



Research Article

Pyrolytic conversion of perennial grasses and woody shrubs to energy and chemicals

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Abstract

Spartina argentinensis, *Panicum prionitis*, and *Arundo donax* are perennial grasses and *Geoffroea decorticans* is a shrub, all of which grow under adverse conditions in the Litoral region in Argentina. The pyrolytic conversion of these biomasses was studied at 550 °C in a fixed bed reactor during 30 min under N₂ flow with a 20 °C min⁻¹ heating ramp starting at room temperature. The main products were liquid, two phases (aqueous and oil) being observed with the aqueous phases being the most important in all the cases (yields from 29.2 to 45.7 wt%). The highest yield for an oil phase (18 wt%) was observed with the shrub and the yield of gases and chars were similar in all the cases. By means of sequential vacuum distillation it was possible to selectively separate water, methanol and acetic acid which were present in the aqueous phases, thus increasing the concentration of high value compounds such as ketones, phenols and furans in the residual fraction. The concentration of phenolic compounds in the residual fraction was 60% higher than the initial one in the aqueous phase. The oil phase mainly contained phenols, ketones and acids with high molecular weight. According to these results, these biomasses can be considered as a source of energy, fuels or chemicals, and it is possible to propose a methodology to upgrade the aqueous fractions in pyrolysis liquids.

Keywords Pyrolysis · Perennial grasses · Rangelands

1 Introduction

Biomass has been a source of energy for humankind for multiple purposes since man began to control fire 1.9 million years ago. Since the Industrial Revolution, the increase in life quality is highly associated to an increase in fossil fuels consumption, as they became a major input not only for industries per se but also for heating and transportation. Two centuries later, environmental problems related to fossil fuel combustion, that had not been initially considered, began to warn society in general and researchers in particular. The Intergovernmental Panel on Climate Change [1] sustained that the steady trend in global temperature increase “is due to the observed increase in

anthropogenic greenhouse gases (GHG) concentrations in the atmosphere”. Modeling different GHG scenarios, IPCC showed with high confidence that global temperature could increase approximately 2 °C relative to pre-industrial levels even with GHG concentrations remaining below 450 ppm CO₂ eq. New energy sources can contribute to reduce GHG emissions. The use of renewable energy has increased in the last decades, associated to technological leaps, but it still represents a small share of the global energy consumption.

Besides solar, geothermal, hydropower, ocean tide, and wind energies, bioenergy is considered one of the major contributors for the mitigation of the climate change [1]. Nevertheless, at present, biomass is used with energetic

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aims mainly to produce first generation biofuels, such as bioethanol from corn and biodiesel from soybean, rapeseed or palm oil, which face severe concerns due to the high demands of energy [2] and fertilization with concomitant nitrogen losses to atmosphere (in the form of NO_x) or groundwater (as NO₃⁻) [3]. Furthermore, these biofuels compete for the same resources with the food industry, and cause loss of ecological services and biodiversity due to land use change [4]. Therefore, considering that cellulose is the most abundant organic compound on Earth, lignocellulosic materials are a sustainable option [5] with positive side effects, such as soil quality improvement [6–9].

C4 perennial grasses emerge as promising lignocellulosic feedstocks for bioenergy, given that a number of advantages are evident in the cases of, for example *Panicum virgatum* L. [10, 11], and *Miscanthus × giganteus* J.M. Greef and Deuter ex Hodk. and Renvoize [12]. These advantages can be attributed, among others, to: (1) high biomass yields even in soils of low fertility, with minimal fertilizers requirement; (2) use of available machinery for their production, and (3) positive energy balance [13]. Recently, some studies were published about the pyrolysis of grasses, which show a rising interest on the possible economic impact of this approach [14–18]; however, sounder studies are required. The pyrolysis of lignocellulosic biomass produces mainly liquid products which, generally, include an aqueous phase and a tarry, insoluble phase [19].

Subtropical rangelands span across Argentina, mostly with C4 perennial grasses that present high biomass production even growing in saline soils, with poor drainage subjected to periodic drought and floods cycles. The main economic activity in those areas is low productivity livestock production [20, 21]. Controlled fires are used as a range management tool in order to improve forage quality.

Spartina argentinensis Parodi (= *Sporobolus spartinus* (Trin.) P.M. Peterson and Saarela) is the dominant species in large inland marshes (circa 30,000 km²); and *Panicum prionitis* Nees [= *Coleataenia prionitis* (Nees) Soreng] grows along the Delta and river valley of the Parana River [21, 22]. Previous results highlight the possibility of using these perennial grasses as bioenergy feedstocks due to (1) their high resilience to disturbances [20, 23, 24] and (2) the possibility of integrating bioenergy with livestock production, considering that newly sprouted leaves are more tender as they present higher digestibility and crude protein levels in comparison with older and senescent leaves.

Chañar, *Geoffroea decorticans* (Gillies ex Hook. & Arn. Burkart) is an Argentinean woody shrub that has a dual reproductive system: sexual by seeds enclosed in stony endocarp and asexual by gemmiferous roots which

enables it to adapt to environments with discontinuous plowing and poor range management [25], restricting man and cattle traffic. Local rangers use bulldozer or fire for controlling this species in order to improve native grasses availability. Previous studies [19] showed that it is possible to obtain up to 50 wt% of liquid products from the pyrolysis of the endocarp in the chañar fruit.

Arundo donax L. is a perennial (rhizomatous) grass, widely distributed in humid temperate areas and though it is considered a problematic weed, many researchers claim that it can be used as an energy crop due to its high annual growth rates [26, 27].

It is the objective of this work is to characterize the products derived from the pyrolysis of three native Argentinian species (the grasses *Spartina argentinensis* and *Panicum prionitis*, and the woody shrub, *Geoffroea decorticans*), and the exotic perennial grass, *A. donax*. The previous description defines that in large territorial extensions such as those mentioned, the supply of these biomasses is very large, that the energy valorization and the production of fuels or chemicals seem promising, and that pyrolysis processes could be an attractive choice. Emphasis is given to the distribution of products and their physicochemical characterization. Subsidiarily, a procedure is proposed in order to improve the composition of part of the pyrolysis products by decreasing their water and acid content by means of vacuum distillation, thus increasing its potential as a raw source for chemicals. Reports in the literature about the pyrolysis of these biomasses are very scarce, if any; then, results from this study are a novel contribution to their feasible exploitation as a source for energy and chemicals.

2 Materials and methods

2.1 Biomass characterization

S. argentinensis and *P. prionitis* were obtained from rangeland near the city of Coronda and San Javier, respectively (Santa Fe province, Argentina). *S. argentinensis* was harvested using a forage cutter and a round baler. Bales were subjected to three consecutive transformations: (1) coarsely chopped; (2) chopped to 25–50 mm mesh (density 66.9 kg m⁻³); and (3) finely grinded to 0.2–0.5 mm particle size (density 165 kg m⁻³). Finally, it was pelletized without any binding agent to obtain pellets that, considering physics parameters, fall in the Enplus-A1 category. *P. prionitis* was bought to local harvesters from San Javier (Santa Fe, Argentina) as it is a grass commonly used for thatched roof. *Arundo donax* was obtained from a population growing in the experimental field of the Facultad de Ciencias Agrarias (Zavalla, Argentina) while *G. decorticans*

was cut in rangelands in the northwestern of Santa Fe province (Argentina). All biomasses were ground in a knife mill to 5–8 mm particle size range and dried in a stove at 100 °C during 24 h before pyrolysis.

The contents of water, volatile matter and ash were determined according to ASTM D3173, D3175 and ASTM D 3174, respectively, and reported on a dry basis. The amount of fixed carbon was determined by difference. The elemental compositions of biomasses were determined in a CHN628 Series Elemental Determinator (LECO) equipment. The higher heating values (HHV) were determined following Dulong's formula [28].

The thermal degradations of the biomasses were studied by means of a thermo-gravimetric/differential thermal analyzer (TGA/SDTA 851 e, Metter Toledo, Switzerland) from room temperature to 950 °C with a heating ramp of 10 °C min⁻¹. Nitrogen (99.99%) was used as carrier gas with a 50 ml min⁻¹ flow. Samples (between 2 and 5 mg) were placed in a 70 µl semispherical capsule.

2.2 Pyrolysis experiments

Raw biomasses were pyrolyzed in a fixed bed stainless steel reactor, 21.0 cm length, 1.9 cm internal diameter, heated electrically in a furnace. Each experiment required from 10 to 15 g of biomass. The heating ramp was 20 °C min⁻¹, from room temperature up to 550 °C, and maintained constant during 30 min. This final pyrolysis temperature was selected according to previous results with various biomasses, which showed that at this temperature the highest yields of liquid products were usually obtained [29, 30]. Before and during the pyrolysis, nitrogen was fed at 20 ml min⁻¹ to remove vapors from the reacting zone and consequently to minimize secondary condensation and carbonization reactions. Effluents from the reactor were passed through a condenser immersed in a salt-water solution at -5 °C where liquid products were retained and gases vented to the atmosphere. Samples were taken from both liquid and solid phases. The masses of residual solid (char) in the reactor and liquid products were determined by weighing of the unit sections before and after the experiment. The mass of gases was determined by difference. Repeated experiments were performed in order to assess standard deviations.

Pyrolysis liquid products were centrifuged at 6000 rpm during 5 min to separate the aqueous phase from the oil phase.

2.3 Enrichment of the product aqueous phase

The product aqueous phase from the pyrolysis of *P. prionitis* was distilled under vacuum in glass equipment using 200 g samples, which were heated in a water bath. Vacuum

was produced by means of a two-stage rotary vacuum pump with paddles in oil bath. Water was used to refrigerate the vapors and five fractions were collected at different temperatures, according to the conditions shown in Table 1.

2.4 Product characterization

The aqueous and oil phases, all the distilled fractions and the gas products were analyzed by conventional capillary gas chromatography in an Agilent 6890 N equipment with flame ionization detection (FID) and a HP-5 column, 30 m long, 0.32 mm of internal diameter and 0.25 µm phase thickness. In order to ease the analysis, oil phase was dissolved at 10% into methylene chloride. Gases were also analyzed on a GS-CARBONPLOT column, 30 m long, 0.53 mm internal diameter and 3 µm phase thickness with thermal conductivity detection (TCD). Product identification was performed by means of standards and GC-MS. The calibration of chromatographic areas was done with response factors for each of the chemical groups, which had been determined using mixtures of standards and a reference compound (tetralin for liquid products and methane for gases). Unidentified peaks were assigned an average response factor.

The characterization of liquid products and char also included elemental microanalysis and density for the case of liquids. Gases elemental composition was determined by means of chromatographic analysis. In the cases of the aqueous phase and the distilled fractions, the content of water was assessed by means of Karl-Fischer titration (IRAM 21320). The contents of water, volatile matter and ash were determined in the same way as for biomasses (see Sect. 2.1). pH in the various aqueous phases was determined with a HANNA HI 8424 pHmeter. Densities were determined conventionally by a conventional volume-mass method.

The high heating values (HHV) of liquid, gases and char were determined with Dulong's formula [28], and corrected in the case of the aqueous phase considering water.

The different oil fractions were subjected to FTIR analysis. Wafers (about 44 mg/cm²) were prepared by

Table 1 Distillation conditions

Fraction	Temperature (°C)	Vacuum pressure (cmHg)
1	65 ± 3	52
2	70 ± 2	52
3	75 ± 4	52
4	45 ± 5	72
5	50 ± 6	72

impregnating KBr with oil fraction from the experiments. The analysis were performed with a Shimadzu Prestige-21 instrument equipped with a high-sensitivity detector (400–4000 cm^{-1} , 40 scans, 2 cm^{-1} resolution).

3 Results and discussion

3.1 Raw materials

The properties of the biomasses are shown in Table 2. The low content of water makes them appropriate as raw material for thermochemical processes. The elemental composition of all raw biomasses and their ash contents were in the typical ranges for lignocellulosic materials [31]. Moreover, it can be seen that the HHV of grasses are lower than that of the woody shrub, in consistency with reports in the literature where, generally, grasses show HHV smaller than those from wood sawdusts [32].

These biomasses were scarcely studied; indeed, just a few reports can be found about the composition of *S. argentinensis*, *A. donax* and *G. decorticans*, or similar species such as *Spartina anglica* [32–37]. For example, 38–55% wt. cellulose, 21–23% wt. hemicelluloses and 8.1 wt% lignin were reported for *S. argentinensis* [33] and *S. anglica* [34]; 35.9 wt% hemicellulose, 29.2 wt% cellulose and 23.3 wt% lignin were reported for *A. donax* [35] and 25.8 wt% hemicellulose, 47.1 wt% cellulose and 19.8 wt% lignin were reported for *G. decorticans* sawdust [37]. No reports were found about the composition of *P. prionitis*, though a closely related grass could be considered comparatively: Imam and Capareda [38] reported 19.2 wt% hemicellulose, 32 wt% cellulose, 18.8 wt% lignin and 18.5 wt% extractives

in *P. virgatum*. Coincidentally, they all report high contents of C and O in the biomasses.

The thermal decomposition of the various biomasses is shown in Fig. 1, where it can be seen that the profiles are typical for lignocellulosic materials [39]. In all the cases the decomposition process involved three steps; in the first one, from the start of heating at room temperature to about 100 °C, corresponds to the loss of water and some volatiles (about 10–20 wt% of the biomass is lost). In the second step, where cellulose and hemicellulose decompose [40], the maximum loss of mass (about 50%) was observed for all the biomasses, the temperature at which the maximum occurred in this second stage being 320 °C (DTG curve). In the particular case of *A. donax*, this maximum shifted to about 300 °C, probably due to the high content of hemicellulose of this biomass, which decomposes before cellulose [35]. The third step develops from 400 °C to the end of the analysis, where lignin and, partially, the residual carbonaceous material decompose. These results are coincident with previous reports from other authors who used the same or similar biomasses [32, 34–36, 38]. The thermal decomposition of the main components of lignocellulosic materials (cellulose, hemicellulose and lignin) has been extensively studied [39, 41–44]. According to those reports, the decomposition of hemicellulose proceeds at temperatures between 220 and 315 °C, that of cellulose between 315 and 400 °C, while lignin decomposes in a wide temperature range from 150 to 900 °C.

3.2 Products in the pyrolysis

Figure 2 shows the product yields in the pyrolysis of the four biomasses. Three product streams were obtained in all the cases: liquid products composed by a water soluble phase (aqueous phase), and a water insoluble phase (oil phase), gaseous products, and a residual solid in the reactor (char). In all the cases, the standard deviations from repeated experiments represented less than 7% for each product yield. The highest aqueous phase yield was obtained with *A. donax*, in consistency with its high content of holocellulose, that is, cellulose plus hemicellulose and volatile matter (see Sect. 3.1). It has been shown that the pyrolysis of this biomass produces larger amounts of volatile organic compounds than lignin and the rest of components of lignocellulosic materials [40].

On the contrary, the lowest yield of liquid products was obtained with *S. argentinensis* and, in turn, the aqueous phase formed showed the highest water content, as it will be discussed later (see Table 4, Sect. 3.3). This can be the consequence, in part, of the higher content of ash and hydrogen in this grass, as compared to the other biomasses (see Table 2). It is known that the content of ash

Table 2 Composition of biomasses (wt%, dry basis)

	<i>Spartina argentinensis</i>	<i>Panicum prionitis</i>	<i>Arundo donax</i>	<i>Geoffroea decorticans</i>
Humidity	6.2	8.1	8.5	11.9
Volatile matter	69.9	71.4	70.9	66.4
Fixed carbon	22.2	24.7	25.4	29.1
Ash	7.9	3.9	3.7	4.5
Elemental composition (wt%)				
C	50.2	41.6	43.5	47.3
H	6.1	5.1	5.3	5.2
O*	35.1	48.2	47.1	42.2
N	0.7	1.2	0.4	0.8
O/C (mol)	0.5	0.9	0.8	–
HHV (MJ kg ⁻¹)	19.6	12.9	14.0	16.0

*O (wt%) = C (wt%) – H (wt%) – N (wt%) – Ash content (wt%)

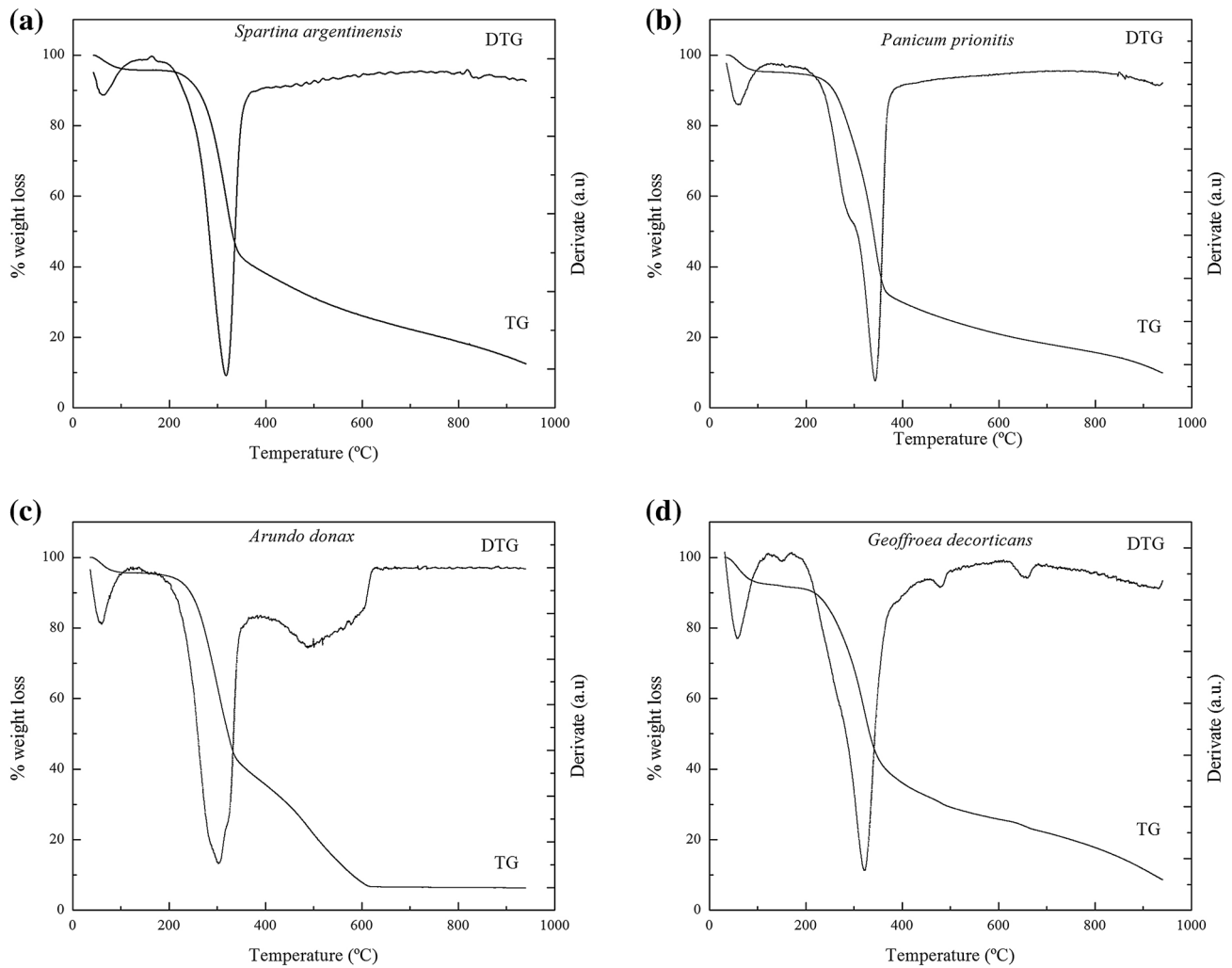


Fig. 1 Thermogravimetric (TG) and derivate thermogravimetric (DTG) curves at 10 °C min⁻¹ heating rate of the biomass

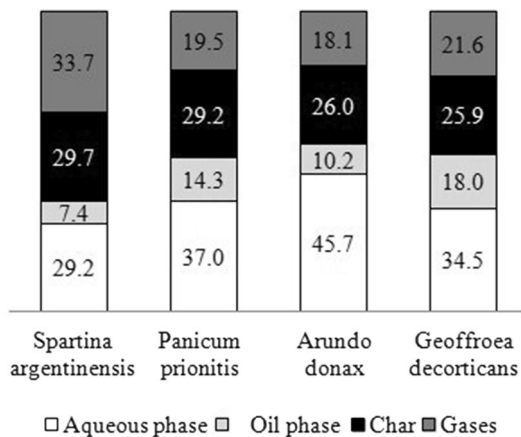


Fig. 2 Yields of products in the pyrolysis of the different biomasses (wt%)

in the raw biomass impacts on the yield of liquid organic products in the pyrolysis, given that ions, mainly K⁺ and Ca⁺², catalyze reactions leading to water and non-condensable gases. For example, Richards and Zeng [45] showed that in the pyrolysis of cotton wood K⁺, Li⁺ and Ca⁺² ions increase the yield of oil phase and decrease the yield of liquid products, which mainly include low molecular weight products. A study by Oasmaa et al. [46], including more than 30 lignocellulosic residua, showed that when the ash content increases from 0.1 to 4 wt%, the yield of liquid products in pyrolysis at 480–520 °C decreases from 60–65 to 40–45 wt% Vasiliev et al. [47] reported that the main components in ash from *P. virgatum* and *A. donax* are SiO₂ (more than 50 wt% in both cases), K₂O (*A. donax*) and CaO (*P. virgatum*).

G. decorticans, produced much more oil phase than the grasses, due to its higher lignin and fixed carbon contents [31] in this biomass.

The highest yield of gases obtained with *S. argentinensis* could also be attributed to its higher content of ash, where some metals can act as catalysts in the pyrolysis process, while char yields were similar with all the biomasses, except in the case of *S. argentinensis*, the biomass with higher C content, where it was slightly higher.

No study was found about the pyrolysis of these biomasses and the respective yields, except some publications where *A. donax* was used to produce aqueous phase and gases with energetic purposes. For example, Saikia et al. [35], who used a fixed bed reactor at temperatures between 350 and 650 °C, reported yields to be between 15 and 25 wt% for oil phase, between 4 and 9 wt% for aqueous phase, between 30 and 37 wt% for char and between 30 and 45 wt% for gases.

Moreover, it is possible to compare these results with others where biomasses from the same botanical families, with similar characteristics, were used. For example, Boateng et al. [48] investigated the pyrolysis/gasification of *P. virgatum* at temperatures between 500 and 1050 °C to evaluate the influence of the physiological maturity stage of the grass on the distribution of products. Those authors reported yields of liquid products between 58 and 76 wt%, gases between 13 and 28 wt% and char between 9 and 13 wt%. In previous studies, the fruit endocarp of *G. decorticans* was pyrolyzed under the same experimental conditions as those used in this work obtaining 47 wt% aqueous phase, 2.4 wt% oil phase and 21.4 wt% gases [19].

These results showed that these biomasses can be used as raw material for thermochemical processes leading to energy and chemical products.

3.3 Characterization of the liquid products

3.3.1 Chemical composition of oil phases

Reports about the chemical composition of pyrolytic aqueous phases and oil phases from the grasses studied in this work are scarce, while unknown in the case of *G. decorticans* sawdust.

The chemical composition of oil phases, the water insoluble fraction in liquid products from pyrolysis, is shown in Table 3.

Its major components were essentially the same ones as in the corresponding aqueous phases, the concentrations being completely different and the phenolic compounds being the most important ones. Most common substituting groups in compounds with phenolic rings in aqueous phases and oil phases are methyl, ethyl, propyl, isopropyl, vinyl, allyl, carboxyl and carboxymethyl [49]. Oil phases derived from grasses showed a higher content of alkylated phenols, about 50% of the group, with phenol, cresol, dimethylphenols and 2-methyl-1,4-benzenediol

prevailing, while oil phase from *G. decorticans* contained much more phenolic ethers, about 80% of the group, with guaiacol, methylguaiacol, syringol, acetosyringone and 2-methoxy-1,4-benzenediol as the major compounds present. Trimethoxybenzene, which was present in the oil phase from *G. decorticans* (2.5 wt%), was not observed in oil phases derived from grasses. These compounds with benzenic structure derive from the pyrolysis of lignin [40, 50]. Other biomasses, such as pine, *Prosopis* and poplar wood sawdusts, yielded phenolic ethers similarly to *G. decorticans* [51], in consistency with the higher lignin content in woods as compared to grasses.

Acids and ketones were also significant in the oil phases. Among acids, propyl glutaric acid and acetic acid were the most abundant compounds, representing between 57 and 88 wt% of the group in the cases of grasses, while 2-methyl-propanoic acid and 4-hydroxy-3-methoxy-benzoic acid were in the case of *G. decorticans* (about 60% of the total). This difference could be due to the fact that propyl glutaric acid and acetic acid derive mostly from the depolymerization and fragmentation of hemicelluloses [40], more abundant in grasses, while the 2-methyl-propanoic acid and 4-hydroxy-3-methoxy-benzoic acid derive from the pyrolysis of lignin, which is present at higher concentrations in the woody shrub.

Ketones were also abundant in all the oil phases, with substituted cyclopentanones and cyclohexanones, both saturated and unsaturated, being the major compounds in all the cases. Particularly in the oil phase from *G. decorticans*, where the concentration of ketones was much higher, the most abundant compound was 3,4-dimethoxyacetophenone, representing 22% of total ketones; this ketone was not observed in oil phases derived from grasses. According to the molecular structure of this ketone, which contains a benzenic ring substituted with methoxy groups, it is possible to infer that is derived from lignin pyrolysis.

The amount of furans and pyrans was 50% higher in the oil phases produced by grasses, due to the higher content of cellulose and hemicellulose in those raw biomasses as compared to the woody shrub.

FTIR spectroscopy can provide complementary information about chemical species present in the oil phase of bio oils. Figure 3 shows the FTIR spectra corresponding to the different oil phases obtained in the pyrolysis experiments, where it can be seen that the absorption bands confirm that, for all the raw biomasses, the same chemical functionalities are observed. They are typical in bio-oils: the band between 3250 and 3750 cm^{-1} correspond to O–H stretching vibrations and hydrogen bond of hydroxyl groups [44]; bands at 2850–2930 cm^{-1} correspond to C–H stretching vibrations of alkanes; bands at 1700 and 1650 cm^{-1} belong to ketones and aldehydes carbonyl

Table 3 Composition of oil phases (wt%)

	<i>Spartina argentinensis</i>	<i>Panicum prionitis</i>	<i>Arundo donax</i>	<i>Geoffroea decorticans</i>
Acids	23.6	28.1	34.8	18.2
Formic acid	5.9	0.3		0.1
Acetic acid	5.3	5.5	11.1	2.9
Isocrotonic acid	0.3	0.5	0.2	0.4
2-Methyl-propanoic acid	2.1	1.7	1.8	4.7
Pentanoic acid	0.5		0.8	0.3
4-Methyl-pentanoic acid				1.6
Propyl glutaric acid	8.0	18.6	19.6	0.9
4-Hydroxy-3-methoxy-benzoic acid	1.5	1.6	1.2	6.1
4-hydroxy-3,5-dimethoxy-phenylacetic acid				1.3
Esters	6.9	3.0	2.7	3.3
Propyl acetate	4.5	1.3	0.3	
Propyl butanoate	1.6	1.3	1.1	1.4
Vinyl 2-butanoate	0.8	0.5	1.3	0.8
Allyl acetylacetate				1.2
Aldehydes	2.2	1.5	2.2	1.8
2-Butenal			1.2	
Cynnamaldehyde	1.2	1.2	0.9	0.8
Octanal	0.7			0.5
Anisaldehyde	0.3	0.3	0.1	0.5
Ketones	11.8	9.0	8.1	15.1
Acetone	0.5	0.4	0.2	0.6
2-Butanone	0.4	0.3	0.4	0.4
4-Hydroxy-3-methyl-2-butanone	0.9	0.4	0.4	0.4
2-Pentanone	0.1	0.2	0.6	0.5
2,3-Pentadione	0.5	0.2	0.3	0.1
1-Hidroxy-2-Propanone	0.1	0.1	0.4	0.1
2-Cyclopenten-1-one	2.7	2.9	2.1	2.0
Cyclopentanone	0.4	0.3	0.1	0.6
3-Methyl-cyclopentenone,	1.0	0.8	0.6	0.9
2-Cyclohexen-1-one	1.3	0.3	1.3	0.8
Cyclohexanone	0.4	0.8	0.1	0.4
2,4-Dimethyl-cyclopentenone	0.7	0.5		1.0
3-Methyl-2-cyclopenten-1-one	0.3	0.4		0.4
2-Hydroxy-3-methyl-cyclopentenone	1.8	1.0	1.0	1.1
4-Hydroxy-4-methyl-2-pentanone				0.1
5-Methyl-5H-furan-2-one				0.1
2-Methyl-2-cyclopenten-1-one				1.0
2-Methyl-cyclohexanone				0.2
2-Methyl-cyclopentanone				0.2
2,3-Dimethyl-cyclopentanone				0.4
3,4-Dimethoxy-acetophenone				3.3
2-Hydroxy-3-ethyl-cyclopentenone	0.7	0.5	0.5	0.5
Furans	6.2	3.7	6.1	4.0
Furfural	0.2			
3-Methyl furan				0.2
2-Furanmethanol	3.5	2.1	2.9	1.9
5-(Hydroxymethyl)-furfural	0.5	0.5	1.6	0.4
2-Acetylfuran	1.1	0.8	0.7	1.0

Table 3 (continued)

	<i>Spartina argentinensis</i>	<i>Panicum prionitis</i>	<i>Arundo donax</i>	<i>Geoffroea decorticans</i>
3,4-Dihydro-2H-pyran	0.9	0.2	0.9	0.4
Alcohols and Ethers	0.2	2.1	2.4	5.0
Methanol		0.6	1.1	2.0
1-Ethoxy-butane				0.3
1,2,4-Trimethoxy-benzene				2.8
1,2,5-Trimethoxy-benzene	0.2	1.4	1.4	
Phenols	31.9	31.5	26.7	35.9
Alkylated phenols	13.1	16.6	11.6	9.9
Phenol	2.6	4.0	2.3	1.9
Methylphenols (Cresols)	2.5	3.1	1.7	2.0
Dimethylphenols	1.7	4.7	2.4	3.2
2-Methyl-hydroquinone				0.3
2,5-Dimethyl-hydroquinone				0.5
Ethylphenol	0.5	0.4	0.2	0.5
Trimethylphenols				0.5
4-Ethyl-catechol				0.5
2-Methyl-1,4-benzenediol	4.9	3.6	3.8	
1-(4-hydroxy-3-methylphenyl)-2-propanone	0.6	0.5	0.8	0.4
2,6-Di-tert-butyl-p-cresol	0.4	0.3	0.3	0.1
Phenolic Ethers	18.8	14.9	15.1	26.0
Guaiacol	1.4	1.3	1.1	1.2
Methylguaiacol	2.7	2.8	1.4	3.3
3-Methoxy-phenol	4.5	3.3	3.3	4.0
4-Methoxy-catechol	0.5	0.5	0.5	0.9
4-Vinyl-guaiacol	0.0	0.1	0.1	0.2
4-Ethyl-guaiacol	1.3	1.0	1.1	1.3
4-Ethyl-3-methoxy-phenol	2.1	2.4	1.9	2.0
Vainillin	0.6	0.3	0.4	0.6
Syringol	3.2	1.7	3.6	3.5
4-(2-propenyl)-syringol				0.5
Acetosyringone				2.1
Eugenol	0.3	0.3	0.3	0.5
4-Propyl-guaiacol	2.0	1.1	1.5	2.0
3-Methoxy-catechol				0.3
2-Methoxy-1,4-benzenediol				2.9
Acetoguaiacone				0.7
Hydrocarbons	0.1	0.1		0.6
Isopropylcyclopentene	0.1	0.1		0.1
2-hexene				0.5
Unknown	17.1	20.9	17.0	16.2
UK1	6.3	4.8	5.4	4.2
UK2	4.5	3.2	2.6	1.6
UK3	6.3	12.8	9.0	10.4

groups and esters groups; bands at 1600 and 1500 cm^{-1} indicate the existence of C=C bonds in alkenes groups and aromatic compounds. Bending vibrations in C-H bonds in alkanes are observed at 1370–1470 cm^{-1} , while C-H in plane bending vibration at 830–1030 cm^{-1} confirm

aromatic compounds and primary alcohols. The band at 1115–1270 cm^{-1} belongs to alcohol and ether functions in oxygenated compounds [52].

A less intense absorption band in the 750–850 cm^{-1} range can be observed in the case of the oil phase derived

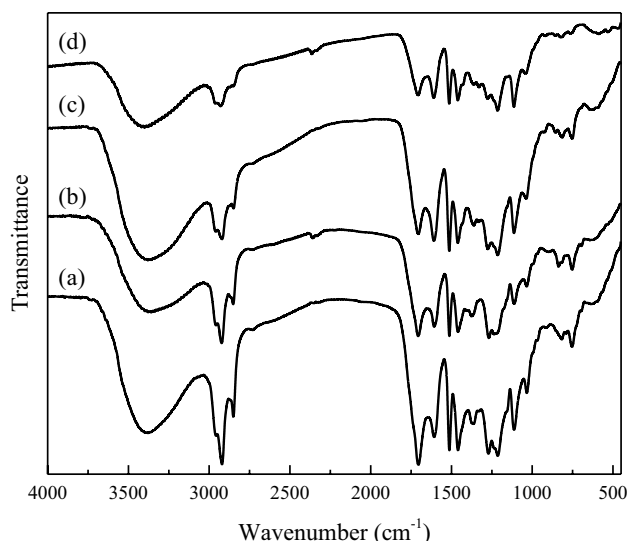


Fig. 3 FTIR spectra of the oil phases derived from the various raw biomasses. **a** *Spartina argentinensis*; **b** *Panicum prionitis*; **c** *Arundo donax*; **d** *Geoffroea decorticans*

from *G. decorticans* as compared to grass biomasses; this absorption zone corresponds to the vibration of C-H bonds out of the plane in positions 2, 5 and 6 in guaiacol units [52]. All these observations are consistent with the compositions of the oil phases shown in Table 3. Moreover, the *S. Argentinensis* spectrum showed lower intensity in the absorption band at 1600 cm^{-1} , consistently with the higher C content of this oil phase.

The composition of aqueous phases and oil phases from the biomasses studied had not been reported so far, with the exception of Saikia et al. [35]. Those authors analyzed the composition of *A. donax* oil phase by means

of different analytical techniques (FTIR, H^1 , C^{13} NMR and GC-MS) and observed the occurrence of functional groups such as alkanes, ketones, aldehydes, alkenes, phenolic and aromatic compounds and identified phenolic and furanic compounds (60% of chromatographic area) and caffeine (40% of chromatographic area). Some authors reported compositions of aqueous phases and oil phases from species of other grasses. Boateng et al. [14] reported water, acetaldehyde, acetic acid and 1-hydroxy-2-propanone in aqueous phase from *P. virgatum*, while Pilon and Lavoie [53] informed that the major compounds in that aqueous phase, obtained at $300\text{--}500\text{ }^\circ\text{C}$, were phenolic derivatives (phenol, cresol, guaiacol, methylguaiacol and vinylguaiacol, between 14 and 23% of the chromatographic area), cyclopentanone derivatives (2-hydroxy-3-methyl-2-cyclopenten-1-one and 2-hydroxy-2-cyclopenten-1-one, between 5.8 and 8.5% of the chromatographic area).

3.3.2 Chemical composition of aqueous phases

All the aqueous phases showed high contents of water (see Table 4), a typical characteristic of these liquids [54]. The main organic compounds were acetic acid, which represented between 35 and 51 wt% of the total, and methanol (between 9 and 24 wt%). The highest contents of acetic acid were observed in the aqueous phases from *A. donax* and *S. argentinensis*, in consistency with the higher contents of hemicellulose of these grasses [31, 35]. The acetic acid is the result of cracking acetyl groups linking xyloses in hemicellulose, where these groups can represent up to 10 wt% [40]. Methanol, in turn, is produced mainly from the fragmentation of methoxy groups substituting glucuronic acid which, together with xyloses, are the major components in angiosperm's hemicellulose [55]. However, the

Table 4 Composition of aqueous phases (wt%, dry basis)

	<i>Spartina argentinensis</i>	<i>Panicum prionitis</i>	<i>Arundo donax</i>	<i>Geoffroea decorticans</i>
Water	44.9	26.7	24.3	39.1
Organic compounds				
Acids	50.6	50.4	58.8	40.3
Esters	1.3	3.4	3.2	3.1
Aldehydes	0.8	4.5	1.9	3.6
Ketones	13.4	11.7	9.7	12
Furans and heterocyclic	3.1	4.8	4.1	4.4
Alcohols and ethers	9.6	13.0	10.3	24.3
Phenols	8.3	7.2	7.9	8.7
Alkylated phenols	4.6	3.3	2.6	3.3
Phenolic ethers	3.6	3.9	5.3	5.4
Hydrocarbons	0.2	0.1	0.1	0.1
Unknown	12.7	4.9	4.1	3.5

highest methanol yield was observed with *G. decorticans*, given that it can be obtained from the decomposition of cellulose [49], which is present at higher contents in this biomass [37] as compared to the grasses [35, 38].

Ketones, particularly cyclic pentanones, furans and phenolic compounds were other important compounds in all the aqueous phases. Cyclopentanones are frequently observed in cellulose [56] and hemicellulose [40, 55] pyrolysis. The highest concentrations of ketones were observed in the aqueous phases from *S. argentinensis* and *G. decorticans*, which are the biomasses with the highest contents of holocellulose (cellulose + hemicellulose) (see Sect. 3.1). The concentrations of furanic compounds in all the aqueous phases were similar (see Table 4), consistently with the cellulose contents in the raw biomasses [32, 35, 38]. The depolymerization and fragmentation of cellulose produces mainly furfural, 5-hydroxymethylfurfural and furanmethanol, together with some compounds containing pyranic rings, as the result of consecutive dehydration reactions of the glucose rings in its structure [40].

Phenolic compounds derive from the pyrolysis of lignin in biomasses [40, 50], their proportions in aqueous phases being similar in all the cases, even though the content of lignin in *G. decorticans* is significantly higher [37]. However, in the group, the amount of phenolic ethers, particularly syringol, was higher in aqueous phases from biomasses with more lignin, that is, *G. decorticans* and *A. donax* [35]. A

much higher proportion of methanol than that of grasses was observed in the pyrolysis of *G. decorticans*, which may in part derive from phenols with monomeric structure. When the pyrolysis temperature is higher than 400 °C, the cracking of substituting methoxy groups in phenolic rings produces methanol and methane [50]. The proportion of phenolic ethers in the oil phase fraction of the products from *G. decorticans* was also much higher than in the cases of the other biomasses, as it will be discussed later.

Unidentified compounds in the aqueous phases were mostly low molecular weight, less than 130 g mol⁻¹.

3.4 Physico-chemical properties of aqueous phases and oil phases

Aqueous phases obtained in the pyrolysis of the four biomasses were all light brown color and contained large amounts of water (see Table 4). Their elemental composition and some physicochemical properties are shown in Table 5, together with those of the respective oil phases. Aqueous phases density (between 0.9 and 1.3 g ml⁻¹) and pH (between 2 and 4) were typical of these liquids [54]. It is to be noted that the aqueous phases contained more oxygen than the parent biomasses, which, together with the high water content, confer them low HHV values. These observations are consistent with previous results: if water and oxygen contents in the

Table 5 Physicochemical properties of liquid products of pyrolysis

	<i>Spartina argentinensis</i>	<i>Panicum prionitis</i>	<i>Arundo donax</i>	<i>Geoffroea decorticans</i>
Aqueous phase				
Density, 25 °C (kg m ⁻³)	1.07	1.09	1.11	1.06
pH	3.5	3.2	3.1	3.6
Elemental composition (wt%, dry basis)				
C	27.0	18.8	18.7	22.6
H	9.0	9.7	10.1	8.7
N	0.8	1.0	0.3	0.6
O*	63.1	70.4	70.8	68.1
EHI (mol)	0.4	0.5	0.8	0.1
HHV (MJ kg ⁻¹)	10.7	7.7	8.2	7.9
Oil phase				
Density, 25 °C (kg m ⁻³)	1.40	1.39	1.38	1.43
Elemental composition (wt%, dry basis)				
C	50.1	55.0	53.8	48.0
H	7.8	7.4	9.6	9.9
N	1.0	1.8	0.9	2.1
O*	41.1	35.8	35.7	40.0
EHI (mol)	0.6	0.6	1.1	1.1
HHV (MJ kg ⁻¹)	20.8	22.9	25.7	23.3

*O (wt%) = C (wt%) – H (wt%) – N (wt%) – Ash content (wt%)

aqueous phases were between 44 and 84 wt% and 32 and 48 wt%, respectively, the HHV values were between 6 and 17 MJ kg⁻¹ [19, 51]. Moreover, it is to be noted that the aqueous phase derived from *S. argentinensis* showed the highest C content, while the higher O contents were those in the aqueous phases from *P. prionitis* and *A. donax*, thus being consistent with the compositions of the raw biomasses (see Tables 1, 5).

Oil phases contained less oxygen, more carbon and were denser than the aqueous phases. Consequently, their heating values were higher than those of the corresponding aqueous phases and even higher than those from other species. For example, HHV in oil phases from wood sawdust typically are between 16 and 19 MJ kg⁻¹ [57]. Considering oil phases from similar biomasses, HHV in oil phases from *A. donax* [35] and *P. virgatum* [53] were reported to be 17 MJ kg⁻¹ and 15 MJ kg⁻¹, respectively. An important observation was that the oil phase with the highest C content was the one obtained with *P. prionitis* (the biomass with the lowest C content, see Table 2), and the oil phase with the highest O content was that from *S. argentinensis* (the biomass with the lowest O content, see Table 2). This means that in the case of *P. prionitis*, concentrating C in the oil phase is much higher than in the other cases; a similar condition can be observed with O and *S. argentinensis*.

According to the characteristics of the aqueous and oil phases, it is convenient to upgrade them into fuels which can be directly used in static applications or transportation fuels and raw materials for the chemical process industry. Interesting options to valorize pyrolysis aqueous phases and oil phases are to process them over acidic catalysts [58] or to co-process them in refineries in partial replacement of fossil feedstocks in well-established processes such as the catalytic cracking of hydrocarbons (FCC) [59]. In that sense, the effective hydrogen index (EHI, [60]) is an important parameter defining how crackable these mixtures are; the higher the EHI, the more efficient the conversion to hydrocarbons. The index shows the neat H/C relationship when heteroatoms are present in the molecules, according to Eq. (1),

$$EHI = \left(\frac{H}{C}\right)_{ef} = \frac{(H - 2O - 3N - 2S)}{C} \quad (1)$$

where H, C, O are the molar percentages of the various elements on a dry basis.

The resulting EHI were very low for all the aqueous phases and slightly higher for the oil phases (see Table 5). In comparison to fossil feedstocks, whose EHI vary from 1 (aromatic residues) to 2 (highly paraffinic cuts) [61], aqueous phases and oil phases can be considered hydrogen deficient.

3.5 Characterization of gas and solid products

The yields of gases were continuously observed during the pyrolysis experiments, two peaks being recorded for all the raw biomasses. The first one was located between 270 and 350 °C and the second one, smaller in magnitude, between 480 and 500 °C. These peaks correspond to the holocellulose (cellulose + hemicellulose) and lignin decomposition, respectively [62].

Table 6 shows the composition and properties of the gas and solid (char) products in the pyrolysis of the different raw biomasses. Gases were mainly composed by carbon dioxide (between 60.0 and 72.5 wt%), hydrogen (between 8.3 and 24.4 wt%) and hydrocarbons (between 11.1 and 16.1 wt%, methane being the most important hydrocarbon in all the cases). Observed carbon dioxide and hydrogen yields were higher than those obtained with other biomasses [63–65]. The yield of hydrogen in the case of *A. donax* pyrolysis was much higher while that of carbon dioxide resulted lower than in the other cases. In turn *G. decorticans* yielded more hydrocarbons than the other biomasses. In relation to the composition of the gases produced by pyrolysis, Boateng et al. [48], as an example, reported gases yields in the pyrolysis/gasification of *P. virgatum* at temperatures between 600 and 1050 °C to be CO between 2.5 and 7.5 wt%, CO₂ between 9 and 18 wt%, methane between 1.3 and 3.7 wt%, ethane and propane between 0.1 and 1.1 wt%.

The HHV of all the gases were similar, in the range of values reported in the literature for various biomasses, that is, between approximately 15 and 30 MJ kg⁻¹ [66], which are lower than that of LPG (50 MJ kg⁻¹). These gases could be used to sustain the own pyrolysis process, thus providing the energy necessary in biomass decomposition reactions.

Chars derived from biomass pyrolysis show polycyclic aromatic structures [40]. The mechanism leading to this solid residue is favored by intra and intermolecular rearrangements, resulting in high reticulation degree and material stability. The most important step is the formation of benzenic rings and its further recombination into polycyclic structures, together with the release of water and non condensable gases [67].

The chars contained less oxygen and more carbon, the HHV being consequently much higher, than the corresponding raw biomasses (see Table 2). Consistently with the compositions shown by the ultimate and proximate results (see Table 2), the char with the highest C content was the one derived from *A. donax*, while that from *S. argentinensis* showed the highest H content. Thus, the chars are solid fuels better than the parent biomasses. Consequently, it was also observed that the atomic O/C relationship was significantly lower in chars (see Table 6), given the decarbonilation,

Table 6 Composition and properties of gases and char (wt%)

	<i>Spartina argentinensis</i>	<i>Panicum prionitis</i>	<i>Arundo donax</i>	<i>Geoffroea decorticans</i>
<i>Gases</i>				
Chemical composition				
Carbon dioxide	72.5	71.7	70.2	69.2
Carbon monoxide	6.7	4.2	5.3	2.6
Hydrogen	8.3	6.6	11.5	11.0
Methane	8.7	13.4	10.1	12.7
Ethane + ethylene	2.2	1.9	1.5	2.3
Propane + propylene	1.6	2.2	1.4	2.2
Elemental composition				
C	32.3	34.9	31.4	33.3
H	11.1	10.6	14.5	14.9
O*	56.6	54.5	54.1	51.8
HHV (MJ kg ⁻¹)	25.1	26.9	25.5	24.5
<i>Char</i>				
Ash	26.6	13.4	14.2	17.4
Elemental composition				
C	61.0	66.5	71.2	69.1
H	3.4	3.3	3.1	3.1
O**	7.8	15.0	10.2	8.7
N	1.2	1.8	1.2	1.7
O/C (mol)	0.1	0.2	0.1	0.1
HHV (MJ kg ⁻¹)	24.2	24.7	26.8	26.4

*O (wt%) = C (wt%) – H (wt%) – N (wt%)

**O (wt%) = C (wt%) – H (wt%) – N (wt%) – Ash content (wt%)

decarboxylation and dehydration reactions during pyrolysis on the biopolymers constituting biomass, leading to aromatic rings crosslinked by aryl–alkyl C–C bonds [68]. Moreover, it is also possible that chars retain oxygenated compounds inside their structures. Pilon and Lavoie [53] showed by means of solvent extraction that char in the pyrolysis of *P. virgatum* contains a wide variety of compounds, the most important ones being alkanes and cycloalkanes with between 11 and 20 carbon atoms per molecule (up to 22% of the extract chromatographic area), phenols (up to 45%, including phenol, ethylphenolguaiacol, ethylguaiacol, and vinylguaiacol among others), cyclopentanone derivatives (up to 11.5%, methylcyclopentenones being the major compounds) and furan derivatives (up to 16%, including furanmethanol, butyrolactone and furfural as major compounds). These authors attributed the occurrence of alkanes to the decomposition of extractives, particularly fatty acids in grasses, which are subjected to decarboxylation and cracking. They also reported that HHV for that char was between 22.2 and 24.5 MJ kg⁻¹.

3.6 Separation of chemicals from aqueous phases

As already mentioned, liquid products from biomass pyrolysis are potentially useful as fuels after deoxygenation upgrading and, moreover, they could be the source of valuable chemicals [69]. Different authors used separation processes such as simple [70] and reactive [71] liquid–liquid extractions, and simple and vapor assisted distillations [72] to recover chemicals from bio-oils. However, many of these publications were limited to simulated bio-oils, composed by mixing model compounds considered representative of true mixtures and, in most of the cases, no information was provided about overall distillation and/or extraction yields

Distillation was used to selectively separate water, methanol and acetic acid present in the aqueous phase of *P. prionitis* pyrolysis products. Selected temperatures and vacuum yielded a residual fraction rich in chemicals of high value (see Table 7) without resorting to organic solvents, which are usually very expensive and highly contaminant.

Table 7 Yields in the vacuum distillation of the aqueous phase of *P. prionitis* bio-oil (wt%)

	Distilled fractions (DF)					Remnant
	1	2	3	4	5	
Fractions	36.3	5.8	8.1	2.4	1.6	45.8
Compounds						
Water	83.3	9.6	6.5	0.5	–	0.1
Acids	8.2	5.9	16.4	6.7	3.8	59.0
Aldehydes	3.5	2.4	–	2.1	1.5	90.5
Ketones	10.3	2.5	3.2	0.3	1.0	82.7
Esters	10.5	6.7	13.4	–	0.8	68.6
Ethers	–	–	–	–	–	100
Furans	7.9	2.8	2.3	0.5	1.5	85.0
Alcohols	71.3	1.8	–	–	–	26.9
Phenols	2.7	1.3	0.9	0.1	0.5	94.5
Unknown	7.7	2.6	3.3	1.6	2.8	82.0

The yields of each fraction were calculated as the relationship between the mass of the fraction and the initial mass of the raw bio-oil aqueous fraction. The yields of the different groups were determined from the yields of each compound, in turn calculated as the relationship of the mass of the compound in the various distilled fractions and the initial mass of in the aqueous phase of the bio-oil. Table 7 shows that the yield of the first step of distillation was very important, significantly decreasing in the following steps. Most of the water and methanol in the bio-oil were separated in the first step. The third step, where the highest temperature was reached, produced the most selective separation of acids (almost exclusively, acetic) and esters (propyl acetate). In general terms, when the five steps were completed, the yields of acids and alcohols were 41% and 73%, respectively. The yields of other important groups were not as significant; for example, 5.5% for phenols, 17.3% for ketones, 15.0% for furans, less than 10% for aldehydes and nil for ethers. Most important distilled compounds were phenol and 3-methoxyphenol among phenols, 2-cyclopenten-1-one, 2-pentanone and

2-cyclohexen-1-one among ketones and 2-furanmethanol and 2-acetylfuran among furans.

The compositions of the various vacuum distilled fractions are shown in Table 8. It can be seen that a significant improvement in terms of water removal was achieved in the residual fraction, with a consequent increase in the concentration of high value compounds such as ketones, phenols and furans.

The other fractions were composed by, mainly, methanol, water and acetic acid. The first two distilled fractions were rich in methanol and water, respectively, the third one being rich in acetic acid. The fraction rich in acetic acid could be directly used in the synthesis of magnesium and calcium acetate de-icers by means of acylation reactions [73] and the production of slow-release nitrogenous organic fertilizers, by taking advantage of the high content of carbonyl groups [74].

The residual fraction showed a concentration of phenolic compounds which is 60% higher than the initial one in the aqueous phase, most important compounds in the group being phenolic ethers (42%), mainly guaiacol and

Table 8 Composition of the distilled fractions and the remnant in the vacuum distillation of the aqueous phase of *P. prionitis* bio-oil (wt%)

	Distilled fractions (DF)					Remnant
	1	2	3	4	5	
Water	73.7	53.1	26.2	6.0	–	0.1
Acids	6.8	30.4	61.4	84.7	71.9	38.5
Aldehydes	0.3	1.3	–	2.7	2.9	6.0
Ketones	2.4	3.8	3.5	0.9	5.6	15.6
Esters	0.7	3.0	4.3	–	1.4	3.8
Ethers	–	–	–	–	–	0.8
Furans	0.8	1.8	1.0	0.8	3.5	6.7
Alcohols	13.4	2.1	–	–	–	4.0
Phenols	0.4	1.2	0.6	0.2	1.9	11.7
Unknown	1.5	3.3	3.0	4.7	12.8	12.8

its alkylated derivatives. On the contrary, acid and alcohols decreased their concentrations in the residual fraction (35% and 65%, respectively), most important remaining acids being acetic and 2-methylpropanoic, and methanol among alcohols.

Ketones, furans and aldehydes also concentrated in the residual fraction, with cyclopentenones (38%), 2-furan-methanol (46%) and cinnamaldehyde (69.2%) being the prevalent compounds in each of the groups.

These facts confirm that this methodology is appropriate to improve the composition of the aqueous phase of bio-oils because valuable compounds such as phenols and ketones can be concentrated. Some of the compounds which showed a high concentration in the residual fraction could be used with specific aims after a more efficient concentration process. For example, guaiacols and their alkylated derivatives are used to produce food flavor additives [75], cyclopentenones and their derivatives inhibit aldo-keto reductases [76], thus being useful to treat pathologies where these enzymes are involved. Moreover, 2-furanmethanol is the raw material for the synthesis of furan resins, which are thermally stable and chemically inert polymers used as cements and binders [77].

Considering these observations, it is possible to propose a methodology to upgrade the aqueous fractions in pyrolysis liquids, decreasing acidity and water content by means of a primary distillation process. However, it is necessary to design further, complementary separation and/or purification steps in order to achieve the purity degrees required in given raw materials.

4 Conclusions

The pyrolysis of three native Argentinian species (two perennial grasses and a woody shrub), and an exotic perennial grass, all them being species with high growth rate in extensive subtropical rangelands areas and conforming a large supply of biomass, produced gas, liquid and solid (char) products. Liquid products were composed by an aqueous phase which mainly contained ketones, methanol and low molecular weight acids and an alquitranous, oil phase which mainly contained phenols, ketones and acids with high molecular weight. The composition of the liquid products indicated that chemicals could be separated from them (for example, acids or alcohols in the aqueous phases, or phenolic compounds in the oil phases, can be found at high concentrations). Moreover, the oil phases showed HHVs in the 21–26 MJ kg⁻¹, much higher than those of the aqueous phases or the raw materials, supporting an interesting fuel potential. However, these options deserve sounder studies.

Simple vacuum distillation upgraded the composition of the aqueous phase in the pyrolysis liquids from one of the perennial grasses (*P. prionitis*) by removing water and decreasing substantially the content of acids and methanol, thus increasing the concentration of more valuable products. The fractions from the distillation enriched in acetic acid (up to 84%) could be appropriate as the reactant for acylation and esterification reactions as well as to produce de-icers such as magnesium and calcium acetate or fertilizers.

The product gases (average HHV 25.9 MJ kg⁻¹) and chars (average HHV 22.4 MJ kg⁻¹), could be used to produce the energy necessary for the own pyrolysis processes or for previous raw biomass conditioning steps.

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Compliance with ethical standards

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

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