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Accepted version:

EFFECT OF MECHANICAL HARVESTING ON THE CHEMICAL COMPOSITION AND COMBUSTION BEHAVIOUR OF SHRUB BIOMASS

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ABSTRACT

Shrub lands are an important source of genetic resources and raw materials for a bioeconomy-based future. The main objective of this study is to determine the effect of mechanical harvesting on the chemical composition and the combustion quality properties of typical shrub formations in the Mediterranean area, whose prevailing species are broom, rockrose and gorse.

Above ground, shrub biomass was collected manually and mechanically and its main properties and chemical composition were compared. Its combustion behaviour was predicted by using fuel indices related to emissions, deposit build-up and ash melting. The predictions were evaluated after performing combustion tests with mechanically harvested shrub pellets.

The chemical composition and combustion behaviour of the biomass differed greatly depending on the prevailing species. Mechanised harvesting can cause the ash content and the levels of several elements, particularly Si, to increase through the inclusion of soil particles, which influence combustion behaviour. The Si/(Ca+Mg) index appears to be a good indicator to predict the slagging tendency of these fuels. However, the K+Na+Zn+Pb index could not accurately predict aerosol emissions and ash deposition. The information provided by this index should be complemented by using the Si/K index, which considers the influence of Si on alkali retention.

KEYWORDS

Broom; combustion behaviour; gorse; harvesting; rockrose; shrub

1. INTRODUCTION

According to FAO statistics, shrub lands (classified as other wooded land) cover more than 1,200 Mha, 9.2% of the world’s land surface, a relevant figure compared to forestlands, which nowadays cover 4,000 Mha.

The countries with the highest relative shrub land area versus total land coverage are Australia (33%), Argentina (24%), South Africa (20%), Chile (20%), Greece (19%), Portugal (19%), Spain (19%) and Turkey (13%) [1].

Even though shrubs cover important areas in many countries [2], their management and use are still very low mainly due to the associated high costs. Their control for fire prevention thus entails a significant cost for public administration and forest owners.

There are many types of natural shrubs forming biotopes in which climatic or edaphic conditions limit the growth of forests. However, in Spain and other countries with Mediterranean climates, most of the area covered by scrubs is anthropogenic in origin. Deforestation, abandonment of agricultural activity, intentional burning to generate pastures and forest fires of different causes usually generate a gradual degradation of the forest soil favouring the pyrophyte scrub species. The most interesting shrub formations for biomass use are precisely those that originate after land abandonment or fire, due to their height and high biomass surface densities, i.e. broom, rockrose and gorse-based scrubs.

Broom-based scrubs are formed by species of the genera *Genista*, *Cytisus* and *Retama*. These formations extend over approximately 1.77 Mha in western Spain [4, 5].

Rockroses are species of the genus *Cistus* and cover approximately 2.3 Mha in central and western Spain [4, 5]. Rockroses grow on open burned lands, pastures and marginal agricultural lands, and as typical undergrowth vegetation under Mediterranean tree covered forests.

Gorse scrubs are shrub formations that are mainly species from the genus *Ulex*. The most abundant species is *Ulex eurapaeus* that is native to western and central Europe but nowadays found in more than 55 countries outside its native range [3]. In Spain, gorse formations cover more than 65,000 ha in the northern regions: Galicia, Asturias, Cantabria and the Basque Country [4, 5].

Scrubs can be highly valuable environmentally and economically as they are an important source of genetic resources and raw materials for a bioeconomy-based future. For this reason, a greater knowledge of these plant communities, their sustainable management and the characteristics of their biomass resources are necessary. The floristic composition of the shrub communities is usually very diverse, even greater than that of many tree forests. For that reason, the study of their biomass must be based on the analysis of the characteristics of the plant mixture and not on a single species since above ground biomass collection is done by machines.

The information available on the characterisation and specific combustion properties of shrub solid biofuels is still relatively scarce. In most cases, analyses are carried out on samples that have been collected manually and the results obtained represent the composition of the raw, clean biomass. As far as we know, there is no literary study on the chemical composition and quality of biomass mechanically collected from shrublands. However, in a real case scenario, the biomass would be harvested and collected mechanically, meaning that its composition could greatly differ from raw, clean biomass, due to the addition of mineral impurities during its collection, transportation and conversion process into a biofuel. The studies by Carrión-Prieto et al. [6], Elvira and Hernando [7], Fernandes and Pereira [8], Núñez-Regueira et al. [9], Viana et al. [10] only focus on the physical properties of the selected biomass materials and on some chemical-energetic properties such as the calorific value and the proximate and elemental analysis. However, trace elements, currently limited by the ISO 17225 series that grades solid biofuels, and the chemical composition of ash are also important properties since they can considerably affect the combustion behaviour of these fuels.

The objective of the present study is to determine the effect of mechanical harvesting on the chemical composition and combustion quality of the biomass from three typical shrub formations in the Mediterranean area. The work also aims to predict the behaviour of these biomass materials during combustion by using predictive indices. The performance of the selected fuel indices was verified after the combustion of pellets produced from mechanised harvested shrub biomass and measurement of the degree of agglomeration of the collected ashes and the emissions and ash deposits generated during combustion.

2. MATERIALS AND METHODS

2.1. Biomass raw materials

Identification, sampling and harvesting of shrub land formations were carried out following the procedures described below.

Commercial pine pellets (class A1, according to ISO 17225-2:2014) were used as reference fuel for combustion tests.

2.1.1. Identification of shrub lands

Based on LiDAR information from the flight campaign of the National Aerial Orthophotography Plan (PNOA) carried out in 2010, spectral information provided by the Operational Land Imager sensor (OLI, Landsat 8 satellite) with images of 2015, and field sampling plots, three biomass collection areas, corresponding to representative shrub lands in the Iberian Peninsula were considered (Table 1). Transect vegetation inventories (0.6 transects per sampling hectare) were established to obtain field data. A base line of 18 m in length with a known direction, and 3 perpendicular transects to the base line of 25 m in length, were defined in each sampling plot for vegetation inventory and cover definition [11].

Table 1. Catchment areas and shrub sampling

Centre of the catchment area	Shrub land sampling area (ha)	Number of vegetation transects	Cover (%)	Prevailing shrub
Las Navas del Marqués	29	18	70% *Genista cinerascens* L 20% *Cytisus scoparius* L 10% *Rubus* spp.	Broom (*Genista cinerascens*)
Garray	55	33	80% *Cistus laurifolius* L. 20% *Rubus* spp.	Rockrose (*Cistus laurifolius*)
As Pontes de García Rodríguez	13	9	85% *Ulex europaeus* L. 10% *Calluna vulgaris* L. 5% *Erica tetralix* L.	Gorse (*Ulex europaeus*)

2.1.2. Manual sampling

Once homogenous and representative shrub lands were located, stratified sampling was carried out taking into account the structural variability of the mass, based on the crown cover and the average height of the vegetation. A total of 30 circular plots with an 11.3 m radius were distributed in each of the three catchment areas to estimate medium shrub height, crown cover, standing biomass load and floristic composition. The detailed methodology is described by Bernal et al. [12]. Secondly, representative samples of fresh biomass (2.5 kg per sampling plot), that included the aerial part of the plants, were collected and sent to a laboratory for their complete characterisation.

2.1.3. Mechanical harvesting and biomass pre-treatment

Biomass was collected using two mechanised harvesting methods, which were previously described by Bados et al. [13]. The methods were selected according to the indications established by the manufacturers and dealers. In that sense, the biomass from Garray and Las Navas del Marqués (with rockrose and broom as the prevailing species) was collected with a harvester-baler (Biobaler WG55) that produces cylindrical shrub bales, more suitable for less dense and shorter shrubs. On the other hand, a harvester-mulcher (RETRABIO), which is more powerful, was used in case of the biomass collected in As Pontes de García Rodríguez (mainly gorse), where the shrubs were denser and taller.

The biomass collected by mechanical procedures was processed in the pre-treatment plants of CEDER-CIEMAT through grinding (pre-shredder type Lince 45/140, 75 kW), drying (rotary drum dryer), milling (fixed hammer mill type HK-AIR 26, 75 kW) and pelletising (flat die type Amandus Kahl 33-500) processes in order to produce pellets (ϕ 8mm) without additives to be used in commercial domestic boilers. The detailed process is described by Bados et al. [14]. With the aim of forming a combined sample to be characterised prior to combustion tests, the samples of pellets were taken from moving material at the outlet of the bagging bin of the pelletisation plant. Therefore, five samples of 1 dm^3 were taken and a combined sample was constituted.

2.2. Analytical procedures

Samples of shrub biomass, shrub pellets and ashes gathered after combustion tests were analysed in the Laboratory of Biomass Characterisation located at CEDER-CIEMAT. The analytical samples were prepared according to ISO 14780:2017 “Solid biofuels. Sample preparation” by means of homogenisation, division, drying and grinding. The analytical tests carried out are shown in Table 2.

Table 2. Parameters analysed and standards used in the Laboratory of Biomass Characterisation at CEDER-CIEMAT

Parameter		**Standard**
Proximate analysis	Moisture	ISO 18134-2:2017
	Ash	ISO 18122:2015
	Volatile matter	ISO 18123:2015
Ultimate analysis	C, H, N	ISO 16948:2015
	S and Cl	ISO 16994:2016
Calorific value		ISO 18125:2017
Major elements (Al, Ca, Fe, K, Mg, Na, P, S, Si, Ba, Mn, Sr, Ti)		ISO 16967:2015
Trace elements (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn)		ISO 16968:2015
Particle size distribution		ISO 17827-1:2016, ISO 17827-2:2016
Crystalline phases in ash (X ray diffraction)		

The level of agglomeration of the ashes collected in the grate after combustion was estimated by measuring their particle size distribution. In this sense, a representative sample of ash was selected by cone and quartering and sieved for 15 min in a vibratory sieving machine. The particle size distribution was determined after weighing the fractions collected in the different sieves. This methodology has been previously applied successfully on the ashes produced after the combustion of other solid biofuels [15-17].

2.3. Statistical analysis

Statistical analyses on the data set were performed using Statgraphics Centurion XVII.I. A variance analysis (ANOVA) was used to determine whether there are statistically significant differences across species for a particular quality property. Fisher´s least significant difference (LSD) procedure was used to discriminate among means. P-values from F-tests below 0.05 denote statistically significant differences across species. Different letters between two means indicate that they are significantly different at the 95.0% confidence level. With this method, there is a 5.0% risk of calling each pair of means significantly different when the actual difference equals 0.

2.4. Fuel indices

Several fuel indices were selected among the most frequently used and recently cited in literature to predict the combustion behaviour of the studied shrubs with regard to emissions, deposit build-up and ash melting issues [18]. Taking into account that Si, K, and Ca are the major ash forming elements present in shrub biomass, and that some sort of mineral contamination is expected after harvesting the studied biomass by mechanical means, only the indices that take into consideration the importance of these elements were included in this study.

K+Na+Zn+Pb (mg/kg, dry basis) is an indicator for aerosol (fine particles smaller than 1 µm: PM1) emissions and deposit build-up on heat exchanger surfaces. Aerosol emissions increase with an increasing amount of K, Na, Zn and Pb in the fuel. Thus, if the index is < 1,000, the tendency towards PM1 emission and deposit build-up is low; if the index has a value between 1,000 and 10,000, the tendency is medium; and, finally, if the index is > 10,000, the tendency is high.

Si/K (molar) can predict K release. A high molar Si/K ratio leads to a preferred formation of potassium silicates, which are bound in the bottom ash. Therefore, K release is reduced, aerosol formation may decrease and SO_x and HCl emissions may increase. For very high Si/K ratios, a high amount of K in the bottom ash prevails. However, for low Si/K ratios (< 2.5), no clear conclusion can be made.

Si/(Ca+Mg) (molar) can provide primary information on ash-melting problems in ash systems dominated by Si, Ca, Mg and K. This index versus the ash sintering temperature for different biomass materials is shown in a graph [9]. As the molar ratio of Si/(Ca+Mg) increases, the ash sintering temperature decreases, and this decrease is remarkable when the index exceeds the value of 1.

2.5. Combustion tests

The pellets produced from the mechanised harvested biomass of the studied shrub lands were combusted in a commercial boiler. Commercial pine pellets (class A1, according to ISO 17225-2:2014) were used as reference fuel. After preliminary combustion tests carried out to define and set the operating conditions with the aim of obtaining the lowest emissions, one combustion test was performed. Each test had a steady state period of 6 h, working as close as possible to the nominal power of the boiler. The steady state was considered to start at the time at which the flue gas temperature did not change more than ± 5 ºC in a period of 30 minutes.

The boiler used has thermal power between 25 and 40 kW, depending on the biomass fuel used. It has been specially designed for agro-fuels and has a lateral feeding burner based on a moving grate with a double forward-backward and upward-downward movement. The feed system has been adapted to feed pellets, chips and chopped biomass. Furthermore, the boiler has a fully automatic ash extraction system. The heat exchanger consists of vertical tubes with three smoke passes. Fumes are blown through by a fan. This boiler does not have any equipment to remove the particles contained in the exhaust gases. The boiler is automatically controlled to ensure low gas emission levels, being classified by its manufacturer as class 3 according to EN 303-5:1999 standard.

The gaseous composition of exhaust gases during the combustion tests was measured with a portable Fourier Transform Infrared (FTIR) Spectroscopy analyser and a zirconium oxide cell (for determining the O_2 concentration). The frequency of data acquisition was 20 s.

Continuous monitoring of the particle content in exhaust gases was carried out with a system that uses electrodynamic probe electrification technology. The electrical current produced by particles interacting with a grounded rod protruding across the stack is measured and correlated with dust concentration by comparing it with the results of an iso-kinetic sample. An automatic iso-kinetic sampler was thus used to measure the particle content in flue gas in certain periods of time following ISO 9096:2017 standard.

Upon completion of the combustion tests, ash was gathered from different locations and weighed. Firstly, all the ash over the grate was gathered and, together with all the ash extracted to the ash-container with the ash extraction system, formed the “bottom ash” sample. Next, all the ash deposited inside the tubes of the heat exchanger was collected using a brush, separating the samples of the 1st and 2nd passes, which were labelled “1st pass tubes” and “2nd pass tubes”, respectively.

3. RESULTS AND DISCUSSION

3.1. Composition of shrub lands. Manual harvesting

The main properties and chemical composition of the studied shrub lands, which are characterised by different prevailing species, is shown in Tables 3 and 4. Samples were collected manually following the procedure detailed in section 2.1.2.

The variance analysis shows that the chemical composition of the biomass collected manually from shrub lands differs greatly, depending on the catchment area and/or the prevailing species, with the exception of Al, Fe, Mg, P, Si and Ti, elements which are usually associated with mineral contamination from soil.

As can be seen in Table 3, the biomass from shrub lands where the prevailing species are broom and gorse showed lower ash contents (1.4-1.5%) than that found for shrub lands dominated by rockrose (2.6%). The highest calorific value was found for broom, followed by gorse and rockrose. Similar values were reported by other authors [6, 10, 19-21].

Table 3. Composition of the biomass collected manually from shrub lands characterised by different prevailing species

Area		Las Navas del M.	Garray	As Pontes de G. R.	ANOVA
Main shrub		Broom	Rockrose	Gorse	
Property	Unit	Average (n = 30)	Average (n = 30)	Average (n = 30)	P-value
Moisture	wt.%, w.b.	37.2b	32.2a	47.2c	<0.01
Ash	wt%, d.b.	1.4a	2.6b	1.5a	<0.01
HHV	MJ/kg, d.b.	20.73c	19.90a	20.12b	<0.01
LHV	MJ/kg, d.b.	19.36c	18.58a	18.78b	<0.01
C	wt.%, d.b.	50.6b	49.4a	50.4b	<0.01
H	wt.%, d.b.	6.3c	6.0a	6.2b	<0.01
N	wt.%, d.b.	1.1c	0.47a	0.85b	<0.01
S	wt.%, d.b.	0.06b	0.04a	0.06b	<0.01
Cl	wt.%, d.b.	0.05b	0.02a	0.07c	<0.01
Al	wt.%, d.b.	0.020a	0.035a	0.020a	>0.05
Ca	wt.%, d.b.	0.17a	0.76b	0.15a	<0.01
Fe	wt.%, d.b.	0.012a	0.046a	0.016a	>0.05
K	wt.%, d.b.	0.31c	0.21a	0.27b	<0.01
Mg	wt.%, d.b.	0.067a	0.068a	0.068a	>0.05
Na	wt.%, d.b.	0.0046a	0.0048a	0.074b	<0.01
P	wt.%, d.b.	0.047ab	0.039a	0.052b	0.04
Si	wt.%, d.b.	0.23b	0.21ab	0.16a	0.05
Ti	wt.%, d.b.	0.0011a	0.0014a	0.0014a	>0.05

n: number of samples; wt.%: weight %; w.b.: wet basis; d.b.: dry basis; HHV: high heating value; LHV: low heating value

Regarding the ultimate analysis, it can be said that the biomass of shrub lands formed by prevailing leguminous species, such as broom and gorse, showed higher N contents than shrub lands where rockrose was the predominant species, due to the higher N fixation capacity of the former in leaves and twigs [22]. Shrub lands dominated by rockrose presented relatively low S (0.04%) and Cl (0.02%) contents. However, higher S (0.06%) and Cl contents (0.05% and 0.07% for broom and gorse, respectively) were observed in the shrub lands where broom and gorse were the prevailing species.

The content of the ash forming major elements is quite similar for the analysed shrub lands, with the exception of Ca, K and Na. The average Ca content of the biomass from rockrose shrub lands is five times higher than those found for broom and gorse. Although significant, K was within the range of 0.21-0.31% for all the characterised shrub lands. It is also worth mentioning the significantly higher contents of Na and Cl of gorse shrub lands (0.07%) in comparison with those found in shrub lands where the prevailing species were broom and rockrose.

Table 4 shows the levels of trace elements found in the biomass collected from all the studied shrub lands. For trace elements, an analysis of variance could not be used as most of the values fell below the quantification limits of the test methods. For this reason, Table 4 shows the average values, when calculations are possible, together with the maximum content found in the analysed samples and the percentage of samples showing levels below the quantification limit of the test method (values shown in brackets).

Table 4. Trace elements of the biomass collected manually from shrub lands characterised by different prevailing species

Area		Las Navas del M.		Garray		As Pontes de G. R.	
Main shrub		Broom		Rockrose		Gorse	
Element	Unit	Aver.	Max.	Aver.	Max.	Aver.	Max.
		(n = 30)		(n = 30)		(n = 30)	
As	mg/kg, d.b.	<0.10 (83%)	0.14	<0.10 (97%)	0.11	<0.10 (87%)	0.26
Cd	mg/kg, d.b.	<0.10 (83%)	0.20	0.37	1.1	<0.10 (47%)	0.88
Cr	mg/kg, d.b.	<1.0 (100%)	<1.0	<1.0 (100%)	<1.0	<1.0 (80%)	3.2
Cu	mg/kg, d.b.	3.3	7.1	2.7	4.0	8.1	145
Hg	mg/kg, d.b.	0.007	0.011	0.007	0.013	0.005	0.030
Ni	mg/kg, d.b.	<1.0 (90%)	2.4	2.0	3.8	2.1	4.1
Pb	mg/kg, d.b.	<1.0 (97%)	1.8	<1.0 (50%)	4.0	<1.0 (93%)	4.2
Zn	mg/kg, d.b.	19	35	23	42	14	41

n: number of samples; Aver.: average; Max.: maximum; d.b.: dry basis;

As can be seen, the levels of trace elements were fairly low, and always within the limits stated in the international standards that grade the quality of solid biofuels (ISO 17225 series). Among the 90 samples collected, only one with an exceptionally high level of Cu (145 mg/kg) exceeded the afore-mentioned limits, which could be due to cross-contamination during the sampling and/or processing steps, or to the origin of the sample, as it was collected in a restored area where there was once a mining slagheap, which highlights the importance of full characterisation of the biomass that comes from restored soils. If this outlier was excluded, gorse biomass would average a Cu content of 3.3 mg/kg.

3.2. Composition of the pellets produced from mechanised harvested biomass

Table 5 shows the main properties and chemical composition of the pellets produced from the biomass collected by mechanical means (see section 2.1.3) and later used in combustion tests (section 2.5). It also includes the characterisation of the fuel used as a reference in combustion tests (commercial pine pellets, class A1). A1 pellets show the best quality properties for combustion, so they are mostly used for small-scale applications.

Table 5. Composition of the shrub pellets produced from biomass collected by mechanical means.

Parameter	Unit	Broom	Rockrose	Gorse	Pine
Moisture	wt.%, w.b.	9.6	7.2	10.8	6.3
Ash	wt%, d.b.	1.4	4.2	3.8	0.5
HHV	MJ/kg, d.b.	20.27	19.94	19.90	20.39
LHV	MJ/kg, d.b.	18.90	18.68	18.57	19.07
C	wt.%, d.b.	50.3	50.2	50.0	51.4
H	wt.%, d.b.	6.3	5.8	6.1	6.1
N	wt.%, d.b.	0.88	0.40	0.97	<0.05
S	wt.%, d.b.	0.04	0.04	0.08	0.02
Cl	wt.%, d.b.	0.03	0.03	0.07	0.01
Al	wt.%, d.b.	0.036	0.063	0.22	0.007
Ca	wt.%, d.b.	0.15	0.67	0.35	0.11
Fe	wt.%, d.b.	0.020	0.046	0.14	0.0070
K	wt.%, d.b.	0.21	0.24	0.30	0.043
Mg	wt.%, d.b.	0.060	0.067	0.10	0.018
Na	wt.%, d.b.	0.011	0.0067	0.095	0.0024
P	wt.%, d.b.	0.046	0.050	0.061	0.0055
Si	wt.%, d.b.	0.15	0.67	0.72	0.033
Ti	wt.%, d.b.	0.0021	0.0059	0.0095	0.00039

wt.%: weight %; w.b.: wet basis; d.b.: dry basis; HHV: high heating value; LHV: low heating value.

The main properties and chemical composition of the shrub pellets produced is comparable to those shown by short rotation wood crops, such as poplar [23] or willow [24, 25]. They are also characterised by higher ash, N, S, and Cl contents and lower calorific values than those shown by A1 pine pellets, usually prepared from debarked wood. Moreover, as noticed in the chemical composition of the shrub biomass collected manually (section 3.1), it is worth mentioning the remarkable N levels found for the pellets produced from leguminous species (roughly 1%) as opposed to those observed in pellets produced from rockrose (0.4%), as well as the elevated Cl and S levels shown by the pellets produced from gorse shrub lands.

By comparing with Table 3 (clean biomass corresponding to manual harvesting), the increase in ash, Al and Si noticed in pellets produced from shrub lands where rockrose and gorse were the prevailing species (Table 5) suggests that mechanical harvesting introduced mineral contamination through the inclusion of soil particles into the biomass collected in these areas. In contrast, no evidence of mineral impurities was found in the pellets produced with the mechanised biomass of shrub lands where broom predominated.

The pellets produced from broom shrub lands fulfilled the requirements of class B wood pellets for commercial and residential applications. However, the inclusion of mineral impurities during the mechanised harvesting of rockrose and gorse shrub lands led to pellets with ash contents of around 4%, exceeding the limits set in the international standard that grades the quality of wood pellets for domestic and industrial uses. In any case, as previously mentioned, the elevated contents of Cl and S naturally present in the studied gorse shrub lands could already limit the use of this biomass to industrial applications.

3.3. Prediction of combustion behaviour through fuel indices

The combustion behaviour of the studied shrubs was predicted by using three selected fuel indices (see section 2.4). Table 6 lists the indices calculated for the biomass collected manually and for the pellets produced from biomass harvested mechanically.

Table 6. Fuel indices across prevailing species and harvesting procedures

Index	Unit	Broom		Rockrose		Gorse		Pine
		Collected manually	Harvested mechanically (pellets)	Collected manually	Harvested mechanically (pellets)	Collected manually	Harvested mechanically (pellets)	Pellets
K+Na+Zn+Pb	mg/kg	3170	2227	2177	2443	3471	4062	465
Si/K	molar	1.0	1.0	1.4	4.0	0.8	3.4	1.1
Si/(Ca+Mg)	molar	1.2	0.9	0.3	1.2	0.9	2.0	0.3

wt.%: weight %

K+Na+Zn+Pb index values are comprised between 1,000 and 10,000 for shrubs. This fact shows a medium tendency towards aerosol emission and, therefore, a medium tendency towards ash deposition on heat exchanger surfaces. As can be seen, the values of the indices are of the same order within the interval (1,000-10,000) and consequently, no differences are expected with regard to the prediction made based on the index.

Si/K index shows values lower than 2.5 for all shrub samples collected by hand and, subsequently, no clear conclusion with regard to K release can be made. However, if the shrub pellets are considered, the index predicts a preferred formation of potassium silicates in the bottom ash, lower aerosol formation, and higher SO_x and HCl emissions during rockrose and gorse pellet combustion. The different prediction between the biomass collected manually and that harvested mechanically is mainly due to the highest values of Si analysed in the biomass coming from mechanised harvesting, which is related to contamination with mineral matter from soil.

The Si/(Ca+Mg) index shows different values if shrub biomass collected by hand or harvested mechanically are considered due to the difference in Si content. So, although the three manually collected shrubs have a similar tendency towards ash melting, the tendency towards slagging increases when mechanised harvested biomass is considered. Consequently, the prediction points to gorse pellets being the biomass with the lowest melting temperature, since it shows the highest value of the index (2.0).

With regard to the prediction for the pine pellets considered as a reference fuel, it can be said that a low tendency towards aerosol emission and deposit build-up can be expected, but no clear conclusion concerning K release can be made and no slagging risk is expected.

3.4. Results of combustion tests and evaluation of the performance of predictive indices

During the combustion tests, lasting 6 hours in steady state conditions, the boiler worked without mechanical problems related to the fuels used. All tests were carried out in similar operating conditions during the steady state: the average boiler load was between 39.0 and 39.3 kW in shrub pellets tests and 43.9 kW in pine pellet test, and water flow and water return temperatures were 70 ± 3 °C and 55 ± 3 °C, respectively, in all the tests. On the other hand, the average temperature at the inlet of the heat exchanger varied between 935 °C (pine) and 848-889 °C (shrubs) and at the outlet of the boiler it varied between 178 °C (pine) and 182-193 °C (shrubs). The emissions measured during the steady state period are shown in Table 7.

Table 7. Emissions during the steady state of the combustion tests with pellets referred to dry gas basis and O_2: 10 %v.

Emissions	Broom		Rockrose		Gorse		Pine	
	Avr.	Std. dev.	Avr.	Std. dev.	Avr.	Std. dev.	Avr.	Std. dev.
O_2 (%v.)	8.0	1.0	8.3	0.8	8.2	0.9	8.1	1.0
CO (mg/Nm^3)	623	518	71	53	22	18	295	210
NO_x (mg/Nm^3)	388	52	373	30	601	59	140	10
SO_2 (mg/Nm^3)	7.0	7.0	59	2.2	132	6.0	13	2.5
HCl (mg/Nm^3)	2.9	0.4	7.4	1.0	60	3.3	0.3	0.5
TSP (mg/Nm^3)	235	154	32	18	40	27	97	20

%v.: % volume; NO_x: NO + NO_2, shown as NO_2; TSP: total solid particles; Avr.: average; Std. dev.: standard deviation.

As can be seen in Table 7, broom and rockrose pellet combustion produced similar NO_x emissions, lower than those obtained from gorse pellet combustion. Considering the N content in the fuels (Table 5), NO_x emissions should be higher in broom combustion compared to rockrose combustion, since N content is higher in broom. This behaviour could be explained by the higher CO emissions obtained during broom combustion and the equilibrium between CO and NO_x during combustion [26].

Concerning SO_2 emissions, the highest values were observed during gorse combustion followed by rockrose. On the other hand, broom and pine pellets showed values of the same order of magnitude. This fact is not consistent with the S content of the different biofuels used (Table 5). However, SO_2 emissions are not only related to S content in fuel but also to content in alkalis or alkaline earth metals (such as Na, Ca and K), which can capture sulphur [27-32].

With regard to HCl emissions, the high value obtained during gorse combustion is remarkable as might be expected from the Cl content in the fuels used (Table 5). Nevertheless, HCl emission was higher during rockrose pellet combustion compared to the value obtained during broom pellet combustion, although the Cl content in both fuels considered was the same. This behaviour is due to the fact that an important percentage of the total chlorine released during biomass combustion is integrated in the ash and it depends mainly on the concentration of alkali and earth-alkali metals and Si in the fuel [33].

Finally, regarding total solid particles (TSP) emitted, the high value observed during broom pellet combustion is remarkable.

3.4.1. Particle emissions and deposition on heat exchanger surfaces

K+Na+Zn+Pb (mg/kg, dry basis) can predict aerosol (PM1) emissions and deposit build-up on heat exchanger surfaces. Although aerosols were not measured during the combustion tests performed, flow of fly ashes, i.e. TSP emitted and ash deposited on the heat exchanger surface (1st and 2nd pass tubes), were calculated considering the continuous measurement of TSP and the ash collected inside the heat exchanger after the combustion tests. These parameters together with bottom ash (both of them free of unburnt matter) are shown in Table 8. As can be seen, broom is the shrub with the highest emissions of TSP and the highest ash deposition on the heat exchanger surface and, consequently, the highest fly ash mass flow (31 g/h). On the contrary, the values corresponding to pine, rockrose and gorse are considerably lower (11, 6.4 and 5.3 g/h, respectively).

Table 8. Average values of TSP and ash flow during the combustion tests

Shrub pellets	Emission	Ash deposition		Fly ash (Emission + Ash deposition)	Bottom ash
	TSP (g/h) (DM)*	1st pass tubes (g/h) (DM)*	2nd pass tubes (g/h) (DM)*	Total mass flow (g/h) (DM)*	Total mass flow (g/h) (DM)*
Broom	24	5.1	1.7	30.8	82
Rockrose	3.4	2.2	0.80	6.4	266
Gorse	3.8	0.96	0.57	5.3	282
Pine	9.1	1.3	0.61	11	23

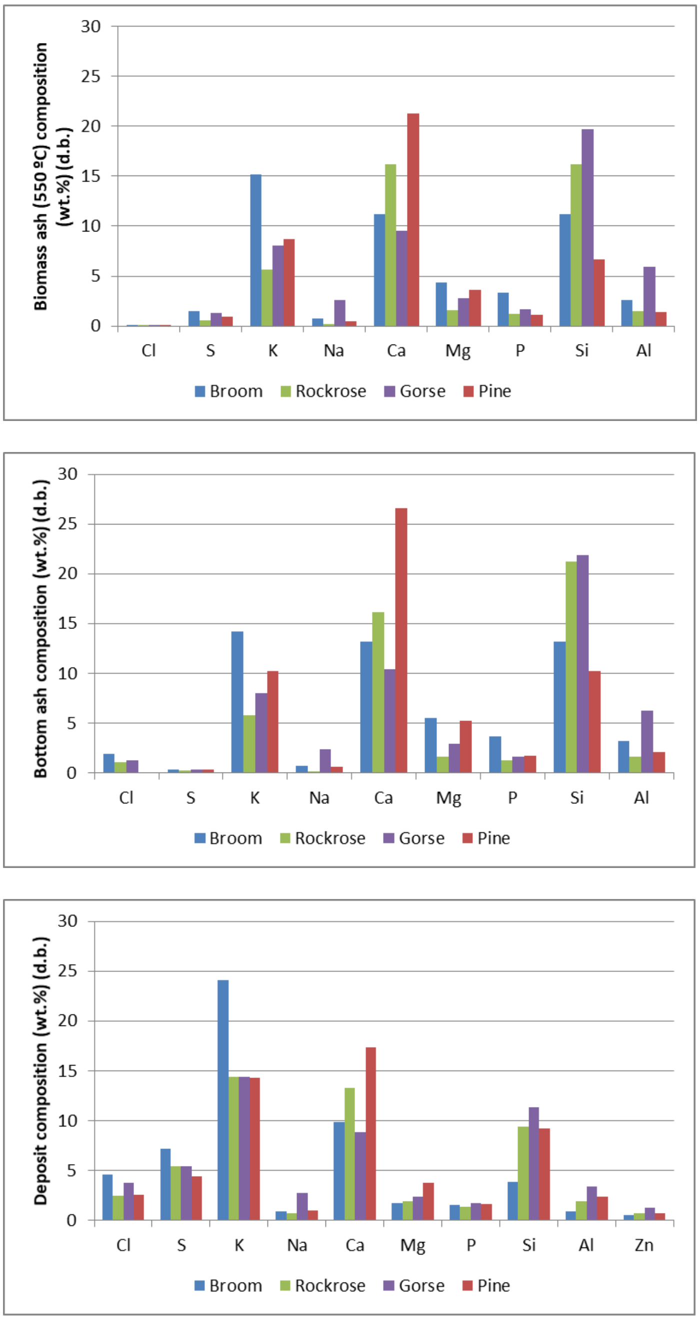
$O_{2,ref}$: reference O_2; %v.: %volume; DM: dry matter; *: free of unburnt matter

By comparing the obtained values with the prediction made by the K+Na+Zn+Pb index calculated on the basis of a laboratory analysis, it can be said that this index is not appropriate for predicting the behaviour of the tested shrubs with regard to TSP emissions and ash deposition since the prediction pointed at a medium tendency towards aerosol emission for all shrubs tested (Table 6). Furthermore, the index predicted a low tendency for pine pellets and the total mass flow of fly ash has been higher for pine pellets than for rockrose or gorse pellets.

Concerning TSP emission, it must be clarified that the index was created to predict aerosol emissions and, although aerosols are included in TSP together with coarse particles, the amount of aerosols and coarse particles has not been determined in this study. On the other hand, the presence of a high Si content in the rockrose and gorse pellets used (due to the contamination of the biomass with soil matter during mechanised harvesting) seems to be the reason why the behaviour of broom is different from rockrose and gorse. In this sense, the Si/K index predicts a preferred formation of potassium silicates in the bottom ash and lower aerosol formation and higher SO_x and HCl emissions during rockrose and gorse pellet combustion. This prediction is endorsed by the behaviour of both shrubs during combustion tests, which showed the lowest fly ash flow and the highest SO_2 and HCl emissions. Therefore, the existence of Si in their composition leads to the fact that not only K, Na, Zn and Pb contents determine the fly ash formation. High concentrations of Si and Al can trap alkali species through the formation of aluminosilicates, which reduces the concentration of alkali chlorides and sulphates [34, 35].

Consequently, the prediction of fly ash formation through the K+Na+Zn+Pb index needs to be complemented by the prediction of the influence of Si and Al on alkali removal.

Ash obtained from pellets at 550 ºC, bottom ash and ash gathered inside the heat exchanger were analysed and the corresponding results can be seen in Figure 1. The high K content and low Si content of broom ash compared to rockrose and gorse ashes can be observed (Figure 1). Furthermore, the presence of K in the ash deposited inside the heat exchanger during the combustion test with broom pellets and the presence of Si in the bottom ash during the combustion tests with rockrose and gorse pellets are remarkable and consistent with the lower emissions of fly ash observed (Figure 1).



wt.%: weight %; d.b.: dry basis

Figure 1. Composition of biomass ash obtained at 550 ºC, bottom ash deposited on 1st pass of heat exchanger (iron-free)

3.4.2. Ash melting behaviour

With the aim of characterising the ash melting behaviour of the different pellets tested, the degree of agglomeration of the ash collected on the grate was studied through the analysis of its particle size distribution (Figure 2).

Figure 2 shows that the most sintered ash corresponded to gorse followed by rockrose and broom and, finally, pine. Considering the behaviour predicted by the Si/(Ca+Mg) index (Table 6), it is evident that the difference predicted between the behaviour of pine (index value: 0.3) and the rest of shrubs (index values between 0.9 and 2.0) can also be observed in the combustion tests carried out. Even a difference between the sintering tendencies of the different shrub pellets tested can be seen, since the index values are: 0.9 for broom, 1.2 for rockrose and 2.0 for gorse. A visual inspection of the bottom ash collected after the tests showed the same differences, because pine pellet combustion produced loose bottom ash, broom and rockrose pellet combustion generated agglomerated bottom ashes and gorse pellet combustion produced bottom ash with melted zones.

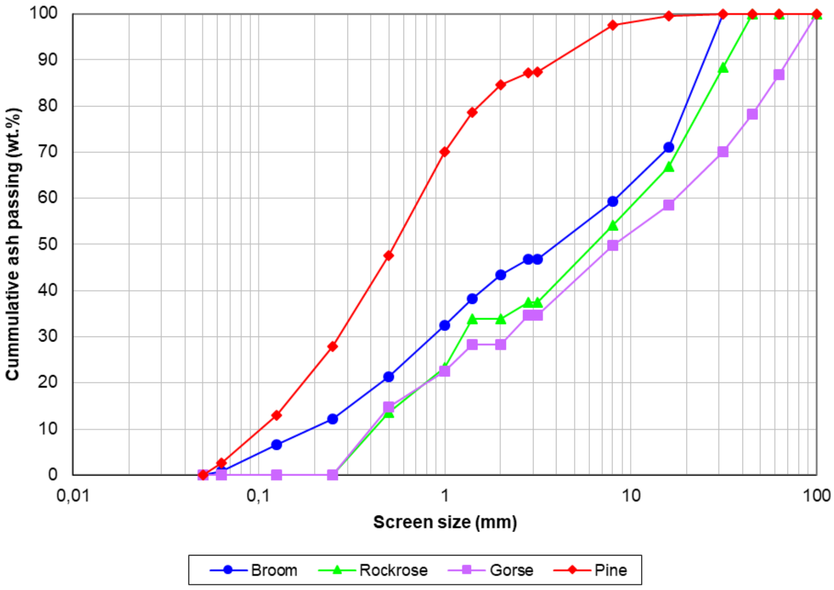


Figure 2. Particle size distribution of the ash gathered on the grate after the combustion tests

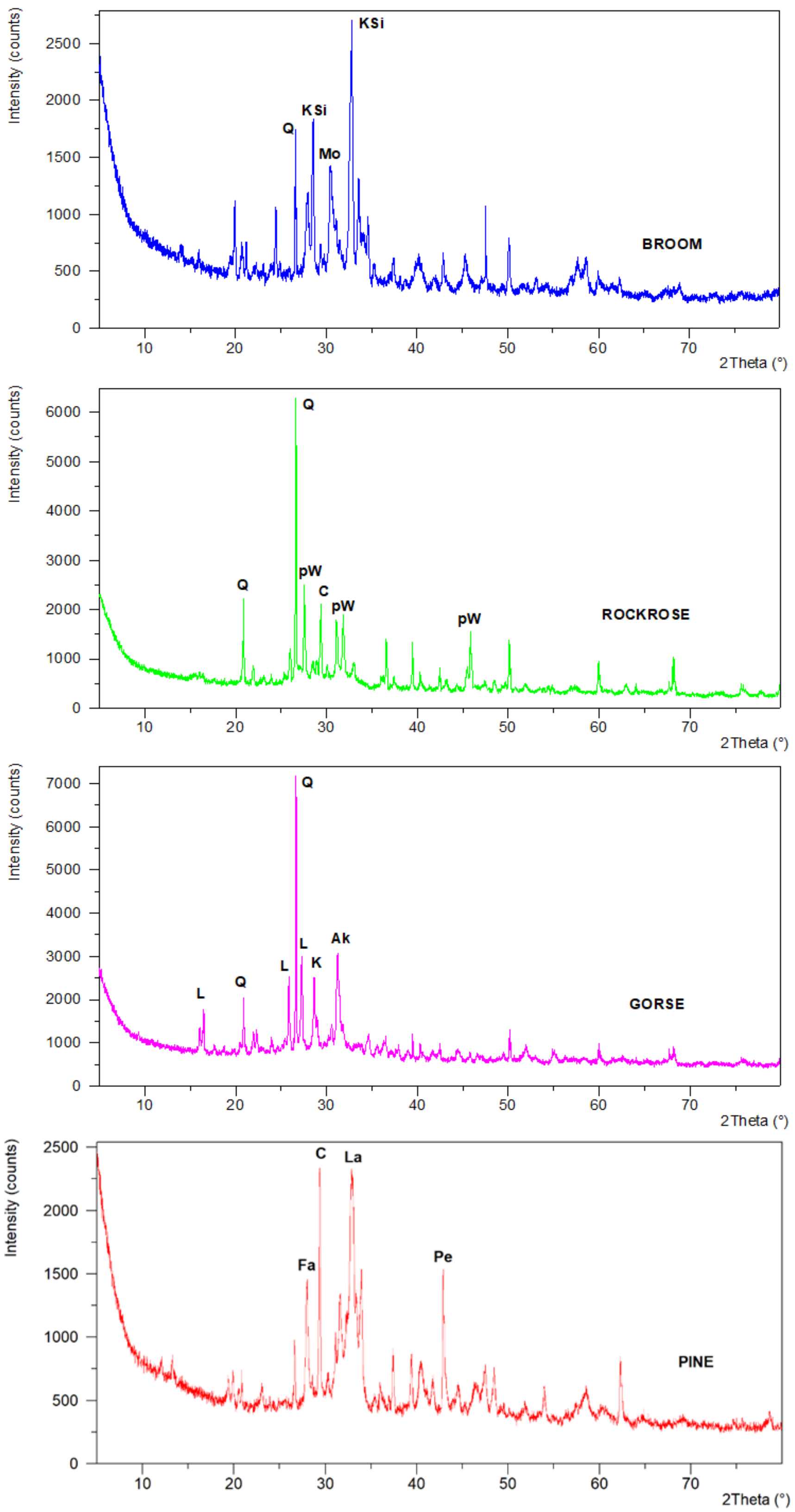
An X-ray diffraction technique was used to analyse crystalline phases in the bottom ash collected after the different combustion tests. Figure 3 shows the corresponding diffractograms, where the intensity (counts) versus the incident angle (2Θ) can be seen.

Diffractograms corresponding to the bottom ashes obtained after the combustion tests with rockrose and gorse show high peaks for quartz. These shrubs had a high silicon content, mainly as quartz (SiO_2), derived from contamination with mineral matter during mechanised harvesting. Although the silicon has reacted partly to form silicates, a fraction of this silicon still stays as quartz.

In general, calcium and/or magnesium silicates such as pseudowollastonite ($Ca_3Si_3O_9$), monticellite ($CaMgSiO_4$) and larnite (Ca_2SiO_4) show melting points (about 1500 ^oC) higher than potassium aluminium silicates, such as leucite ($KAlSi_2O_6$) or kalsilite ($KAlSiO_4$). It is known that leucite and kalsilite have melting points of about 1600 ^oC; however, considering the phase diagram for SiO_2-Al_2O_3-K_2O, liquid curves indicate melting points between 900 °C and 1700 °C for compositions in equilibrium with these compounds [36].

Potassium aluminium silicates, such as leucite ($KAlSi_2O_6$) or kalsilite ($KAlSiO_4$) are mainly found in the bottom ash of gorse. Another potassium aluminium silicate ($KAlSiO_4$) is found in the bottom ash of broom. This potassium compound has the same molecular formula as kalsilite and the difference is due to the fact that kalsilite crystallises in a hexagonal system and the silicate found in the broom ashes crystallises in a monoclinic system.

On the other hand, pseudowollastonite ($Ca_3Si_3O_9$), monticellite ($CaMgSiO_4$) and larnite (Ca_2SiO_4) are found in rockrose, broom and pine bottom ashes, respectively. The detection of these phases together with the calcite ($CaCO_3$) found in pine can be the cause of the better melting behaviour of rockrose, broom and pine in comparison with gorse. Furthermore, the detection of high melting point compounds such as periclase (MgO), which melts at about 2800 °C, can justify the best melting behaviour of pine pellets during the combustion tests.



Q: quartz; L: leucite; K: kalsilite; KSi: potassium alumosilicate; Ak: akermanite; Mo: monticellite; pW: pseudowollastonite; C: calcite; Fa: fairchildite; La: larnite; Pe: periclase

Figure 3. X ray diffractograms of the bottom ashes collected after the corresponding combustion tests.

3.4.3. Effect of mechanised harvesting on the combustion behaviour of shrub biomass

As shown in previous sections, mechanised harvesting of shrub lands can introduce mineral contamination by the inclusion of soil particles into the biomass collected, depending on factors such as soil texture, type and operation of the mechanical equipment, or the logistics process. If mechanised harvesting is optimised, a reduction in ash content and some elements like Al, Mg, Na, and Si can be achieved. In such cases, the chemical composition of the biomass harvested by mechanical means is not supposed to differ significantly from the biomass collected manually, as observed when comparing the biomass that was collected manually or by mechanical means from broom shrub lands.

During the combustion of broom pellets (0.15% Si), Si did not play an important role in K capture, in accordance with the prediction of the Si/K index. The biomass manually collected from all the studied shrub formations showed low, similar Si levels as well, ranging 0.16-0.23%. Considering this, it could be said that, if mechanised harvesting had not introduced mineral particles from soil, all shrub pellets would have shown similar Si-K interactions, and their behaviour would have been close to what was observed during the combustion tests performed on broom pellets. In such a case, a considerable part of K would not be retained by Si, and thus the K+Na+Zn+Pb index would presumably predict a medium tendency for aerosol emissions and deposit build-up during the combustion of rockrose and gorse pellets, which occurred when broom pellets were tested. Consequently, K would supposedly be retained by Cl and S forming ash deposits and particle emissions, and thus HCl and SO_2 emissions would be lower than those observed during the combustion tests of rockrose and gorse (Table 7). At the same time, the Si/(Ca+Mg) ratio would decrease and, therefore, lower slagging problems would be predicted and observed for rockrose and gorse.

4. CONCLUSIONS

The main properties and chemical composition of shrub biomass differ greatly, depending on the prevailing species (broom, rockrose and gorse). Shrub lands mainly formed by a leguminous species, such as broom or gorse, are characterised by higher N contents than those formed by other species such as rockrose. In addition, biomass collected from gorse shrub lands showed relatively high levels of Cl and S, which could definitely limit its use in small-scale applications.

The biomass from the studied shrub lands naturally showed mean ash contents below 3.0%. However, the mechanised harvesting of shrub biomass can greatly affect its chemical composition and quality properties by increasing the content of mineral impurities through the inclusion of soil particles. Increases in ash contents and the levels of several elements, particularly Si, have influenced the combustion behaviour of the fuels. On the one hand, the introduction of Si avoided K release by trapping K compounds in bottom ashes, which increased their slagging tendency while decreasing deposit build-up and TSP emissions. On the other, as K was less available to form KCl and K_2SO_4 in fly ashes, higher emissions of HCl (g) and SO_2 (g) were released.

The Si/(Ca+Mg) index appears to be a good indicator to predict the slagging tendency of shrub biomass. However, the K+Na+Zn+Pb index could not accurately predict the actual aerosol emissions and ash deposition of the studied fuels, probably because it does not take into account the influence of elevated Si contents in the fuel. In this regard, the use of the Si/K index might provide additional information and clarify the influence of Si on alkali retention.

Mechanised harvesting of shrub lands without introducing mineral contamination is feasible. The improvement of mechanised techniques to harvest shrub lands, particularly by reducing the inclusion of soil particles, would increase the quality properties of the fuels produced from this biomass and therefore their combustion behaviour.

Acknowledgements

This work has been partially funded by the LIFE+Programme, Project number LIFE13 ENV/ES/000660. Furthermore, equipment co-funded by the European Regional Development Fund has been used: a biomass conditioning and pre-treatment line (project CIEM09-3E-275) and a biomass harvester-baler machine (project CIEM13-3E-2505).

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