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TRANSFORMING THE LIGNIN-RICH RESIDUES OF SUGARCANE BAGASSE BIOCONVERSION INTO BIO-OIL AND BIOCHAR

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ABSTRACT

The commercial advance of cellulosic ethanol from sugarcane bagasse generates vast amounts of enzymatic hydrolysis residue (EHR). The characteristics of this residue depend on the conditions of pretreatment and enzymatic hydrolysis (e.g., severity, extent of carbohydrate conversion, alkali used in pH control, among others). This work evaluates the EHR as a pyrolysis feedstock to co-produce bio-oil and biochar, aiming to understand the peculiarities of these products generated from EHR and the possible applications to mitigate greenhouse gas (GHG) emissions. In addition to having higher yields of bio-oil and biochar than raw and pretreated biomass, biochar from EHR showed higher mechanical, chemical, and thermal stability, with a predominance of carbon forming C-C/C=C bonds. Characteristics such as lower oxygenation and slight enrichment in aromatics were observed for the EHR bio-oil. Biochar application in agriculture to mitigate GHG emissions and bio-oil application as a substitute for fossil fuel seems to be viable paths for EHR valorization.

Keywords: Pyrolysis. Biomass. Enzymatic hydrolysis. Bioprocess. GHG emissions.

1 INTRODUCTION

Sugarcane is one of the main crops produced in Brazil. The processing of sugarcane stalks in the sugar-energy sector generates bagasse as an abundant residue. In the sugarcane mills that process bagasse to produce 2G ethanol, the enzymatic hydrolysis residue (EHR)[1] is also generated. The EHR is often considered a fuel for sugarcane mills' heat and power units. However, the EHR has characteristics that could make it suitable as a substrate for biochar and bio-oil production, such as high lignin content, since most of the polymeric carbohydrate fraction was solubilized in the hydrolysis step.[2] Therefore, EHR adds further value to the biorefinery products and may help mitigate GHG emissions.[3] One significant possibility is the application of biochar in agriculture because biochar is a technology for carbon dioxide removal, and agriculture is Brazil's second-largest GHG source. Factors related to biomass pretreatment and enzymatic hydrolysis can interfere with the characteristics of the bio-oil and biochar obtained from EHR. For example, the cations from the alkali (NaOH, KOH, Ca(OH)$_2$, and others) used in pH control of the hydrolysis reaction may remain adhered to the biomass, acting as catalysts[4], as well as altering the surface of the biochar, affecting its characteristics. Therefore, this highly processed biomass has completely different characteristics from raw biomass, making it necessary to understand its peculiarities for possible applications. In this way, this study aimed to understand the characteristics of biochar and bio-oil produced from EHR and their potential uses as a strategy for mitigating GHG emissions.

2 MATERIAL & METHODS

A sugarcane mill in the state of São Paulo kindly provided sugarcane bagasse. The bagasse was pretreated by a steam explosion at 190ºC for 10 minutes in a continuous reactor (SüPR-2G, AdvanceBio) at the LNBR/CNPEM pilot plant. The slurry was centrifuged in a basket centrifuge. Hydrolysis of the pretreated slurries was conducted using two sets of tests. At first, the pretreated biomass was subjected to enzymatic hydrolysis in a 3.9 L reactor (INFORS, Labors 5 BioEtOH), with 10% solid loading, at 50°C, 80 rpm agitation, pH 5 (NaOH 1M), during 96h. Chloramphenicol (7 ppm) was added to avoid microbial interference. In the second set of tests, the pretreated biomass was hydrolyzed with the same parameters as the first set, but the alkali used to maintain pH 5 in the reactor was changed to KOH or Ca(OH)$_2$ to evaluate the influence of the different cations. The obtained EHR was dried, milled (1 mm), and pyrolyzed at 450ºC for 30 minutes, with a heating rate of 20°C/min under a nitrogen flow of 5 mL/min in a horizontal tubular reactor. *In natura* bagasse (BIN) and steam-exploded bagasse (SEB) were investigated as control samples. The biochar was characterized by Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Thermogravimetric analysis (TGA), and Raman Spectroscopy. The bio-oil was characterized by 2D Heteronuclear Single Quantum Coherence (HSQC) and [31]P Nuclear Magnetic Resonance (^{31}P NMR), Gel permeation chromatography (GPC) and Gas chromatography-mass spectrometry (GC-MS). Stability tests also evaluated biochar by crushing it with a high-energy ball mill (Emax RETSCH). The influence of the grinding time on the biochar particle size was investigated. For this purpose, 0.8 g of biochar was added to 20 mL of water in 50 mL ZrO$_2$ grinding vessels containing 71 g of 5 mm ZrO$_2$ beads. After 15, 60, and 360 minutes, the samples were removed and dried in an oven at 100°C overnight. The oxidative chemical aging process was carried out according to the protocol proposed by Cross and Sohi[5].

3   RESULTS & DISCUSSION

The percentages of carbohydrates and lignin of the feedstocks and the pyrolysis yields of bio-oil and biochar are shown in Table 1. At first, the biochar yield is affected by the lignin content in the feedstocks; as the lignin content increases, so does the biochar yield. It is also worth noting that, despite the biomass processing, the EHR still contains more than 30% residual cellulose and 8.3% hemicellulose. The scanning electron microscopy (SEM) images show differences in the structures of the biochar from BIN, SEB, and EHR (Figure 1A). While the BIN biochar has a fibrous appearance like the one found in raw biomass, the SEB and EHR biochars have more disrupted structures and smaller particle sizes due to the previous bagasse processing (pretreatment and enzymatic hydrolysis). Furthermore, the XPS analysis shows that the biochar surface composition is primarily carbon-based, with the EHR biochar being the least oxygenated. This trend is more evident in the biochar surface O/C ratio, which is 0.08 for the EHR biochar and 0.11 for the BIN biochar. In addition, C-C/C=C bonds are also predominant in EHR. However, it is also possible to observe that inorganic elements (e.g., Si) are present in the biochar, raising questions on possible interference from inorganics in the pyrolysis process[4]. Raman analysis showed two peaks in 1350 cm^{-1} (D-band) and 1590 cm^{-1} (G-band) regions, which are characteristic of biochar, and the profile presented corresponds to carbon materials with a high degree of amorphization, numerous oxygenated functionalities and defects, and small (~2 nm) graphitic domains. Due to the changes that biochar can undergo when applied to soil, its thermo-physical-chemical stability was assessed. Increasing grinding time resulted in smaller particles in all three biochars (<900 nm). Compared with the BIN and SEB biochars, the EHR biochar retained larger particles at 15 and 60 minutes, indicating that it is mechanically more robust. Due to oxidative wear, the EHR biochar behaved similarly to the BIN biochar. For the TGA tests, it was observed that EHR and SEB lost less mass than BIN, suggesting that the processing of biomass favors its thermal stability. The mechanical stability of the EHR biochar may favor its application in the soil since the disintegration into smaller particles that translocate through the environment is a potential concern.

Table 1 Chemical composition of the evaluated sugarcane feedstocks and yields of biochar bio-oil in the pyrolysis reactions.

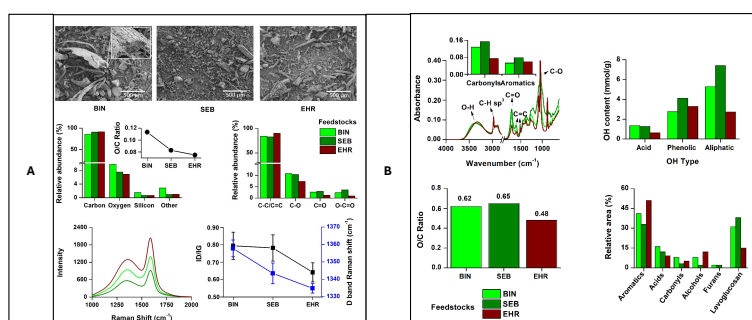| Component (wt.%)	*In natura* Bagasse (BIN)	Steam-exploded Bagasse (SEB)	Enzymatic Hydrolysis Residue (EHR)
Lignin	25.1 ± 0.2	33.5 ± 1.3	51.8 ± 0.3
Cellulose	40.5 ± 1.1	52.1 ± 2.3	34.7 ± 0.5
Hemicellulose	28 ± 0.6	12.2 ± 0.2	8.3 ± 0.11
Ashes	3.0 ± 0.2	1.8 ± 0.2	2.8 ± 0.2
Extractives	3.8 ± 0.5	nd	nd
Closure	100.2 ± 1.1	100.6 ± 1.3	98.3 ± 1.0
Biochar yield	25 ± 1	23 ± 1	31 ± 1
Bio-oil yield	13 ± 3	20 ± 3	21 ± 3

Nd: not determined.

Figure 1. (A) Panel of biochar characterization. (top) Scanning electron micrographs of BIN, SEB, and EHR. (center, left) Relative abundance of elements, (inset) atomic O/C ratio, and (center right) relative abundance of carbon oxidation states as determined by XPS. (bottom, left) Raman spectra and (bottom, right) the deconvoluted ID/IG ratios and D band Raman shift. **Figure 1B** Panel of bio-oil characterization. (top, left) FTIR spectra and inset comparing band intensities of carbonyls (1710 cm^{-1}) and aromatics (1510 cm^{-1}). (top, right) ^{31}P-NMR quantification of acid, phenolic, and aliphatic hydroxyls. (bottom, left) Mean O/C atomic ratio and (bottom, right) relative abundance of classes of compounds based on relative areas of the peaks identified in GC-MS. All graphs compare the three pyrolysis feedstocks (BIN, SEB, and EHR).

The peculiarities of the EHR bio-oil are presented in Figure 1B. The EHR bio-oil presents lower overall oxygenation, mainly through lower carboxyl content and a slight aromatic enrichment than BIN bio-oil. Against this background, the reduced carbohydrate (and, therefore, oxygen) content of the EHR feedstock is translated into a lower oxygenation (and presumably higher stability) of the bio-oil, indicating an advantageous quality. On the other hand, the aromatic enrichment of the EHR bio-oil (Figure 1B) is much lower than the feedstock lignin content (Table 1), suggesting limited prospects for the EHR bio-oil as an enriched source of aromatics. These characteristics might be changed under different enzymatic hydrolysis conditions, such as changing the alkaline cation K$^+$ or Ca^{2+} used in pH control. Further advancing the understanding of the variations of the EHR and the consequences for the EHR pyrolysis process and products is needed to scale up this technology.

4   CONCLUSION

The enzymatic hydrolysis residue (EHR) from sugarcane bagasse is a novel feedstock available at scale. The EHR characteristics depend on pretreatment and enzymatic hydrolysis conditions. The results of this study show that EHR can be a valuable feedstock for pyrolysis to co-produce bio-oil and biochar, diversifying the product portfolio and enhancing the GHG mitigation potential of 2G biorefineries. Compared to *in natura* (BIN) and steam-exploded bagasse (SEB), the investigated pyrolysis conditions resulted in higher yields of biochar and bio-oil from EHR. In

addition, characterization showed that bio-oil and biochar from EHR were less oxygenated, and the biochar was mechanically, thermally, and chemically more stable. Further studies are advocated to understand the impacts of the pretreatment and hydrolysis conditions (severity, choice of alkali, extent of carbohydrate bioconversion) on the pyrolysis process, the bio-oil and biochar characteristics, and the potential applications of these products.

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