

Exploring the potential of fast pyrolysis of invasive biomass species for the production of chemicals

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ABSTRACT

The pyrolysis of five invasive plants crowded in Colombia (*Liquidambar styraciflua*, *Sambucus nigra*, *Cecropia telenitida*, *Ruta graveolens*, and *Clusia orthoneura*) has been studied for the first time in order to assess their potential for the production of liquid and solid fuels and chemical products. The volatiles produced from the fast pyrolysis of these biomass species at three different temperatures (500, 600 and 700 °C) were analyzed by Py-GC/MS. In spite of the different nature of the feedstock, the bio-oil produced from the pyrolysis of all the biomasses at the three temperatures studied is mainly composed of phenols (with a relative content in the 19–26.5 % range), acids (14.6–19.5 %), ketones (13.4–19.2 %) and levoglucosan (6.7–15.4 %). Temperature has a moderate effect, leading to a decrease in the relative content of all component families, except aldehydes and hydrocarbons, when it is increased. Biochars produced at 500 °C show high calorific values, as well as low H/C and O/C ratios, which prove their high stability in the soil. These results are clear evidence that the valorization of these invasive plants by pyrolysis may be an effective strategy for the mitigation of their associated impacts.

1. Introduction

The colonization of invasive plants has posed different threats to local biodiversity, ecosystem services, environmental quality, and human health, involving a significant cost on the global economy [1]. In this regard, the Intergovernmental Platform and Ecosystem Services of the United Nations (UN) has foreseen that almost a fifth of the earth's surface is at risk due to biotic invaders [2]. Therefore, the management of these plants is crucial in order to mitigate their negative impact. Nevertheless, the elimination of these invasive species does not always involve a total or partial recovery of native biodiversity, which is evidence that their management often becomes intrinsically complex [3]. Indeed, the removal of these plants produces significant volumes of residual biomass, which are dumped outdoors with negative effects on water and soil quality, in addition to contributing to summertime fire hazards.

In Colombia, it is estimated that there are more than 300 invasive species, with the most studied ones being prickly broom, giant snail, bullfrog, lionfish, poet's eye, water hyacinth and African palm [4,5].

However, there are other plants of growing concern that have disrupted several ecosystems in Colombia and other American countries in the last few years, which have hardly been studied. Thus, elderberry (*Sambucus nigra*), red gum (*Liquidambar styraciflua*), rue (*Ruta graveolens*) or yarumo (*Cecropia telenitida*) are invasive and colonizer species that are causing major ecological problems. Furthermore, certain plants, such as wax flower (*Clusia orthoneura*), account for a huge volume of residues and are responsible of several wildfires. Therefore, there is an urgent need of reducing their presence in the affected areas, while contributing to circular economy by means of their appropriate management [6]. However, to date, there have been few studies on the characterization of these species, and research on their valorization via biological or thermal processes is even scarcer. In particular, conversion of biomass residues by means of thermochemical processes, such as pyrolysis, gasification and combustion, are well-known and encouraging routes for their high efficiency, which may contribute to controlling biological invasion, seeking reuse and achieving energy recovery [7]. Within the aforementioned thermochemical processes, pyrolysis is the most efficient one for obtaining products involving the highest contribution to

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circular economy, due to its lower greenhouse gases (GHG) emissions [8, 9].

Biomass fast pyrolysis, which is carried out at high heating rates and for short residence times of the volatile compounds, leads to high bio-oil yields (60–75 % wt%), a gas yield in the 5–25 wt% range and a biochar production between 15 and 35 wt% [10,11]. Bio-oil is a complex mixture of oxygenated compounds, whose composition varies depending on the biomass features and operating parameters (mainly temperature, heating rate and residence time). This liquid product may have several applications, such as source of chemicals or fuel for boilers, or may be upgraded to transportation fuels and chemicals by means of several catalytic processes [11,12]. However, the economic viability of the biomass pyrolysis process requires recovering also the solid product. Indeed, it has been reported that the biochar derived from invasive plants present an excellent porous structure, adsorption properties and chemical stability, and therefore turn out to be as suitable as the biochars derived from the traditional biomasses used for environmental remediation and agricultural soil amendment applications [6]. Therefore, research involving the production of both bio-oil and biochar from biomass is appealing to academic and industrial communities, as it proves to be effective in resource utilization and contributes to promoting circular economy [13].

Pyrolysis coupled with gas chromatography and online mass spectroscopy (Py-GC/MS) is a well-established and reliable technique that is useful for directly analyzing the volatile stream from pyrolysis [14,15]. Thus, this process allows comparing and assessing the products evolved from the pyrolysis of different biomasses under a controlled temperature program, providing valuable information of their valorization potential [14]. The aforementioned advantages have led to numerous studies dealing with the pyrolysis of various biomass feedstock using Py-GC/MS. However, the valorization of invasive biomass species has been scarcely studied in the literature.

This work aims at contributing to the management by pyrolysis of five invasive biomass species of growing concern in Colombia (elderberry, rue, red gum, wax flower and yarumo), which have not been studied in the bibliography, neither in relation to their characterization, nor to their valorization. Thus, firstly, the chemical properties of the biomasses were determined. Secondly, the pyrolysis of these species is addressed, focusing on the production of bio-oil and biochar. A detailed description of the pyrolysis behavior by Py-GC/MS under different operating temperatures was carried out, relating the effect of both temperature and composition of the biomasses with the product distributions obtained and assessing the feasibility of their use for the production of fuels and chemicals. Furthermore, biochar has been also characterized in order to ascertain its fuel properties and soil amendment capacity.

2. Materials and methods

2.1. Preparation and characterization of the biomass samples

Five different types of biomasses have been selected, which are invasive or colonizer species in Colombia, leading to major management problems and threats to the ecosystems, as well as wildfires hazards. Elderberry (*Sambucus nigra*), native to Europe, Northwest Africa and Southeast Asia, is a species found in Colombia, United States, Bolivia, Chile and Ecuador [16]. The *Altingiaceae* family's red gum (*Liquidambar styraciflua*), originally from Northeast America, is a 20- to 25-meter-tall hardwood, deciduous, monoecious and aromatic tree, which is widely distributed in the United States, Mexico, Central America, Colombia, and Brazil [17]. Rue (*Ruta graveolens*) is a species of *Rutaceae* that is native to Southern Europe, which is found in temperate and tropical regions around the world. It is usually cultivated as an ornamental garden plant, especially for its tolerance to dry soils and heat, but has also been used as a medicinal herb and seasoning [18]. Yarumo (*Cecropia telenitida*) is native to the Andes from Venezuela to Peru,

including the Colombian mountain range. This species has been also selected because of its significant ecological impact due to its rapid growth rate, which makes it the first colonizer of deforested tropical areas, and therefore an invasive species in non-native regions [19]. Finally, wax flower (*Clusia orthoneura*), a shrub found in tropical America [20], is a plant that has been reproduced in large quantities and causes forest fires during summer season.

The biomass samples were collected on the premises of the Universidad de los Andes (Bogotá, Colombia) and taken from the Environmental Engineering Research Center, where they were dried at room temperature for 72 hours. Finally, they were crushed in a Retsch SM 2000 mill (Retsch, Haan, Germany) into a particle size of 0.125 mm - 0.25 mm and stored in Ziploc bags to prevent moisture adsorption.

The ultimate analysis of the biomasses has been carried out following the ASTM-D5373 standard in a Vario-Macro elemental analyzer. The higher heating value (HHV) has been measured following the ASTM-D5865 standard, by means of a Parr 6200 isoperibolic bomb calorimeter (Parr Company, Moline, USA). The chemical composition, i.e., hemicellulose, cellulose, and lignin contents, has been determined according to a methodology previously proposed, based on the deconvolution of the Derivative Thermogravimetry (DTG) curve obtained through a thermogravimetric analysis [21–23]. Finally, the proximate analysis, which evaluates fixed carbon, ash, volatile matter and moisture contents, was performed according to ASTM D5142, using a TGA 5500 Discovery equipment (TA Instruments, New Castle, USA).

2.2. Py-GC/MS analysis

The pyrolysis–gas chromatography/mass spectrometry has been carried out in a CDS Pyroprobe® Model 5150. The biomass sample, 1 mg, was introduced into the pyrolysis tube surrounded by quartz wool. The experiments with each biomass were conducted at 500, 600 and 700 °C for 40 s, and the volatiles generated were injected into the gas chromatography/mass spectrometry analyzer (GC/MS) (QP2010 Shimadzu) by means of a thermostated line. The chromatograph was provided with a BPX-5 column (30 m x 0.22 mm ID, 0.25 µm film thickness) and the temperature sequence of the oven started with steady heating from 45 °C to 295 °C followed by a ramp of 4 °C min⁻¹ for separating the volatile products, with this temperature being kept for 5 min to remove all products from the column. The analyzed compounds were identified based on the National Institute of Standards and Technology (NIST) library. The runs were repeated at least 3 times to ensure reproducibility and standard deviations were calculated. The quantity of each compound was determined by the average values of the areas under the peak in Total Ion Chromatograph (TIC) and Selected Ion Monitoring (SIM) modes.

2.3. Biochar production

In order to assess the potential of both the bio-oil and the biochar obtained from these invasive biomasses, biochar was produced at 500 °C in a fixed-bed reactor previously described in other studies [24–26]. Biochar samples were analyzed by measuring the higher heating value (HHV) and ultimate analysis to obtain the H/C and O/C ratios required to determine their degradation conditions over time.

3. Results and discussion

3.1. Characteristics of the starting materials

Table 1 shows the proximate and ultimate analyses, the higher heating values and the compositional analyses of the five biomasses studied. It is observed that the amount of volatile matter in all species is between 68 and 77 wt%, which is similar to those reported for other plant species [27,28]. These values evidence the high potential of these biomasses for their valorization by pyrolysis, as volatile matter

Table 1
Characterization of the studied biomasses.

	Elderberry	Rue	Red gum	Wax flower	Yarumo
Proximate analysis^a					
Moisture content (wt%)	1.20 ± 0.025	1.02 ± 0.021	1.69 ± 0.035	1.24 ± 0.026	1.69 ± 0.035
Volatile matter content (wt%)	74.28 ± 1.560	72.73 ± 1.527	73.40 ± 1.541	77.91 ± 1.636	68.67 ± 1.442
Ash content (wt %)	7.37 ± 0.155	5.75 ± 0.121	7.74 ± 0.163	8.73 ± 0.183	17.12 ± 0.360
Fixed carbon (wt %)	17.15 ± 0.360	20.50 ± 0.431	17.18 ± 0.361	12.10 ± 0.254	12.52 ± 0.263
Ultimate analysis^b					
Carbon (wt%)	44.49 ± 0.934	40.11 ± 0.842	46.62 ± 0.979	42.13 ± 0.885	38.37 ± 0.806
Hydrogen (wt%)	5.47 ± 0.115	4.28 ± 0.090	4.12 ± 0.087	4.11 ± 0.086	4.02 ± 0.084
Nitrogen (wt%)	4.06 ± 0.085	2.97 ± 0.062	0.45 ± 0.009	1.01 ± 0.021	0.89 ± 0.019
Oxygen (wt%)	45.53 ± 0.956	52.26 ± 1.0997	48.64 ± 1.021	52.55 ± 1.104	56.53 ± 1.187
Sulfur (wt%)	0.45 ± 0.009	0.39 ± 0.008	0.18 ± 0.004	0.19 ± 0.004	0.20 ± 0.004
H/C ratio	0.12 ± 0.003	0.11 ± 0.002	0.09 ± 0.002	0.10 ± 0.002	0.11 ± 0.002
Higher heating value^a					
HHV (MJ/kg)	20.11 ± 0.422	17.24 ± 0.362	18.94 ± 0.398	17.41 ± 0.366	16.94 ± 0.356
Compositional analysis^a					
Cellulose (wt%)	25.2 ± 0.529	24.58 ± 0.516	23.31 ± 0.490	29.01 ± 0.609	25.65 ± 0.539
Hemicellulose (wt%)	17.75 ± 0.373	21.58 ± 0.453	18.11 ± 0.380	22.05 ± 0.463	19.49 ± 0.409
Lignin (wt%)	48.69 ± 1.022	47.25 ± 0.992	49.36 ± 1.037	39.36 ± 0.827	36.70 ± 0.771

^a As received basis

^b Ash free basis

represents the fraction of the fuel that can be easily volatilized. Fixed carbon contents are comparable to those reported for other species. Thus, rue stands out for having a fixed carbon content of 20 %, which is comparable to what is found in nut and olive seeds [22]. Interestingly, the ash content of these biomasses is of around 6–9 wt%, with this value being slightly higher than those reported for wood and woody biomass, but lower than the ones found in grasses and agricultural residues [28, 29]. Yarumo is the exception, whose ash content is as high as 17.12 wt%, which is attributed to its tendency to colonize degraded areas. High ash contents are related to high biochar and gas yields in pyrolysis, as well as the risk of creating inorganic vapors when devolatilization occurs at high temperatures [10,30,31].

Low nitrogen and sulfur contents in the biomasses is an encouraging fact for their use in thermal conversion processes, as this leads to low pollutant emissions. However, elderberry and rue have a high nitrogen content, which enhances the formation of NH₃ and HCN in the gaseous phase [32]. All the biomasses are characterized by having a high carbon content, with red gum having the highest one (46.62 wt%), which favors the production of a bio-oil with best perspectives for its valorization, as well as a biochar with a high calorific value [10]. Nevertheless, yarumo has the lowest carbon content, which is associated with its trend for colonizing degraded areas.

Regarding the higher heating value (HHV) of these plants, values above 16 MJ/kg have been measured. Elderberry is the one with the highest HHV of 20.11 MJ/kg, which is similar to those reported for seeds of different plants used for biofuel production, such as olive stone (20.36 MJ/kg) or nut shell (20.12 MJ/kg) [22]. In addition, rue and red gum have HHV values close to those reported for other invasive species, such as *Ulex europaeus* and *Genista monspessulana*, i.e., between 18 and 21 MJ/kg [4,5]. These figures are evidence of the great potential of these types of species for producing biofuels through thermal processes, thus

allowing their exploitation in areas where they have been introduced, and therefore reducing the environmental impacts associated with these species in tropical zones. In contrast, wax flower and yarumo have a lower HHV compared to the other invasive species, but still high in relation to other residual biomasses, such as rice husk, which has been extensively studied and used in thermal processes [22].

Finally, it is noteworthy that all the biomasses studied have high lignin contents, with this constituent being the most abundant one, followed by cellulose and hemicellulose. This particular sequence, Lignin-Cellulose-Hemicellulose, has also been found in other herbageous, agricultural and forestry biomass varieties [29,33,34]. High lignin contents are associated with high biochar yields [35], which is evidence of the interest of the valorization of these biomasses seeking for the production of both bio-oil and biochar. Knowledge of the composition of the three biomass polymers is essential for the prediction of pyrolysis fraction yields and their composition (especially that of bio-oil), as well as for understanding the pyrolysis reaction kinetics [31,35,36].

3.2. Py-GCMS results

According to numerous biomass pyrolysis studies, hemicellulose and cellulose undergo pyrolysis between 290 and 450 °C, while lignin degradation starts at lower temperatures (250 °C) and extends up to 600 °C [31,36,37]. Accordingly, 500 °C, 600 °C, and 700 °C have been selected as suitable experimental temperatures for Py-GC/MS runs. The organic volatile compounds evolved from the pyrolysis of the five biomass species have been grouped into functional groups, namely, acids, ketones, aldehydes, phenols, alcohols, furans, saccharides, hydrocarbons and others (heterocyclic compounds).

Fig. 1 shows the peak area percentage of the organic functional groups detected in the pyrolysis volatile streams of the biomasses studied in this work at different temperatures, whereas Table 2 displays those of the main individual compounds identified. It is observed that the pyrolysis of these biomass species leads to a wide range of organic compounds, with variable yields depending on the biomass type and pyrolysis temperature. Thus, these two variables, apart from the reactor type (which encloses the heating rate and volatiles residence time), have been reported as the main parameters affecting bio-oil yields and properties in the literature [10,12,30].

3.2.1. Effect of biomass type on pyrolysis volatiles

As shown in Fig. 1 and Table 2, phenols are the main compounds identified for the five plant species, which is clearly attributed to the high lignin content of these biomasses (Table 1) [31,35,36]. Furthermore, it has been reported that cellulose significantly promotes the synthesis of these lignin derived compounds, leading to high productions in the pyrolysis of lignin and cellulose rich biomasses, such as the ones employed in the current study [38,39]. As observed in Fig. 1, phenolic content is remarkable for rue and yarumo, whereas wax flower leads to the lowest peak area values. These compounds have been grouped in the literature into three lumps: catechols (benzenediols), guaiacols (methoxyphenols) and alkyl-phenols. According to the results displayed in Table 2, alkyl phenols are the main compounds from elderberry, wax flower and yarumo, whereas catechols arise mainly from rue and red gum, and their content is also significant in the remaining species. The content of guaiacols is meaningful only in the volatile stream from the pyrolysis of elderberry and rue, whereas they have not been detected for wax flower and yarumo. Thus, these last two species present the highest cellulose/lignin ratio, which has been reported to promote lignin demethoxylation [40]. As aforementioned, Py-GC/MS has been used for assessing the valorization potential of several biomass species differing in their character [14]. The studies published in the literature report that phenols are the main compound family in the pyrolysis of leguminous species [41,42], switchgrass and doob grass [43,44], as well as olive pomace, nut and almond shell [45].

Apart from phenol compounds, acids and ketones are the most

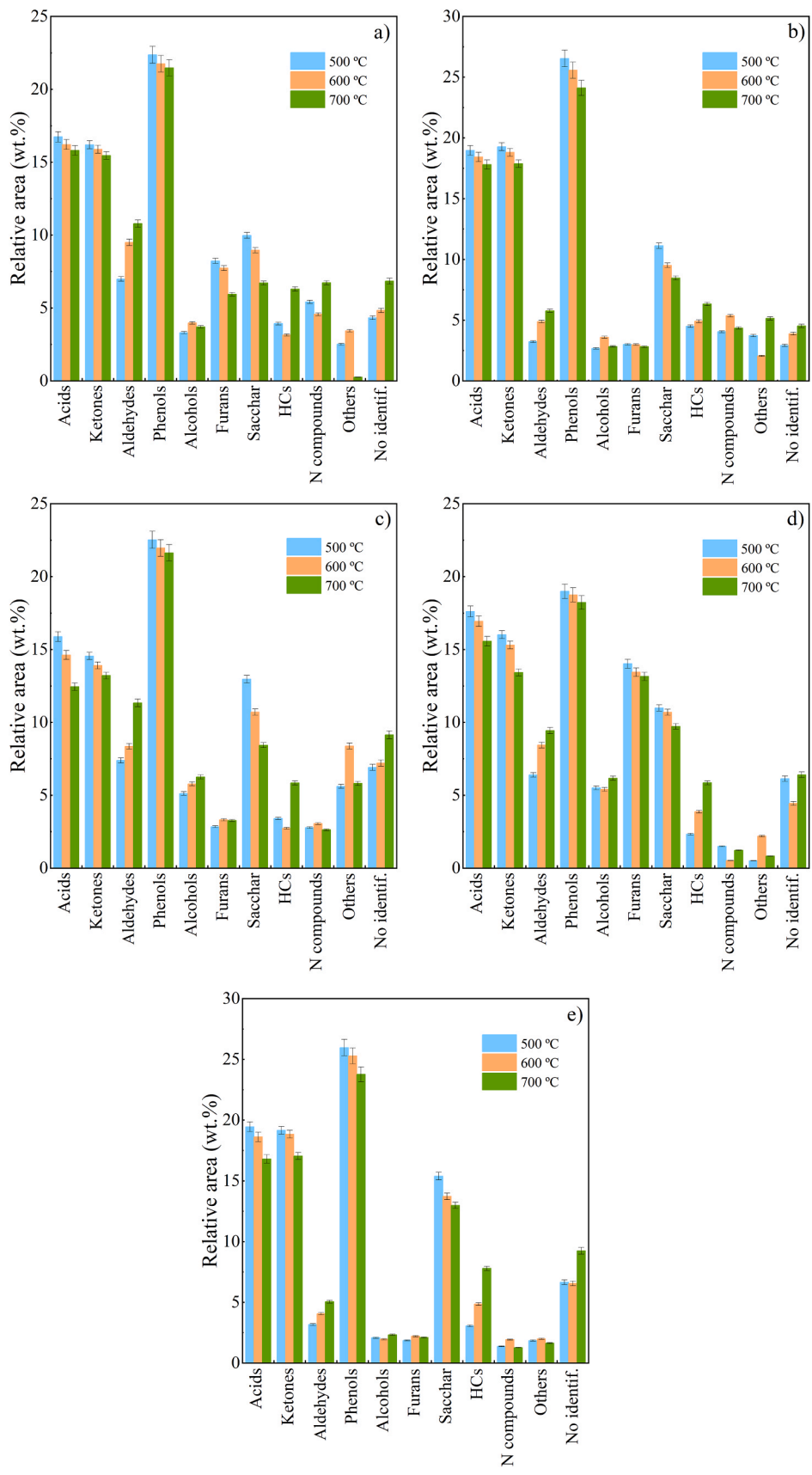


Fig. 1. Effect of temperature on the production of functional groups in Py-GC/MS runs. a) elderberry, b) rue, c) red gum, d) wax flower, and e) yarumo.

Table 2

Relative peak areas of the main volatile products produced by the pyrolysis of the five biomasses in Py-GC/MS runs.

Groups	Compounds	Formula	Elderberry 500°C/600°C/ 700°C	Rue 500°C/600°C/ 700°C	Red gum 500°C/600°C/ 700°C	Wax flower 500°C/600°C/ 700°C	Yarumo 500°C/600°C/ 700°C
Acids	Total		16.74/16.21/ 15.81	18.97/18.43/ 17.81	15.88/14.62/ 12.45	17.61/16.94/ 15.56	19.45/18.62/ 16.81
	Acetic acid	C ₂ H ₄ O ₂	8.09/7.23/6.16	11.03/10.25/7.12	6.13/5.35/4.24	7.18/6.28/4.64	12.78/11.61/ 11.24
Ketones	Tetradecanoic acid	C ₁₄ H ₂₈ O ₂	3.88/8.60/0.00	7.94/8.18/7.19	7.25/5.79/8.04	8.30/10.28/6.40	6.67/7.01/5.56
	Total		16.20/15.89/ 15.46	19.27/18.81/ 17.88	14.55/13.90/ 13.21	16.01/15.30/ 13.42	19.16/18.83/ 17.04
Aldehydes	2-Propanone, 1-hydroxy-	C ₃ H ₆ O ₂	5.41/4.75/3.72	7.77/6.36/3.88	0.71/0.57/0.33	4.24/3.51/1.99	5.43/4.75/3.72
	2-Cyclopenten-1-one	C ₆ H ₈ O ₂	1.68/-/0.74	1.07/0.50/0.70	0.44/1.29/-	0.85/0.74/0.93	1.36/1.99/0.92
	Total		6.99/9.50/10.79	3.23/4.88/5.77	7.39/8.36/11.34	6.40/8.44/9.43	3.17/4.06/5.04
Phenols	Furfural	C ₅ H ₄ O ₂	-/0.40/1.40	0.16/1.48/0.82	1.09/1.21/1.19	2.05/2.53/4.09	1.20/2.37/1.98
	Benzaldehyde	C ₇ H ₆ O	0.58/0.71/0.93	0.45/0.54/1.31	0.58/0.89/0.14	0.35/0.45/1.51	0.23/0.89/0.64
Alcohols	Total		22.37/21.75/ 21.48	26.54/25.58/ 24.11	22.52/21.93/ 21.63	18.99/18.75/ 18.22	25.97/25.29/ 23.76
	Alkyl phenols		14.60/16.53/ 19.28	4.37/5.51/4.87	6.25/10.50/11.90	10.97/7.64/8.12	12.21/14.91/ 14.22
Furans	Catechols		4.58/4.99/2.20	16.61/17.66/ 15.63	13.65/11.46/9.74	8.02/11.11/10.11	13.77/10.37/9.55
	Guaiacols		3.19/2.47/-	5.56/4.10/3.62	2.63/-/-	-/-/-	-/-/-
Alcohols	Total		3.31/3.97/3.70	2.67/3.59/2.83	5.12/5.78/6.26	5.51/5.40/6.17	2.08/1.95/2.33
	Lineal		2.71/3.97/3.70	2.67/3.06/2.38	5.12/5.78/2.14	4.03/4.93/6.17	2.08/1.5/2.33
Furans	Cyclic		0.60/-/-	-/0.53/0.45	-/4.12	1.48/0.47/-	-/-/-
	Total		8.23/7.73/5.94	3.01/2.98/2.81	2.84/3.31/3.27	14.02/13.44/ 13.15	1.86/2.20/2.10
Saccharides	Benzofuran, 2,3-dihydro-	C ₈ H ₈ O	4.85/5.91/5.26	1.59/1.59/1.59	-/0.38/-	-/1.89	-/1.10/1.72
	2-Furanmethanol	C ₅ H ₆ O ₂	0.90/0.94/0.67	0.60/0.89/0.45	0.79/1.55/0.71	0.52/0.33/0.27	0.49/1.11/0.38
	2,5-Furandione, dihydro-3-methylene	C ₅ H ₄ O ₃	-/-/-	-/0.50/0.77	-/0.40	7.59/7.01/3.19	-/-
Hydrocarbons	Total		9.98/8.97/6.71	11.12/9.51/8.47	12.96/10.70/ 8.43	10.99/10.70/ 9.72	15.39/13.72/ 12.98
	Levoglucosan	C ₆ H ₁₀ O ₅	9.98/8.97/6.71	11.12/9.51/8.47	12.96/10.70/8.43	10.99/10.70/9.72	15.39/13.72/ 12.98
N-compounds	Total		3.93/3.14/6.30	4.50/4.91/6.33	3.41/2.74/5.85	2.33/3.87/5.85	3.06/4.85/7.79
	Aliphatic		0.94/0.58/1.53	1.63/1.65/3.71	3.41/1.50/5.65	2.33/1.87/3.37	3.06/4.85/6.65
Others	Aromatic		3.10/2.57/4.78	2.87/3.26/2.62	-/1.24/0.20	-/2.00/2.48	-/1.14
	Total		5.42/4.57/6.73	4.04/5.37/4.35	2.78/3.05/2.63	1.50/0.52/1.23	1.37/1.93/1.26
Not identified	Pyrrrole	C ₄ H ₅ N	1.96/1.24/2.46	2.37/2.56/1.69	0.62/0.22/0.27	0.79/0.52/1.23	1.37/1.93/1.26
	Total		2.51/3.43/0.26	3.73/2.05/5.14	5.62/8.37/5.81	0.51/2.20/0.83	1.85/1.99/1.64
	Total		4.32/4.83/6.84	2.93/3.88/4.53	6.91/7.21/9.14	6.13/4.44/6.41	6.65/6.55/9.25

abundant ones in all the biomasses (Fig. 1). Thus, the content of ketones in the stream from rue and yarumo surpasses that of acids, whereas that of acids is higher in the stream from wax flower, and both contents are similar in the case of elderberry and red gum. As observed in Table 2, acetic acid is the main compound in all the biomasses studied, but the presence of a high molecular weight compound, i.e., tetradecanoic acid, has been also detected. Acetic acid has been reported to be mainly derived from hemicellulose pyrolysis [35,37], and is one of the major compounds identified in the bio-oil produced in the Py-GC/MS of several biomass types [14]. Similarly, high molecular weight acids, such as hexadecanoic acid, were also detected in the Py-GC/MS of sawdust and different lignocellulosic agricultural residues [46], tobacco waste [47] and waste dahlia flower [48]. Regarding ketones, acetol (hydroxypropanone) is the main product identified in all cases, except red gum, with the content of 2-cyclopenten-1-one being significant in all biomasses. Ketones are mainly produced from the decomposition of both cellulose and hemicellulose, resulting from the ring-opening and cracking of monosaccharide units [31,38]. Acetic acid and acetol were also typically identified as the main compounds in the acids and ketones families obtained in the Py-GC/MS of date palm [49], bamboo [50], different leguminous biomasses [41], flowering plants [48,51] and several agricultural residues [46,47].

Levoglucosan has been the unique compound identified in the saccharides group (Table 2), whose formation from cellulose has been reported in literature [36]. Although the cellulose content in all the biomasses studied is rather low, a high relative content of levoglucosan was obtained from all them, especially from yarumo. Indeed, high ash

and lignin contents have been regarded as levoglucosan formation suppressors due to the catalytic effect of the former and the interference in the levoglucosan chain-end mechanism of the later [31,38]. However, other authors observed that certain types of lignin, specifically those containing a significant number of covalent lignin-cellulose bonds, hinder the cellulose-lignin interactions that lead to a decrease in the levoglucosan yield [39,52].

The presence of furans stands out in the pyrolysis volatiles of wax flower, which is associated with its high hemicellulose content (Table 1) [31]. The main compounds identified were furandione from yarumo and benzofuran from elderberry (Table 2). Aldehydes are more abundant in the volatiles derived from elderberry, red gum and wax flower than from the remaining biomasses, and they stem from the decomposition of hemicellulose [35]. Furfural has been the major compound identified in the volatiles evolved from the five biomass species, although benzaldehyde contribution is also important. The content of alcohols is relatively low for all the biomasses studied. Although both linear and cyclic alcohols have been identified in the pyrolysis of these species, long chain alcohols are the prevailing ones. Lignin is the main responsible for alcohol formation, even though, as previously mentioned, the main products derived from this biomass constituent are phenols [31]. These results are consistent with the findings in other studies involving Py-GC/MS of other biomasses [41–43,49–51].

Finally, several hydrocarbons have also been obtained in the pyrolysis of these biomass species. As observed in Table 2, the content of non-aromatic compounds is higher than that of aromatic ones, except for elderberry and rue, which is consistent with the findings reported in the

Py-GC/MS of certain nutshells [53,54]. Long chain paraffins and olefins have been typically identified, whereas toluene has been the main aromatic compound. Nitrogen containing compounds are also present in the volatiles formed in the pyrolysis of all the biomasses, with pyrrole being the major one identified. The volatile streams from elderberry and rue lead to the highest contents of nitrogen compounds due to their higher nitrogen contents in the initial biomasses (Table 1). Several hydrocarbons and nitrogen-containing compounds were also reported in the Py-GC/MS of date palm [49], leguminous biomasses [41,42] switchgrass [43], agricultural wastes [45,47] and flowering plants [51]. Indeed, certain biomasses, such as waste groundnut shell [55] or abolition stalk waste [54], have been reported to produce a bio-oil with a prevalence of nitrogen containing compounds. It is therefore to highlight the low nitrogen proportion in the volatiles evolved from wax flower and yarumo.

Numerous studies have been published in recent years dealing with the effect biomass composition has on the composition of the volatiles produced, the pyrolysis mechanisms and the products of the main biomass constituents, as well as the interactions occurring among them [31,35,36]. However, due to these interactions between hemicellulose, cellulose and lignin, as well as those involving other biomass constituents, such as extractives and ash, it is very complex to predict the composition of the volatiles formed in the pyrolysis process [31]. In addition to the biomass composition, other characteristics, such as biomass morphology, play an important role in the final product distribution due to their effect on heat transfer and diffusion processes [38]. Although the biomasses studied in the current study have differences in their character, their chemical composition follows the sequence Lignin-Cellulose-Hemicellulose, resulting in bio-oils that contain the same main functional groups, whereas there are the relative contents of the individual compounds the ones changing depending on the biomass species. These results give rise to the possibility of their joint valorization by pyrolysis. Moreover, the similar composition and lignocellulosic nature of these species leads to the formation of similar volatile compounds as those obtained in the pyrolysis of typical woody biomasses (pine, eucalyptus, beech and so on) and agricultural residues (such as rice husk). Indeed, various studies reported that phenols, ketones and acids were the main functional groups in the bio-oils obtained from these conventional biomasses [56–59]. Therefore, the results obtained for the volatile stream composition reinforce the suitability of pyrolysis for the management of these invasive species.

3.2.2. Effect of temperature on pyrolysis volatiles

The results displayed in Fig. 1 and Table 2 reveal a moderate effect of temperature on the relative peak areas of the volatiles formed in the pyrolysis of the five biomass species. Furthermore, the trends observed are consistent with those previously reported in the literature for similar raw materials. Thus, low temperatures (below 500 °C) enhance the production of condensable volatile components, whereas temperatures above 500 °C enhance cracking reactions leading to incondensable gaseous products [10,36]. Therefore, as observed in Fig. 1, the content of almost all the functional groups decreases as pyrolysis temperature is increased from 500 to 700 °C, except for aldehydes and hydrocarbons.

Analyzing the influence temperature has on the relative peak area of the individual components (Table 2), the content of acetic acid is reduced as temperature is increased in all cases, but the one of tetradecanoic acid peaks at intermediate temperatures (except for red gum). At high temperatures, decarboxylation of acids hinders their formation, which has also been observed in the Py-GC/MS of date palm [49], gumweed [51], several agricultural wastes [46,60], nut shells [53,54] and switchgrass [43].

Similarly, the contribution of ketones to the volatile stream formed at 700 °C is lower than that obtained at the lowest temperature used in this study, 500 °C. The main responsible of this reduction is acetol (1-hydroxy-2-propanone), whose content is considerably reduced with temperature for all the biomasses studied (Table 2). The yield of heavier compounds shows a similar trend (though more pronounced for

elderberry and yarumo), i.e., an overall decrease in the ketones content due to the cracking occurring at high temperatures. These trends are similar to those reported for other biomasses [51,53,60,61].

As previously mentioned, aldehydes are the only oxygenated compound group whose content increases with temperature. Table 2 shows that the relative peak areas of furfural and benzaldehyde (the two main identified compounds) have a clear upward trend in the pyrolysis of elderberry and wax flower, whereas other compounds are responsible for the increase in these oxygenated compounds at 700 °C in the pyrolysis of the remaining species. Other authors observed a similar trend for several agricultural residues [46,54] and flowering plants [48,51,61], which was attributed to the secondary reactions occurring at high temperatures that diminished acids and ketones, leading to the formation of aldehydes [62].

The reduction in the peak area of phenols at high temperatures is more evident for rue and yarumo than for the remaining species (Fig. 1). In spite of the small effect temperature has on the total peak area of phenols, its influence on the distribution of the different subgroups is more evident. Thus, the presence of guaiacols reduces when temperature is increased, as they are converted into alkyl-phenols and catechols due to secondary side-chain C-C cracking reactions [37,63]. The content of catechols peaks at an intermediate pyrolysis temperature (600 °C) for elderberry, rue and yarumo. According to the relevant literature, temperatures of around 550 °C lead to a reduction in the content of catechols at the expense of the formation of incondensable gaseous compounds (mainly carbon monoxide) [63]. This is not the case for alkyl-phenols, which are stable even at high temperatures and their content increases or remains constant as pyrolysis temperature is increased.

The influence of temperature on the peak area of alcohols and furans changes depending on the type of biomass. Thus, the content of alcohols is highest at the highest temperature for red gum, wax flower and yarumo, whereas peaks at 600 °C for elderberry and rue. As far as furans is concerned, elderberry, rue and wax flower lead to a downward trend when temperature is increased, whereas in the case of red gum and yarumo their content peaks at 600 °C. Therefore, the effect of the feedstock composition makes it difficult to predict the effect of temperature on the formation of these products, thus suggesting the occurrence of strong interactions between the biomass constituents [64].

Levoglucosan content shows a gradual decline when pyrolysis temperature is increased for the five biomasses studied. The low thermal stability of this compound has been widely reported in the literature; that is, its content decreases when pyrolysis temperatures are higher than 530 °C [37,38]. However, Table 2 shows that the relative peak area of levoglucosan is high even at 700 °C for the five biomasses, which may be attributed to the complex cellulose-lignin interaction occurring in these biomasses pyrolysis. Indeed, Wu et al. [38] proposed that high temperatures weaken the cellulose-lignin bonds, thus diminishing the interactions that suppressed levoglucosan formation. A slight decrease in levoglucosan peak area as temperature was increased was also observed in the Py-GC/MS of several agricultural residues [46], date palm [49] or poplar [64].

The relative content of hydrocarbons shows an upward trend as temperature is raised for the five biomasses studied. Thus, the content of both aliphatic and the aromatic compounds increases for almost all the species studied (Table 2) due to decarboxylation and aromatization reactions occurring at high temperatures, which lead to the formation of more stable hydrocarbons [63]. This behavior is common to the pyrolysis of other types of biomasses, as a similar trend was observed for hydrocarbons in the Py-GC/MS of several agricultural residues [46,53,54,60], flowering plants [48,51] and grasses [43,44,55]. Finally, the content of nitrogen-containing compounds peaks at 600 °C in the pyrolysis of all species, except elderberry and wax flower, for which an inverse peak is observed. Nitrogen compounds undergo several complex cracking reactions with the increase in pyrolysis temperature, which lead to a high variability in their composition [65].

In view of the obtained results, it may be concluded that the organic volatile compounds obtained in the pyrolysis of the five biomass species studied in a wide temperature range are suitable for their upgrading by means of catalytic cracking, hydrodeoxygenation or reforming processes, or they are a valuable source of chemicals [66,67]. Thus, the high contents of phenols and levoglucosan make their extraction a viable alternative for the production of resins, polymers or other chemicals [68]. Moreover, the high concentrations of acids and ketones, specifically of acetic acid and acetol, encourage their subsequent steam reforming for H₂ production, as these compounds allow attaining high reforming rates [69]. Furthermore, the high hydrocarbon content is an encouraging fact for use of the pyrolysis liquid fraction in boilers or engines. In fact, this content may be further increased by means of catalytic cracking or hydrodeoxygenation (HDO) processes [70]. Indeed, the low content of furans in the volatile stream of all biomasses (except yarumo) makes these bio-oils suitable for their upgrading via HDO, as furans have been regarded as very refractory compounds to deoxygenate [71]. The nitrogen-containing compounds may entail undesirable emissions, and so must be removed by catalytic hydrodenitrogenation in the corresponding facilities [72]. It should be noted that the current study conducted in a Py-GC/MS deals with the composition of the organic components in the volatile stream, but temperature has also an influence on the water content of the bio-oil and, furthermore, leads to a decrease in the yield of bio-oil by promoting that of the incondensable gaseous fraction [10,30].

3.3. Analysis of the biochars produced at 500 °C

The biochars produced from the five biomass species in a fixed bed reactor have been chemically characterized in order to evaluate their stability in soil amendment applications. A temperature of 500 °C was selected because it has been widely reported in the literature that moderate temperatures favor biochar yield, as well as provide maximum bio-oil yields [10,11].

Table 3 shows the ultimate analysis and HHV of the five biochars. As expected, all the solid products have high carbon contents, with elderberry, rue and red gum being the ones that lead to the highest amount of this element. High carbon contents are closely related to favorable physicochemical properties, as are high cation exchange capacity (CEC), high porosity and large surface area, among others [73,74]. In addition, the application of biochar to crops can improve soil properties, for which the presence of nitrogen is also beneficial [75]. Furthermore, using biochar for soil applications aids carbon sequestration and reduces the concentration of CO₂ in the atmosphere, leading to a reduction of up to 12 % per year in the global amount of greenhouse gas (GHG) emissions [76].

The ultimate analysis shown in Table 3 is evidence of a biochar with superior fuel qualities compared to the raw materials (Table 1). Thus, carbon content was incremented by 55–65 %, while hydrogen content was decreased by 85 %. Accordingly, the higher heating values of the biochars were also improved by 70 %, which is consistent with the data published in the literature for other invasive plants of a similar nature, such as trees, bushes or flowering plants [6,77].

Table 3

Properties of biochar produced at 500 °C.

Parameter		Elderberry	Rue	Red gum	Wax flower	Yarumo
Ultimate analysis ^a	Carbon (wt%)	73 ± 1.533	72.66 ± 0.896	72.69 ± 1.526	70.93 ± 1.490	67.96 ± 1.427
	Hydrogen (wt%)	0.8 ± 0.017	0.63 ± 0.630	0.6 ± 0.013	0.6 ± 0.013	0.59 ± 0.012
	Nitrogen (wt%)	0.67 ± 0.014	0.49 ± 0.490	0.07 ± 0.001	0.17 ± 0.004	0.15 ± 0.003
	Oxygen (wt%)	9.32 ± 0.196	12.07 ± 0.253	11.54 ± 0.242	8.23 ± 0.173	10.44 ± 0.219
	Sulfur (wt%)	0.17 ± 0.004	0.15 ± 0.003	0.07 ± 0.001	0.07 ± 0.001	0.08 ± 0.002
H/C ratio		0.13 ± 0.003	0.10 ± 0.002	0.10 ± 0.002	0.10 ± 0.002	0.10 ± 0.002
O/C ratio		0.10 ± 0.002	0.12 ± 0.003	0.12 ± 0.003	0.09 ± 0.002	0.12 ± 0.003
HHV (MJ/kg)		28.56 ± 0.600	24.48 ± 0.514	26.89 ± 0.565	24.72 ± 0.506	24.05 ± 0.505

^a As received basis

The H/C and O/C ratios of the biochars are indicators of the stability of these materials, thus involving a higher carbon sequestration capacity [78]. It has been reported that H/C and O/C ratios below 0.4 are required in order to ensure biochar stability [78,79]. As observed in Table 3, all the biochars have O/C ratios lower than 0.2, with this value being estimated to have a minimum half-life of 1000 years [79]. However, as the oxygen content of the samples is calculated by difference, whereas that of hydrogen was determined experimentally, it is more reasonable to use H/C ratio for evaluating stability. Accordingly, as all the biochars have H/C values of around 0.1, a half-life in nature higher than 1000 years can be estimated [80]. Pyrolysis temperature plays a crucial role in this regard, as biochars produced at 500 °C have been reported to have a half-life ranging from 100 to 1000 years when incorporated into the soil, making this temperature optimal for their production [81].

Fig. 2 displays the Van Krevelen diagram for the biochars obtained in this study, together with the ones reported in the literature for other chars obtained at 500 °C for different biomasses, such as wood, agricultural straw and stalk, grasses, chicken manure, cotton hulls and others [82]. As observed, all the biochars produced in the current study meet the IBI (International Biochar Initiative) and EBC (European Biochar Certificate) requirements in terms of H/C and O/C ratios, which are an H/C limit of 0.7 and O/C of 0.4 [78]. The low H/C ratios (below 0.13) obtained in this study make these biochars more stable than the ones produce from other biomass sources, such as pine or oak sawdust, and close to the ones reported for the char produced from agricultural wastes, such as rice, wheat, corn and rape straw [82]. Notably, the stable chemical properties of the biochar products formed in the pyrolysis of

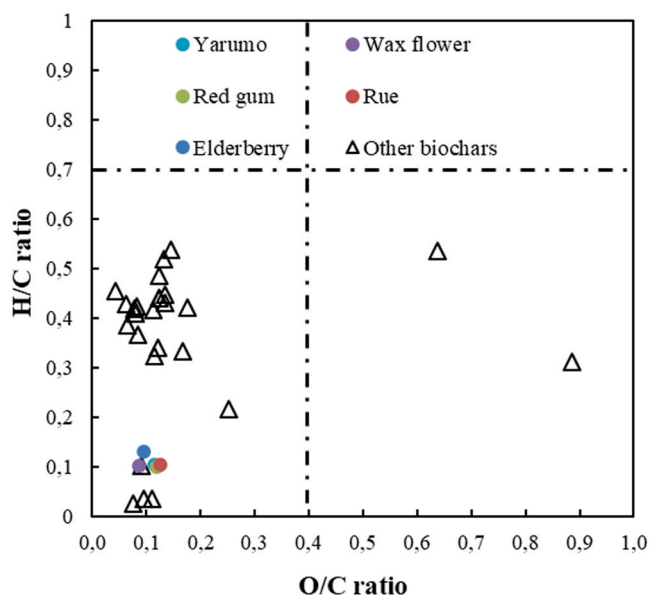


Fig. 2. Van Krevelen diagram for biochars obtained at 500 °C from the biomasses studied. Other biochars were taken from Ippolito et al. [82].

these invasive species may contribute to minimizing their negative impact on the environment [6].

4. Conclusions

The valorization by pyrolysis of five invasive biomass species (elderberry, rue, red gum, wax flower and yarumo) that cause severe problems in Colombia was assessed for the first time. Initially, the biomass samples were chemically characterized, revealing in general terms moderate ash, low sulfur and nitrogen, and high lignin contents. The results obtained by pyrolysis coupled with gas chromatography and online mass spectroscopy (Py-GC/MS) show that the prevailing groups evolved from the pyrolysis of these biomasses at the studied temperature range are phenols, acids and ketones, along with saccharides (levoglucosan) to a lower extent. In spite of the different nature of the feedstock, their compositional analysis follows lignin > cellulose > hemicellulose sequence, which leads to the formation of the same functional groups in the pyrolysis volatile stream, with their composition differing depending on the type of biomass. These results encourage their joint valorization, as well as the co-feeding with other typical pyrolysis feedstock, such as woody biomass or agricultural residues, which would highly improve the efficiency and economic viability of the management of these invasive plants.

An increase in pyrolysis temperature decreased the content of the main functional groups, raising that of aldehydes and hydrocarbons, although its effect turned out to be moderate in the 500–700 °C temperature range. Accordingly, the high relative contents of phenols (19–26.5 %) and levoglucosan (6.7–15.4 %) obtained with the five biomass species make feasible the use of the produced bio-oils as a source of chemicals. Furthermore, the remaining functional groups (ketones, acids, furans, aldehydes and hydrocarbons) have a suitable composition for their subsequent valorization by steam reforming, catalytic cracking or hydrodeoxygenation. It is noteworthy that this last upgrading process reduces the concentration of nitrogen-containing compounds, which otherwise hinder the direct application of these bio-oils as fuel.

The biochars produced at 500 °C have high carbon contents, which means an improvement in the heating value of up to 70 %, with respect to the initial biomass. Moreover, the low H/C and O/C ratios of the biochars lead to their high stability (>1000 years) in the soil, thus promoting soil amendment and carbon sequestration. Accordingly, the suitable properties of these biochars (similar to those obtained from agricultural residues) make their use an interesting option in order to promote environmental remediation in the areas where these invasive species were settled.

The result obtained in this study are highly encouraging for the proposal of future research aimed at developing the valorization of these invasive biomasses based on pyrolysis. The combined production of bio-oil and biochar turns out to be an effective upgrading approach for these species, which is evidenced by the high quality of the products obtained.

CRedit authorship contribution statement

Maite Artetxe: Writing – review & editing, Validation, Supervision, Project administration, Funding acquisition. **Gartzzen Lopez:** Writing – review & editing, Validation, Project administration, Funding acquisition, Formal analysis. **Laura Santamaria:** Writing – review & editing, Validation, Methodology, Formal analysis. **Enara Fernandez:** Writing – original draft, Visualization, Investigation. **Maidier Amutio:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **Julian E. Lopez:** Investigation, Formal analysis, Data curation. **Martin Olazar:** Writing – review & editing, Supervision, Project administration, Funding acquisition. **Juan F. Saldarriaga:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data Availability

Data will be made available on request.

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