



Pyrolytic coproduction of bio-char and upgraded bio-oils from abundant agro-industrial wastes

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Abstract

The co-production of bio-char and upgraded bio-oil by fast pyrolysis of raw and sulfuric-acid pretreated agro-industrial wastes (corn cob, sugarcane bagasse and sunflower seed hull) was investigated to valorize wastes as sources of value-added products (VAPs) following the circular bio-economy system. To this end, proximate and elemental analyses were performed, and adsorption properties were determined in pyrolysis products. Bio-char and bio-oil yields from raw wastes ranged 28–33% and 30–35%, respectively. For all wastes, acid pretreatment increased the solid fraction and caused a reduction of the liquid one, compared to untreated wastes. Pyrolysis of raw wastes led to the co-production of bio-chars and bio-oils with different applications. Bio-chars could be put in for soil amendment, primarily due to high ashes concentration, mesoporosity, and elevated cation exchange capacity; whereas, bio-oils could be upgraded by water addition, leading to a source for carrying out reforming reactions in the context of hydrogen production. Properties of bio-chars from acid washed biomasses enabled them for pollutant remediation, due to their high specific surface and microporosity features. The corresponding bio-liquid was a stable-to-storage material, being a practical source of furfural. These findings emphasize that lignocellulosic wastes can be envisaged as starting materials for producing VAPs via pyrolysis.

Keywords Pyrolysis · Sugarcane bagasse · Corn cob · Sunflower seed hulls · Bio-char · Upgraded bio-oil

Introduction

Corn, sugarcane, and sunflower are three ubiquitous crops worldwide and large amounts of their wastes are associated with the industrial use of these biomasses (Jain et al. 2010; Miranda et al. 2018). In Argentina these wastes are currently used for cattle grazing, soil conservation, landfill, and heat and power generation; still, idle amounts are available reaching for corn cob an annual net availability of 454,886 tons (Agroindustria 2020), and 611,339 tons for sugarcane bagasse (Centro Azucarero 2019). As for sunflower, processing by-products from sunflower edible oil industries in this country originate 55,000 tons of hulls per year that are open air stored (World Atlas 2017; Casoni et al. 2019a). Thus, this scenario shows that these wastes could be valorized as sources for fuels and chemicals production, promoting the circular bio-economy system and entailing a proper management of their processing and production to avoid adverse environmental impacts.

Although gasification of biomass for producing heat and power is a consolidated technology, large amounts of waste are needed in order to ensure sustainability. Pyrolysis

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is other thermal process to harness energy as it can convert lignocellulosic wastes into three main fractions: liquid (bio-oil), solid (bio-char) and gaseous (non-condensable gas), being it possible to adapt this technology to different quantities of waste biomass (Bridgewater 2012; Casoni et al. 2019a). Parameters affecting pyrolysis of lignocellulosic biomass (Kan et al. 2016; Dhyani and Bhaskar 2018; Varma et al. 2018; Bamboriya et al. 2019; Hu and Gholizadeh 2019) were extensively reviewed. Biomass or waste valorization and conversion into value added products (VAPs) using this thermochemical process were reported (Casoni et al. 2019a; Dellarose Boer et al. 2020; Mondal et al. 2020.), as well as factors affecting pyrolysis process for optimum bio-oil production (Akhtar and Saidina Amin 2012; Zhang et al. 2019; Dai et al. 2019). More recently, the potential of pyrolysis bio-oils from lignocellulosic waste to protect wood from fungi and subterranean termite (Boer et al. 2020) and to develop novel bioinsecticides as an alternative to the use of conventional synthetic pesticides (Urrutia et al. 2020) were investigated. However, a feasible and concrete application of all the products is rarely addressed. Tsai et al. (2006) have investigated the fast pyrolysis of sugarcane bagasse focusing on bio-liquid production and obtaining high yields of this fraction; however, they have concluded that upgrading of this product should be carried out before applications as a fuel. Cob corn pyrolysis has been performed following a torrefaction for improving bio-liquids properties (Klaas et al. 2020). Even though relatively high bio-oils calorific values (21 MJ/kg) were obtained, the corresponding pH values were notably low (2–3), which would prevent the liquids from being employed as fuels. A study on sunflower seed hulls pyrolysis aimed at improving the knowledge of alternative uses of bio-char proposed that this material could be employed for soil amendment, even when porosity, specific surface, and cation exchange capacity were not measured (Colantoni et al. 2016).

Herein, bench-scale fast pyrolysis of raw and acid-pre-treated cob corn, sugarcane bagasse, and sunflower seed hulls was achieved and their liquid and solid fractions were fully characterized with the aim of investigating the feasibility of producing VAPs simultaneously from both bio-char and bio-oil. Possible applications of the products are discussed in the light of their physicochemical properties.

Materials and methods

Biomasses

The biomasses used for the pyrolysis were corn cobs (CC) from corn (*Zea mays* L.) hybrid DK70-10 VT3 PRO, bagasse (SB) from sugarcane (*Saccharum* spp.) cultivar L 91-281, and sunflower seed hulls (SS) from a pool of sunflower

(*Helianthus annuus* L.) hybrids. These raw materials were submitted to a pre-treatment by washing the wastes with 10 wt% sulfuric acid solutions. The corresponding acid-treated biomasses were named TCC, TSB and TSS. Raw and pre-treated samples were dried at 60 °C and ground to particle sizes of between 10 and 100 µm, as measured with a laser diffraction analyzer (HORIBA LA-950). The alkaline metal concentration was measured by induced coupled plasma spectroscopy (Shimadzu Simultaneous 9000 apparatus) following EPA standard 200.7. Hemicellulose, cellulose, and lignin contents were determined by the method described by Van Soest (1991) in an Ankon 200/220 fiber analyzer. CC, SB and SS were studied by thermogravimetric analysis (TGA), differential thermogravimetric analysis (DTA) and proximate analysis in a Discovery TGA equipment. N₂ was used for purging the scale for 20 min in order to avoid any traces of oxygen. Approximately 20 mg of the biomasses were heated at 10 °C/min from room temperature to 900 °C. Then the flow was switched to air for the determination of ashes.

Pyrolysis

Pyrolysis of CC, SB, SS, TCC, TSB, and TSS was carried out at 470 °C with a nitrogen flow (200 mL/min) in a vertical reactor. Approximately 10 g of biomass were introduced into the reactor in a metal basket. The vapors produced during reaction were collected at the end of the equipment using a water/ice bath.

The yields of bio-oil and bio-char were measured from the corresponding masses. The quantity of gases was calculated as the difference with the one corresponding to the liquid and the solid fractions. Repeatability errors for measuring yields were lower than 1%.

Pyrolysis products characterization

The bio-oil chemical characterization was carried out by gas chromatography in a GC–MS Perkin Elmer CLARUS 500 chromatograph coupled with a mass spectroscopy detector, using an Elite-5 MS column (60 m, 0.25 mm ID). A semi-quantitative analysis of the products was carried out from the chromatographic peak areas.

Bio-chars produced via pyrolysis from raw biomasses were named with an acronym starting with “C” followed by the name of the corresponding biomass. Thus, six bio-chars were studied: CCC, CSB, and CSS (for raw wastes) and CTCC, CTSB, and CTSS (for acid-pre-treated wastes). These bio-chars were assayed by TGA, DTA and proximate analysis. The elemental analyses were determined in an Exeter Analytical CE-400 instrument. Nitrogen sortometry at 77 K was used for obtaining isotherms at – 196 °C in a Nova 1200e Quantachrome instrument. The

specific surface areas (S_{BET}) were measured according to the Brunauer–Emmett–Teller (BET) theory (Lowell et al. 2012). Pore volume and pore diameters were calculated following Barrett–Joyner–Halenda (BJH) method. Cation exchange capacity (CEC) was determined following the method developed by Munera-Echeverry (2018). Briefly, approximately 1 g of bio-char was washed with deionized water and treated with NH_4OAc 1 M for 24 h under continuous stirring. Then, four consecutive washes with 20 ml isopropanol were performed under stirring for 30 min. Complete removal of NH_4OAc was attained by washing with KCl 2 M. The amount of ammonium was determined by UV spectroscopy.

Statistical analyses

Statistical analyses were performed with Infostat Software v. 2017 (Di Rienzo et al. 2017). Analysis of variance (ANOVA) and DGC multiple comparison test were used to determine statistical differences in the properties of raw wastes and bio-chars derived from raw and acid-pretreated wastes.

Upgrading of bio-oils by water addition

The liquid fraction corresponding to the pyrolysis of the raw biomasses (CC, SB and SS) was added to water at 1–2 °C drop to drop, till the water: bio-liquid volume ratio was 1:1. In this way two phases were formed and the chemical analysis of the upper aqueous phase was carried out in a similar way as for the bio-oils.

Results and discussion

Raw biomass characterization

Several physicochemical properties of raw CC, SB and SS biomasses are shown in Table 1. The proximate analysis delivers information associated with the burning quality of biomass (Varma and Mondal 2017). Volatile matter revealed an opposite trend compared to fixed carbon across wastes (Table 1). While CC raw waste accounted for the highest volatile matter content and lowest fixed carbon value, the other way around occurred for SB raw waste (Table 1). Ash content in SB biomass was almost 1.5 and 3.0 times the amount determined in SS and CC biomasses, respectively (Table 1), and was similar to the ash content reported in SB biomasses obtained from South Africa (Carrier et al. 2011) and India (Varma and Mondal 2017). This shows that the amount of ash content depends on the nature of biomass, and because it is an incombustible material it can lower the burning rate of the biomass, further playing a disadvantageous effect. All three raw wastes

Table 1 Proximate analysis, elemental content and major cell-wall components in raw biomasses of corn cob (CC), sugarcane bagasse (SB) and sunflower seed hulls (SS)

	CC	SB	SS
Volatile matter, VM (dry basis %)	82.3	78.1	79.8
Fixed carbon, FC (dry basis %)	16.7	19.0	18.1
Ashes (dry basis %)	1.0	2.9	2.0
Fuel ratio (FC/VM)	0.20	0.24	0.23
Na^+ (mg/Kg)	40	120	100
K^+ (mg/Kg)	700	1700	10,400
Ca^{++} (mg/Kg)	10	1300	3200
Mg^{++} (mg/Kg)	11	1470	1900
Hemicellulose (dry basis %)	23.9	15.2	18.4
Cellulose (dry basis %)	37.2	43.3	39.1
Lignin (dry basis %)	18.0	19.5	20.4
Others ¹	20.9	22.0	22.1

¹Pectins, resins, extractives, etc., expressed as mg/Kg

contained very low fuel ratios (fixed carbon/volatile matter) due to the elevated levels of volatile matter (Table 1). Similar SB fuel ratios were reported (García-Pérez et al. 2002; Varma and Mondal 2017; Boer et al. 2020). Fuel ratios below 1 are extremely low compared to anthracite that has a fuel ratio of 12 (Chae et al. 2020).

Lignocellulosic biomass feedstocks such as agro-industrial wastes contain water, cellulose, hemicellulose, lignin, and small fraction of inorganic matter such as mineral matter (K, Ca, Mg, Na). The relative mass ratios of both organic and inorganic compounds varied across the three agro-industrial wastes (Table 1). The uppermost values of the major cell-wall compounds hemicellulose and cellulose were detected in the raw biomasses of the monocots, i.e., CC accounted for the highest concentration of hemicellulose and SB for cellulose; whereas lignin content showed an opposite tendency and was highest in the raw waste of the dicot sunflower (Table 1). The maximum value arising from the sum of cellulose plus hemicellulose corresponded to raw CC biomass (61.1) and was accompanied by the highest volatile matter content (82.3) in the same raw waste (Table 1), supporting the fact that, in general, cellulose and hemicellulose tend to produce more volatiles (Akhtar and Saidina Amin 2012). Higher amounts of lignin, on the other hand, reduced the amount of volatile (Table 1), in accordance with the correlation proposed by Raveendran et al. (1995) for the effect of mineral matter constituents and amount of lignin on the volatiles yield of biomass pyrolysis. The content of three main polymeric components, i.e. cellulose, hemicellulose, and lignin, in the initial raw agro-industrial wastes (Table 1) fell within the range values of the cell-wall compounds already reported (Kim and Day 2011; Ioelovich 2014;

Pointner et al. 2014; Casoni et al. 2018, 2019a; García et al. 2019).

Mineral matter showed substantial compositional variations in biomass species (Table 1). The main elements present in ashes were Na, K, Ca and Mg. Na concentrations were fairly similar in SB and SS residues, but were more than two times the concentration detected in CC biomass. K concentration in raw SS waste was by far the highest among elements and across raw wastes. Values of Ca and Mg were high in raw SS biomass, intermediate in raw SB biomass, and negligible in CC biomass. Average mineral matter content for raw CC, SB and SS wastes was 190, 1148, and 3900, respectively, and appeared to be negatively influencing volatiles yield (Table 1) (Akhtar and Saidina Amin 2012).

Pyrolytic fraction yields across raw and acid-pretreated agro-industrial wastes

Liquid, char, and gas are three major products of pyrolysis process. To investigate their yields in abundant agro-industrial wastes, fast pyrolysis of raw (CC, SB, and SS) and sulfuric-acid pretreated corn cob (TCC), sugarcane bagasse (TSB), and sunflower seed hulls (TSS) biomasses was performed.

Pyrolysis yields to liquid and solid fractions varied across the raw agro-industrial wastes (Fig. 1). Bio-oil in raw biomasses ranged from 30 to 35%, whereas in bio-char from 28 to 33%. Temperature and composition of biomass (cellulose, hemicelluloses, lignin, and inorganic matter) species played an underlying role in the yield of these pyrolysis fractions. While intermediate pyrolysis temperatures (500–550 °C) usually maximize the liquid bio-oil yield, lower temperatures, such as the ones used in this and in previous investigations (Casoni et al. 2018), led to the formation of char (Akhtar and Saidina Amin 2012). The effect of this parameter was reflected in untreated wastes as the bio-char yield

was above the bio-oil yield with the exception of CC biomass (Fig. 1). Considering that the gas fraction yield was quite uniform across the untreated wastes, the augment of CC bio-oil yield necessary represented a reduction of the CC bio-char yield (Fig. 1) which might be explained by the low amounts of lignin and inorganic metal compounds that appear in pyrolysis ash (Tables 1 and 2) (Akhtar and Saidina Amin 2012). Alkaline earth metals also influenced the distribution of the pyrolysis products on two-step pyrolysis of CC in such a way that while their content decreased, the bio-oil yield increased and the bio-char yield decreased (Zhang et al. 2019).

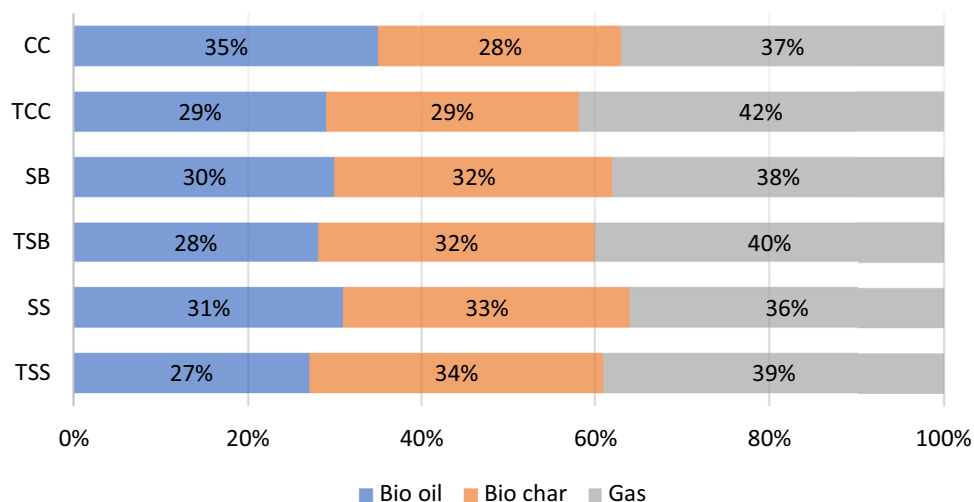
On the other hand, the highest SS bio-char yield (Fig. 1) was accompanied with the highest amounts of lignin and K (Tables 1 and 2). Pyrolysis of 13 biomass samples including CC and SB showed higher liquid yields on demineralization of mineral matter except for three biomass types which had high amounts of lignin and potassium metal and showed an increase in char yield, suggesting that potassium is supposed

Table 2 Chemical properties and elemental content of bio-chars obtained via pyrolysis of raw biomasses of corn cob (CCC), sugarcane bagasse (CSB), and sunflower seed hulls (CSS)

	CCC	CSB	CSS
Volatile matter, VM ^a	31	22.3	23.5
Fixed carbon, FC ^a	65.8	70.6	70.4
Ashes ^a	3.2	7.1	6.1
Fuel ratio (FC/VM)	2.12	3.17	3.00
Na ⁺ (mg/Kg)	99	302	248
K ⁺ (mg/Kg)	1702	4302	25,403
Ca ⁺⁺ (mg/Kg)	26	3123	8021
Mg ⁺⁺ (mg/Kg)	30	3600	4690

^aDry basis %

Fig. 1 Pyrolysis yields to bio-oil, bio-char and bio-gas for raw (corn cob CC; sugarcane bagasse, SB; and sunflower seed hulls, SS) and acid-pretreated (corn cob, TCC; sugarcane bagasse, TSB; and sunflower seed hulls, TSS) wastes



to facilitate gas and charring reactions (Akhtar and Saidina Amin 2012).

For all wastes, acid pretreatment caused a depletion of the liquid fraction and increased solid and gas fractions, compared to untreated wastes (Fig. 1). The effect of acid on the bio-oils yields can be attributed to the hydrolysis that this pretreatment causes in the biomass structure. It mainly affects cellulose and hemicellulose which are degraded to smaller molecules and this is the reason why the gas yield is increased after pyrolysis. Moreover, it should be taken into account that the treatment also dissolve part of the holocellulose which contributes to the depletion of the liquid phase after the reaction (Casoni et al. 2019a).

Bio-char characterization following pyrolysis of raw and acid-pretreated agro-industrial wastes

To study the potential applications of bio-chars in agriculture and environmental issues, several properties of bio-chars obtained via pyrolysis of raw biomasses of corn cob (CCC), sugarcane bagasse (CSB), and sunflower seed hulls (CSS) and the corresponding acid-pretreated wastes (CTCC, CTSB, and CTSS) were determined and analyzed (Tables 2 and 3). Proximate analysis revealed underlying differences in properties (volatile matter, fixed carbon, ashes, and fuel ratio) of bio-chars derived from pyrolysis of raw and

acid-pretreated wastes (Tables 2, 3). Pyrolysis led to a significant reduction in volatile matter of bio-chars from acid-pretreated wastes compared to untreated wastes (Tables 2, 3). As could be expected, pyrolysis led to an increase in fixed carbon, a highly desirable property associated with carbon sequestration which furthermore indicates that bio-chars present high resistance to degradation. (Tables 1, 2, 3). Sulfuric acid pretreatment enhanced even more fixed carbon content (Tables 2, 3, and 4). Because pyrolysis influenced volatile matter and fixed carbon contents in opposite ways compared to the corresponding values measured in starting wastes, fuel ratio (fixed carbon/volatile matter) was improved, by definition, by this thermochemical process (Tables 1, 2, 3, and 4). Ashes in bio-chars obtained through pyrolysis of acid-pretreated wastes were statistically lower than the ones produced from pyrolysis of untreated biomasses (Tables 2, 3, and 4) indicating that the acid-pretreatment removed alkaline cations depleting levels of inorganic salts in bio-chars.

The concentration of metallic species varied strongly in bio-chars, regardless of the nature of the waste and whether it was pretreated or not (Tables 2, 3). The accumulation of potassium in pyrolyzed wastes was the highest among the analyzed elements and across all three agro-industrial wastes. In this respect, the ratio $K + Na + Ca + Mg$ was 11.0 for CCC, 2.0 for CSS, 1.9 for CTCC, and 1.7 for CTSS (Tables 2, 3).

Adsorption properties such as cation exchange capacity (CEC), specific surface area (S_{BET}), pore volume and diameter differed significantly in bio-chars, depending on whether their feedstocks were untreated or pretreated with acid (Table 5), leading this dichotomy to potentially different applications of these bio-chars. CEC, an essential property corresponding to the material's ability to hold positively charged ions, was a challenging variable to assay in bio-chars because it is traditionally measured in soils. On one hand, elevated CEC values, measured according to a method specifically developed for bio-chars (Munera-Echeverry 2018), were in the 25–27 mEq/kg range for raw wastes bio-chars (Table 5), indicating that these materials would be suitable for fixation of nutrients in soils. This feature, coupled with the fact that bio-chars from pyrolysis of raw biomasses developed mesoporosity

Table 3 Chemical properties and elemental content of bio-chars obtained via pyrolysis of acid-pretreated biomasses of corn cob (CTCC), sugarcane bagasse (CTSB), and sunflower seed hulls (CTSS)

	CTCC	CTSB	CTSS
Volatile matter, VM ^a	24.0	18.9	19.6
Fixed carbon, FC ^a	75.0	78.3	78.1
Ashes ^a	1.0	2.8	2.3
Fuel ratio (FC/VM)	3.13	4.14	3.98
Na ⁺ (mg/Kg)	500	20	330
K ⁺ (mg/Kg)	7500	16,600	3400
Ca ⁺⁺ (mg/Kg)	700	14,430	1010
Mg ⁺⁺ (mg/Kg)	2700	410	690

^aDry basis %

Table 4 Averages of chemical properties for raw wastes and bio-chars derived from raw and acid-pretreated wastes

	Raw wastes	Bio-chars from raw wastes	Bio-chars from acid-pretreated wastes
Volatile matter (dry basis %)	80.1 ± 2.1 ^a	25.6 ± 4.7 ^b	20.8 ± 2.8 ^c
Fixed carbon (dry basis %)	17.9 ± 1.2 ^c	68.9 ± 2.7 ^b	77.1 ± 1.9 ^a
Ashes (dry basis %)	2.0 ± 1.0 ^b	5.5 ± 2.0 ^a	2.2 ± 0.9 ^b
Fuel ratio	0.2 ± 0.0 ^c	2.8 ± 0.6 ^b	3.8 ± 0.6 ^a

Different letters indicate significant differences among raw wastes and bio-chars derived from raw and acid-pretreated wastes for DGC test ($p < 0.05$)

Table 5 Adsorption properties for bio-chars from raw and acid acid-pretreated corn cob (CC), sugarcane bagasse (SB), and sunflower seed hulls (SB) wastes

		CC	SB	SS	Aver	Change (%)
CEC (mEq/kg)	RW	27	25	26	26.0 ± 1.0 ^a	
	APW	25	18	23	22 ± 3.6 ^b	-15
	Change (%)	-7	-28	-12		
S _{BET} (m ² /g)	RW	8	6	9	7.7 ± 1.5 ^b	
	APW	107	56	96	86.3 ± 26.8 ^a	1021
	Change (%)	1238	833	967		
Pore volume (cm ³ /g)	RW	0.12	0.15	0.13	0.1 ± 0.0 ^b	
	APW	0.22	0.17	0.21	0.20 ± 0.0 ^a	54
	Change (%)	83	13	62		
Pore diameter (nm)	RW	17	15	22	18.0 ± 3.6 ^a	
	APW	10	7	8	8.3 ± 1.5 ^b	-54
	Change (%)	-41	-53	-64		

Different letters indicate significant differences between bio-chars derived from raw (RW) and acid-pretreated (APW) wastes for DGC test ($p < 0.05$)

(Table 5) due to vapors released at high temperature, provided evidence that CCC, CSB, and CSS could be employed as solid fertilizers in soils. An intensive crop market such as floriculture could be an ideal commercial niche for the use of this type of bio-char, particularly as a fertilization vector of cut flower and ornamental plants that are grown in pots. On the other hand, the S_{BET} and pore volume measurements revealed a statistically significant increase in surface area and microporosity upon acid pretreatment, being 1.021% the average increment for S_{BET} and 54% for pore volume (Table 5). Typically, this range of areas are reached applying acid treatments to lignocellulosic materials (Casoni et al. 2019a, b). These findings are likely due to the formation of vapors in a pyrolytic environment that combined high temperature and sulfuric acid, which in its turn led to microporous bio-chars due to the rupture of unions among phosphates and sulfates with the biomass structure which are formed during the pretreatment. These ruptures originate “holes” producing a porous material. Taken together, these properties indicate that CTCC, CTSB and CTSS displayed improved adsorption properties, and concomitantly, they could be employed as adsorbent materials, e.g., for the removal of contaminants in water (Casoni et al. 2019b). The S_{BET} values of these bio-chars were even higher than the corresponding value reported for Kans grass bio-chars used as effective adsorbent for toxic metals immobilization in aqueous solutions (Baig et al. 2012). On the other hand, high S_{BET} areas, ranging from 259 to 452 m²/g were measured for bio-chars obtained from the vacuum pyrolysis of sugar cane bagasse, (Carrier et al. 2012). Despite these values were higher than the one determined for CTSB (56 m²/g, Table 4) the main drawback of vacuum pyrolysis is that it yields much lower char than fast pyrolysis. This last statement is also valid for sunflower waste bio-chars, where the S_{BET} value (96

m²/g, Table 4) from CTSS produced by fast pyrolysis was lower than the value reported with vacuum pyrolysis of sunflower waste (177 m²/g) (Silva et al. 2020). Cob corn bio-char produced by fast pyrolysis using a pilot scale fluidized bed reactor displayed null S_{BET} and relatively low yield (almost 19%) (Mullen et al. 2010), compared to the high yield and the specific surface area values determined by fast pyrolysis of CTCC. These results are in line with the fact that fluidized bed reactor are designed to maximize yields to the liquid fraction.

Despite both series of bio-chars showed properties in line with their application for soil amendment, bio-chars obtained from pyrolysis of raw wastes appeared to be more suitable materials for fixation of nutrients so they could be used as soil fertilizers, whereas bio-chars resulting from pyrolysis of acid pretreated wastes could be preferentially used for pollutant remediation, i.e., adsorption of contaminants in water.

Other evolving nonagricultural markets for bio-char applications may include: (1) replacement for carbon black which is used as a filler and dye in various types of plastics and in tires; (2) high value composting: adding 10–20% bio-char in the initial stages of composting could reduce processing time, retain more nutrients, boost long-term carbon content, and increase heating temperatures which kill more pathogens or weed seeds; (3) Livestock farming: bio-char could be used as bedding or as part of a manure management system to improve its carbon content, reduce odors, and retain nutrients; (4) improve stormwater management by increasing infiltration of water while reducing toxins; and (5) climate change mitigation tool: bio-char was highlighted as one of only six negative greenhouse gas emissions technologies recognized by the Intergovernmental Panel on Climate Change as it can sequester atmospheric carbon in a stable soil carbon pool (Draper 2019).

Sulfuric acid pretreatment leads to furfural enrichment in bio-oils

To examine the possibility of detecting value-added compounds in the pyrolysis liquid fraction, a chemical analysis was performed in non-pretreated and sulfuric-acid pretreated wastes (Fig. 2). Bio-oils isolated from the pyrolysis of CC, SB and SS residues showed very complex compositions, with several oxygenated compounds (Fig. 2), in agreement with previous reports regarding lignocellulosic materials (Bridgewater 2012; Casoni et al. 2019b). Phenolic compounds and acetic acid exhibited contrasting tendencies of accumulation in SB and SS wastes, carrying CC wastes intermediate levels of both compounds. Phenolic compounds content was higher in the monocots wastes, compared to the dicot waste. Conversely, acetic acid content was the highest in the dicot waste, representing more than twice the amount measured in SB waste (Fig. 2). Negligible levels of levoglucosenone were only detected in CC residue (Fig. 2). Furfural and 1-hydroxy-2-propanone showed opposite trends of accumulation in CC and SB residues, carrying SS wastes intermediate amounts of both compounds. Furfural accumulation was highest in CC residue and 1-hydroxy-2-propanone in SB residue (Fig. 2). For all the bio-liquids low pH values were measured in the 2–3 range. Alike with other lignocellulosic feedstocks, the bio-liquids from pyrolysis all three raw wastes were corrosive and viscous and exhibited a polar nature (Naik et al. 2010).

The addition of water to the bio-liquid just obtained from the pyrolysis of raw SS resulted in the separation of two phases: an aqueous and an oily one. Scholze and Meier (2001) proposed the addition of water to bio-liquids to separate the light from the heavy compounds in two phases. While a remarkable increase in acetic acid (48%) and a lesser extent increase in furfural (7%) occurred in the aqueous phase of SS bio-liquid, phenolic compounds were not detected at all. The light compounds enriched bio-liquid was

stable to storage and its composition remained unaltered for weeks. The high amount of acetic acid in the aqueous phase indicates that this bio-liquid could be employed for reforming to produce hydrogen. Previous works, from Resender et al. (2015) and Maidana et al. (2019) concluded that bio-oils with high concentration of acetic acid can produce high hydrogen yield from steam reforming reaction.

The composition of bio-oils obtained from acid-washed wastes was much simpler than those obtained from raw materials (Fig. 3). On one hand, the highest compound concentration in the bio-oil composition corresponded to furfural. This is supported by two non-mutually exclusive findings: (1) hemicellulose, the main source of furfural, showed enhanced levels in the raw agro-industrial wastes (Table 1); and (2) the acid pretreatment led to the activation of the holocellulose by depolymerization and concomitantly to a higher furfural yield (Casoni et al. 2019a) (Fig. 3). Alike furfural, levoglucosenone also augmented, but to a lesser extent (Fig. 3).

On the other hand, acetic acid decreased dramatically and phenolic compounds were almost completely removed compared to the untreated wastes (Fig. 3). This is also a favorable feature since methoxyphenols are responsible for the instability of the pyrolysis liquid fraction during storage, due to the fact that these compounds repolymerize to lignin, being separated from the liquid, in a solid phase (Casoni et al. 2015; Ramirez-Corredores 2013). Bio-liquids containing small traces (e.g. TCC and TSB) or, even better, without phenolic compounds (e.g. TSS) are much more stable during storage, and could be considered a concrete source for furfural production. Furfural, which can be used as selective solvent in the refining of lubricating oils (Ibrahim et al. 2017), as a fungicide and weed killer, and in the production of tetrahydrofuran, an important industrial solvent (Ebert 2008), could be preferentially isolated from the bio-oil of TSB waste as its composition lacks acetic acid and this facilitates furfural isolation. Moreover, bio-oil enriched

Fig. 2 Chemical composition of bio-oils isolated from raw biomasses of corn cob (CC), sugarcane bagasse (SB) and sunflower seed hulls (SS)

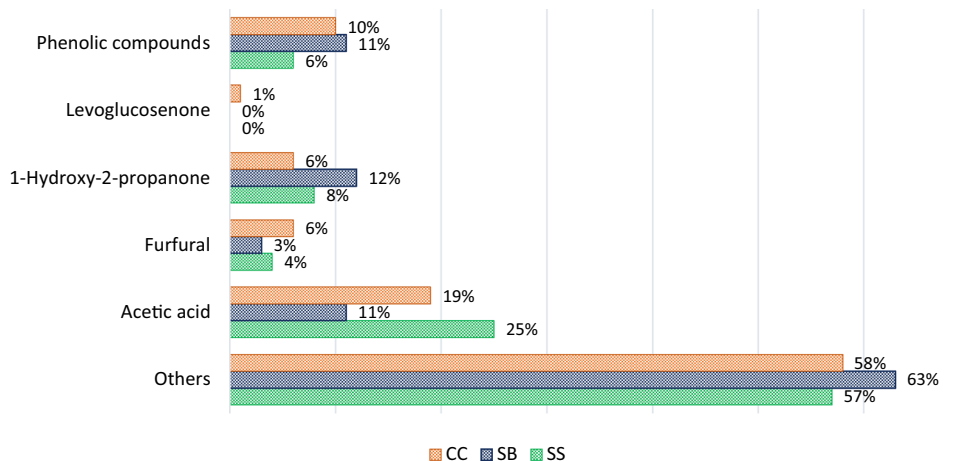
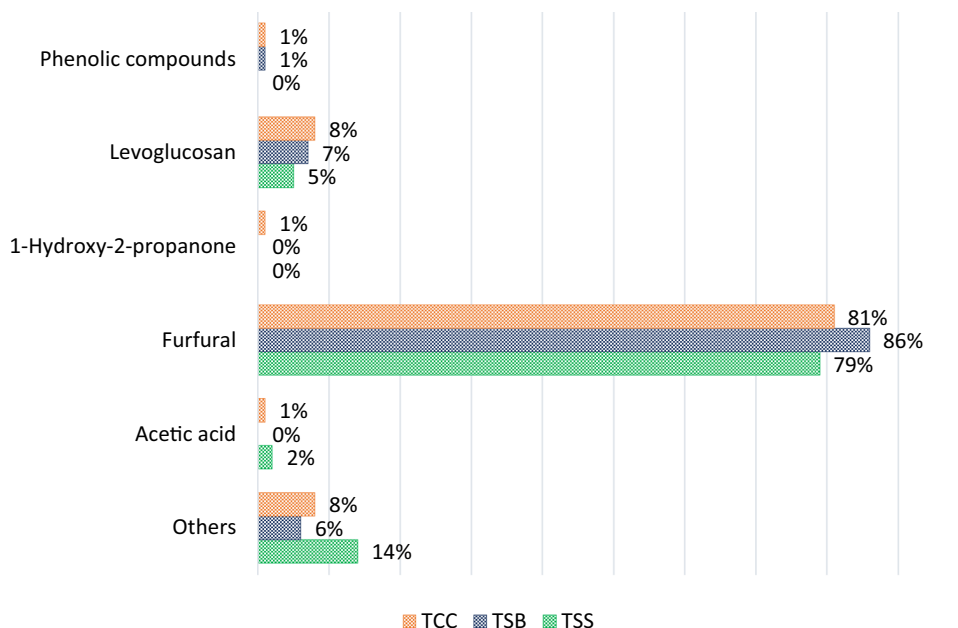


Fig. 3 Chemical composition of bio-oils isolated from sulfuric-acid pretreated biomasses of corn cob (TCC), sugarcane bagasse (TSB), and sunflower seed hulls (TSS)



in furfural produced lethal activity and induced changes in locomotory behavior and nutritional physiology of the insect pests *Sitophilus oryzae*, *Lasioderma serricorne* and *Tribolium castaneum* (Urrutia et al. 2020), underscoring the biological activity of pyrolysis bio-oil from TSS on insects of stored grain and products.

Relevance of this study and conclusions

This research is aligned with the concept of Circular Economy as it refers to three crops (corn, sugarcane, and sunflower) that produce several primary food products (cereals, sugar and edible-oil) and agro-industrial wastes (cob, bagasse, and seed hulls) that become feedstocks for further processing and obtaining of high value products. Pyrolysis is, within the circular bio-economy system, a feasible technology for converting wastes into VAPs. Pyrolysis of raw biomasses led to the co-production of bio-chars and bio-oils with different applications. While the solid fraction could be applied for soil amendment, mainly due to high ashes concentration, mesoporosity and elevated CEC; the liquid fraction could be upgraded by water addition, leading to a source for carrying out reforming reactions in the context of hydrogen production.

The properties of the bio-chars produced from acid washed biomasses enabled them for pollutant remediation, due to the high specific surface and the microporosity features of these materials. The corresponding bio-liquid was a stable-to-storage material, being a practical source of furfural. Based on the present findings, bio-char and upgraded bio-oils could be co-produced with relatively high yields

from acid-washed wastes. Bio-char yields ranged 29–34%, whereas the furfural-rich liquid fraction reached yields in the 27–29% range. Thus, approximately 434 kt/y of bio-chars could be obtained from the conversion of these wastes, representing a significant positive impact on agricultural activities, mainly in regions with naturally poor soils. As for furfural, the production would be around 395 kt/y, being also a remarkable contribution to industrial activities.

It is worth noting that the co-production of both bio-based products from wastes would replace products obtained from dedicated crops, avoiding conflicts with food and feed availability, reducing environmental hazards, and underscoring the fact that abundant lignocellulosic wastes can be envisaged as starting materials for producing VAPs via feasible processes.

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Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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