comparing to other studies, In the literature, we can cite the review work of Yu I. et Al. which reported the highest yield of HMF (18 %) from pinewood feedstock for the non-catalytic reaction using a salt bath [54]. Cai X. et Al reported in their last review that the conversion of chitin into HMF yielded 19 % using a catalytic process [55] it is important to note that most previous studies were based on glucose, fructose, and chitosan as simple polysaccharide to produce HMF where most reactions are based on catalytic way [56]

In this study, the use of ball milling pretreatment was not very efficient for biomass conversion and the products' yield distribution were similar to those obtained for the untreated samples, which could be related to the high lignin content in our biomass samples, the presence of lignin can hinder the conversion. The ball milling pretreatment mainly impacts the size and accessibility of the cellulose and hemicellulose fractions, and may not successfully target the lignin fraction [57, 58], presents in high content in our biomass samples. However, the use of IL allows the conversion of cellulose and hemicellulose by hydrolysis reaction without the use of any catalysts, converting simple sugars into valuable chemicals. The Assai stone shows good reactivity with water solvent even before any pretreatment.

4. Conclusion

Waste biomass samples (AS and CS samples) have been studied as substrates of conversion reactions to obtain high-added value chemicals. The proportion of the macrocomponents in each biomass has been determined by TG

and dTG data. Ball milling and ionic liquid pretreatments have been used and compared in attempts to weaken the macrocomponents structure of the biomasses as well as to facilitate their conversions in hydrothermal reactions. The pristine non-pretreated biomass gives approximately similar yields of C₆, C₅ and C₂ compared to the pretreated ones. The ball-milling treatment promoted a slight increase in the conversion, while the IL treatment was very effective and conversion was quite high (about 90%) although the yield of the interesting products decreased. Biomass AS gives the best results, pointing out a 66% conversion without any pretreatment. This makes Assai stone a promising Amazonian residue to be converted into high-added value products in the bio-refineries concept. The hydrothermal process used in this study for the liquefaction of such biomass wastes is promising as a green and economical route that could be further developed to increase selectivity into the desired products.

Acknowledgments

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Ethical Approval

No applicable.

Competing interests

The authors declare no competing interests.

Authors' contributions:

F.-Z. Azar: prepare the samples, design and perform the experiments, data analysis, and write the original draft preparation; *A. El Kasmi* : revision of the manuscript and data interpretation; *O. F. Cruz Jr* : provide the raw samples, contribute in data analysis and writing; *M. Ángeles Lillo-Ródenas*: review and editing, funding acquisition, supervision; *M.C. Román-Martínez*: review and editing, funding acquisition, supervision.

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Data Availability

All data generated or analyzed during this study are included in this published article.

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