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Research paper

Effect of citric acid leaching on the demineralization and thermal degradation behavior of sugarcane trash and bagasse

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ABSTRACT

The effect of leaching with citric acid on the ash fraction removed and the resulting changes in thermal degradation behavior of sugarcane trash (SCT) and sugarcane bagasse (SCB), was studied. A comparison between citric acid and well-known leaching agents including H_2SO_4, HCl and water, was made considering their effects on chemical, structural and thermal properties of the leached SCT and SCB. Demineralization and potential biomass hydrolysis was evaluated based on proximate and elemental analyses, Fourier transform infrared spectroscopy (FTIR-ATR) and thermogravimetric analysis (TGA). For citric acid and the reference leaching solutions, the mass fraction of ash removed was in a narrow range (between 38.9 and 54.1%) regardless of biomass type and leaching conditions (temperature and time) tested. The nonparametric bifactorial analysis of results revealed that the nature of leaching solution and its interaction with contact time are of major significance when demineralizing both SCT and SCB. Interestingly, no significance of temperature and its interaction with contact time was found. In acid-treated samples, the 1730 cm^{-1} IR-band was sharpened while the signal at 1600 cm^{-1} was largely attenuated, which could be attributed to the modification of the xylan fraction and to the substitution of C=O by OH groups. These mild structural changes, caused by hydrolysis, demonstrated to be very important for subsequent thermal degradation. The later was confirmed by the disappearance of the hemicellulose decomposition peak in the derivative thermogravimetric (DTG) curve.

1. Introduction

Sugarcane bagasse and trash are lignocellulosic materials that have attracted interest as potential feedstock for the production of biofuels (eg. ethanol, bio-oil and syngas) or specialty chemicals *via* thermochemical-catalytic routes [1]. Sugarcane bagasse (SCB) is the solid residue obtained after extraction of the juice from sugarcane (*Saccharum officinarum*) [2], while sugarcane trash (SCT) is the plant residue obtained during harvesting and it is usually left on the field and/or at the cleaning stations.

An attractive alternative technology to process these residues is fast pyrolysis [3], whereby solid biomass is converted mainly to bio-oil. Specifically, bio-oil has the potential for being a fuel or a feedstock for the extraction and/or synthesis of more valuable chemical compounds. Despite its proven application in heating (boilers and turbines) and blending with petroleum fractions, the high heterogeneity and poor fuel quality of crude bio-oil (i.e. high oxygen (> 30%) and water mass fraction (15–30%), high acidity (2 < pH < 3), high viscosity (40–100 mPa s)) impose the need for upgrading processes. The upgrading could be addressed prior to the pyrolysis (by pretreatment) or during/after the thermochemical conversion (by catalytic and fractionation methods).

Current research efforts in pretreatment have been conducted to address problems associated with the presence of naturally occurring alkali and alkaline earth metals (AAEMs) in biomass [4–6]. In terms of specific elements, Si, Na, K, Mg and Ca are generally the major inorganic components in sugarcane [7,8]. During fast pyrolysis, these elements act as catalysts and possess large potential to reduce the yield in bio-oil and to alter the resulting bio-oil composition in a negative way. Most notably, AAEMs appear to suppress the pyrolytic production of levoglucosan (an anhydrosugar) out of cellulose and favor the production of lighter oxygenates (including glycolaldehyde and hydroxyacetone) instead [9]. Additionally, these inorganics present in sugarcane residues could lead to reduced bio-oil stability (i.e. its tendency

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to degrade in terms of fuel quality over prolonged periods of storage) as well. As these inorganic compounds are present within the char particles, some of these finer char particles tend to be carried over or be entrained into the bio-oil during fluidized bed pyrolysis [7,9,10]. Once in the condensed bio-oil, the inorganic compounds could act as catalysts for further degradation reactions during oil storage. In order to overcome these difficulties in pyrolysis of sugarcane bagasse and particularly in pyrolysis of sugarcane trash with its higher ash mass fraction, the feedstock materials can be pretreated prior to pyrolysis to reduce their ash mass fraction [7,8].

Thus, the removal or passivation of the AAEMs is required for controlling the reaction and improving bio-oil quality and stability [11,12]. During passivation, the AAEMs are mainly converted into thermally stable salts that are catalytically inactive but also buffer the system at pH levels that favor glycosidic bond breakage [6], that would otherwise result in the formation of C_2 and C_3 compounds containing a carbonyl group [13]. On the other hand, pretreatment by leaching with water, acidic solutions and organic solvents [8,14–17] leads to the extraction of the AAEMs into the solution.

The SCB leaching with sulfuric acid (H_2SO_4) [18–24] is one of the most widely investigated treatments with acids, but other compounds such as hydrochloric acid (HCl) [7,23], hydrogen fluoride (HF) [7,25,26], nitric (HNO_3) [24,25] and phosphoric (H_3PO_4) [21,27] acids have also been studied (see overview in Table 1).

Despite the potential in removing inorganics, these well-known leaching agents have some disadvantages such as high mass reduction during treatment (i.e. HCl) [7] and environmental concerns (i.e. leachates of HF, HCl and H_2SO_4) [7,28]. In pretreatments with HCl, HF, H_2SO_4, or H_3PO_4 hydrolysis also occurs in which hemicellulose and cellulose in SCB are converted into smaller, extractable molecules [7,29], while HNO_3 changes the chemical interactions between the lignocellulosic structure and the native inorganics [25]. On the other hand, very few studies report on the pretreatment of SCT, whereby the pretreatment served different goals than the use of the material in fast pyrolysis. Existing SCT pretreatment studies include physical (size reduction) pretreatment for the production of energy or animal feed [30], or microbial pretreatment for the production of alcohol [31]. However, taking into account that the chemical composition of SCB and SCT does not differ to a large extent, the same pretreatment strategy can be suggested for both sugarcane residues.

Table 1
Literature reported acidic pretreatments tested on different biomass feedstocks.

Refs.	Acid	Concentration	Feedstock	Pretreatment conditions
[18]	H_2SO_4	20–60 g dm^{-3}	SCB	100–128 °C 0–5 h
[19]	H_2SO_4	2.5–10 g dm^{-3}	Switchgrass	160–190 °C, 0–4 h
[7]	HCl HF	5 mol dm^{-3} 50, 30 g dm^{-3}	SCB	1 h at 25 ± 2 °C
[20]	H_2SO_4	0–30 g dm^{-3}	SCB	112.5–157.5 °C, 0.08–0.58 h
[25]	HNO_3 HF	0.5 mol dm^{-3} (HNO_3, 0.55 kg kg^{-1}) 30 g dm^{-3} (HF, 0.38–0.40 kg kg^{-1})	SCB	1 h, room temperature
[26]	HF	30 g dm^{-3} (HF, 0.48 kg kg^{-1})	Rice straw	1 h, room temperature
[21]	H_3PO_4 H_2SO_4	5, 20, 35 g dm^{-3}	SCB	0.25, 1.63, 3 h, 130 °C
[22]	H_2SO_4	5–50 g dm^{-3}	SCB	24 h
[23]	HCl H_2SO_4 H_3PO_4	30, 70 g dm^{-3} 70 g dm^{-3} 70 g dm^{-3}	Rice husk	2 h, room temperature
[24]	HNO_3 followed by H_2SO_4	1 g dm^{-3} 1, 2, 3 g dm^{-3}	SCB	2 h, constant agitation Stirring every 0.33 h for 4 h

An alternative to the sugarcane biomass pretreatment could be the leaching (washing) with citric acid (CA, $C_6H_8O_7$). This organic acid has the possibility of acting as both a chelating agent and as a weak triprotic acid. Citric acid is a naturally occurring fruit acid and can be produced through three fermentative methods: floating culturing, superficial culturing, and solid state fermentation [32] (e.g. by using sugarcane bagasse [33]). CA has the advantage of being a more environmentally friendly leachant as compared to inorganic acids such as HCl and H_2SO_4 [28]. Citric acid has been widely used in the washing of contaminated soil, sewage sludge or contaminated mine soils to reduce levels of Cd, Cu, Zn, Cr and Pb [34–36] suggesting the potential of CA as a biomass demineralization agent.

Therefore, the main goal of this study is to investigate the effectiveness of citric acid for removing AAEMs from SCT and SCB and to compare its effectiveness to that of other (i.e. more conventional) leachants such as demineralized water, HCl and H_2SO_4. Accordingly, leaching effects on remaining solid (eg. treated SCT and SCB) structure, thermal behavior and chemical composition are analyzed based on compositional analyses (elemental, proximate and inductively coupled plasma optical emission spectrometry (ICP-OES)), Fourier transform infrared spectroscopy (FTIR-ATR) and thermogravimetric analysis (TGA). The influence of leaching temperature and contact time on the removed ash fraction was assessed by using the nonparametric bifactorial analysis of variance proposed by Sokal and Rohlf [37].

2. Materials and methods

2.1. Sugarcane trash bagasse and trash

Two types of biomass were chosen: 1) sugarcane trash, which holds potential as a fast pyrolysis feedstock and 2) sugarcane bagasse, which is an already well-studied residue of sugarcane (*Saccharum officinarum*) production. The original materials (variety of sugarcane: Cuba 1051-73) used in this work were provided by the sugar mill "Ifraín Alfonso" in Villa Clara, Cuba. SCT was manually harvested, and the SCB was sampled two hours after milling. The original SCT and SCB had an initial water mass fraction of 141 and 324 g kg^{-1}, respectively. Both materials were naturally dried in ambient atmosphere during three days until the equilibrium water mass fraction was achieved, after which they were ground using a Retsch mill and sieved to obtain particles with a size ranging from 1 to 2 mm. These materials (further labeled in this study as "untreated") were stored afterwards in plastic bags at room temperature. The properties of untreated SCT and SCB are reported in Table 2.

Table 2
Proximate and ultimate analysis (in kg kg^{-1} dry basis) of the untreated SCT and SCB, the standard deviations are provided.

Proximate analysis			Ultimate analysis		
	SCT	SCB		SCT	SCB
Volatile matter	0.739 ± 0.002	0.798 ± 0.000	Carbon (C)	0.401 ± 0.001	0.441 ± 0.002
Fixed carbon[a]	0.208 ± 0.003	0.183 ± 0.001	Hydrogen (H)	0.053 ± 0.002	0.060 ± 0.000
Ash	0.053 ± 0.001	0.019 ± 0.001	Nitrogen (N)	0.005 ± 0.000	0.002 ± 0.000
			Oxygen (O)[b]	0.488 ± 0.002	0.478 ± 0.002
			Sulphur	BDL	BDL

The water mass fraction was 72 g kg^{-1} in SCT and 67 g kg^{-1} in SCB, both on as received basis.

[a] Fixed carbon (kg kg^{-1} dry basis) = 1 – Ash (kg kg^{-1} dry basis) – Volatile matter (kg kg^{-1} dry basis).

[b] Calculated by difference.

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