

Assessment of the energy potential of agricultural and forestry biomass sources from the Canary Islands

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Abstract. A selection of some biomass sources from the Canary Islands, such as agricultural biomass (vineyard, VB; tomato plant, TPB), forestry biomass (Canary pine needles, CPB) and invasive species (*Pennisetum setaceum*, PSB) were evaluated to determine their potential as solid biofuels due to their abundant level, availability and low supply cost. In this work, the main physico-chemical properties (moisture content, ash content, volatile matter, fixed carbon, CHNOS content, mineral content, heating value, density, etc.) of the four biomasses were evaluated. From the results of this study it can be concluded that the TPB is not considered suitable due to its very high ash content and its relatively low content of volatile matter. However, VB, CPB and PSB proved to be potential candidates for energy generation through thermochemical conversion.

Key words. Biomass, pyrolysis, gasification, combustion, thermochemical treatment.

1. Introduction

The more developed technologies for obtaining energy or fuels from biomass are those based on thermochemical treatments, such as pyrolysis, gasification and combustion. In both economic and environment point of view, combustion, pyrolysis and gasification processes constitute an attractive alternative for the use of biomass as a fuel.

Both pyrolysis and gasification are technologies for producing biofuels, which are then stored, transported or used in subsequent transformation processes. Nevertheless, when energy (heat or electricity) is desired, the combustion of vegetable biomass has advantages concerning operating conditions and fuel flexibility.

A large number of studies have been reported on a variety of biomass for their possible use as renewable fuels. The conversion of these materials by thermochemical processes can significantly and immediately reduce the mass and volume of wastes, allowing for energy recovery. In this work, a selection of some biomass sources from the Canary Islands, such as agricultural biomass (vineyard, VB; tomato plant, TPB), forestry biomass (Canary pine needles, CPB) and invasive species (*Pennisetum setaceum*, PSB) were evaluated to determine their potential as solid biofuels due to their abundant level,

availability and low supply cost. The characteristics of the four biomasses were analyzed in order to determine which of them is the most suitable for each of the thermochemical processes: combustion, pyrolysis and gasification.

2. Experimental

A. Biomasses

Four biomass sources: two agricultural (vineyard, VB; tomato plant, TPB), one forest (Canary pine needles, CPB) and one invasive plant (*Pennisetum setaceum*, PSB) were chosen for this study, due to their abundant level and low supply cost. All biomasses were obtained from Tenerife (Canary Islands). Prior to characterization experiments, the samples were cut and oven-dried at 70°C for 24 hours to facilitate grinding. After drying, each material was crushed on a planetary ball mill (Pulverisette 6, Fritsch) and sieved. The fraction less than 500 µm was selected.

B. Biomass characterization

Proximate analysis was performed according to standards analytical methods UNE-EN ISO 18134:2015, UNE-EN ISO 18122:2015, UNE-EN ISO 18123:2015 for moisture content (MC), ash content (AC) and volatile matter (VM), respectively. The fixed carbon (FC) was calculated by subtracting ash and volatile matter contents from 100% (in a dry basis). Furthermore, a VM/FC ratio was estimated to establish a comparative among the samples.

Ultimate analysis was used to determine the concentration of carbon, hydrogen, nitrogen, oxygen and sulphur content of the biomass samples. The chemical composition was obtained by CHNS elemental analysis using FlashEA 1112 Organic Elemental Analyzer. The oxygen content was estimated by subtraction.

The content of metals in the samples were determined by wet digestion, 0.5 g of the sample digested in 10 mL of nitric acid (99,9%) at atmospheric pressure in a digestion tube with reflux, the digested samples were analyzed by inductively coupled plasma- mass spectroscopy (Agilent Technologies Inc., Agilent 7900 ICP-MS).

The analysis on mineral matter content in each sample was performed using Energy-Dispersive X-ray Fluorescence (EDXRF) spectrometer, model Bruker S2-Puma (500W).

Empirical correlations have been used for calculating the higher heating value (HHV) from the values obtained in the proximate analysis and DTG curves, proposed by Channiwala and Parikh [1] and Parikh et al. [2] for comparison purposes.

Moreover, the lower heating value (LHV) was determined from the HHV considering the content of hydrogen and moisture in the biomass and 2260 kJ kg⁻¹ as latent heat of vaporization [3].

The skeletal density of the samples was measured by gas pycnometry (Micromeritics Instruments, Accupyc 1330) using a 3,5 cm³ sample module and helium as filling gas (99.995% pure).

3. Results and discussion

A. Characterization of biomasses

To assess the potential of agricultural and forestry biomass sources to serve as feedstock for thermochemical conversion processes, its main physicochemical characteristics were studied: moisture content (MC), ash content (AC), volatile matter (VM), fixed carbon (FC), CHNOS content, mineral content, as well as the heating values and the density. The choice of biomass mainly depends on its inherent properties, determining the conversion process and any subsequent processing difficulties that may arise [4]. Table I shows the proximate and ultimate analyses, the mineral content, the density and heating values of VB, TPB, CPB and PSB. The VM/FC ratio and the atomic ratios of O/C and H/C are also provided.

The proximate analysis gives an idea of how good is the biomass to be converted into energy. Feedstocks with low moisture content (less than 50 wt.%) are required for thermochemical conversion processes. High moisture contents decrease the heating value of the fuel and impair the overall energy balance for the conversion process due to drying processes [5]. The results from Table I show that all biomass samples are characterized by relatively low moisture contents, ranging from 10.5-12.7 wt.%. Manić et al. [6] found similar moisture contents in several agricultural residues: 8.58 wt.%, 11.63 wt.% and 9.27 wt.% for corn brakes, wheat straw and hazelnut shell, respectively.

It is appropriate that biomasses subjected to thermochemical processes have a low ash content and a high volatile matter content. A high ash content can lead severe agglomeration, fouling and corrosion in boilers or gasifiers [7]; however, the main problems caused by ashes (erosion, deposit formation, etc.) are conditioned more than by their quantity, by their composition, especially if they contain alkali metals such as potassium or halides such as chlorine [3]. The ash content of the biomasses studied is very wide, ranging from 3.32-28.64 wt.% (Table I). The CPB and the VB are the biomasses with the lowest ash content, which gives them global conversion

advantages over PSB and TPB. The TPB shows a very high ash content (28.64 wt.%) and a relatively low content of volatile matter (59.2 wt.%), so it is not considered suitable for thermochemical processes. The other biomasses are suitable to be subjected to thermochemical processes, due to their high content of volatile matter.

The fixed carbon content of the biomasses studied is in the range 11.8-20.8 wt.%. These values are in the range of those found for wood (12.28-29.90 wt.%) [8]. The volatile matter/fixed carbon (VM/FC) ratio is a way of representing the chemical energy stored in the biomass. Biomass typically has a VM/FC ratio >4.0, while the VM/FC ratio for coal is almost always <1.0. In this work, the VM/FC ratios for the biomasses are in the range 3.65-6.17. Thus, for biomass fuels, the predominant form of combustion will take place via the gas-phase oxidation of the volatile species [9]. The higher the VM/FC ratio is, the more reactive the biomass and the larger the available energy that biomass is able to be released [4]. PSB is the biomass with the highest VM/FC ratio; while the CPB has the lowest VM/FC ratio. Therefore, the PSB is the most reactive biomass followed by the TPB, the VB and, finally, the CPB.

The results obtained for ultimate analysis are also reported in Table I. For all biomasses, carbon is the majority element with 33-49 wt.%, followed by oxygen with 28-43 wt.%. It is observed that the CPB and the VB are the biomasses with the highest content of C and H; while the lowest values correspond to the TPB. The importance of the content of carbon, hydrogen and oxygen in the thermochemical processes to be applied is noticeable, while sulfur and nitrogen are possible sources of polluting emissions.

The TPB has a lower content of oxygen compared to other biomasses, which may indicate creation of smaller amount of inorganic vapors during combustion; however, this biomass showed a slightly high sulfur content, which is not advantageous from an environmental point of view, since it could release SO₂ and H₂S in the gaseous product during the thermochemical process. The sulfur content in biofuels generates SO₂ that forms sulfates, which can condense in the heat exchanger walls or generate ashes. Therefore, low levels of S in the fuel are required [8]. No sulfur was detected in the composition of the other biomass samples.

All biomasses have nitrogen levels less than or equal to 3 wt.%. Similar values were found by García et al. [8] when analyzing the N content of more than 200 biomass samples. The low percentage of N present in the biomasses indicates that its contribution to NO_x in waste gases is lower than from the air, which has a contribution nearly 15 or 20 times higher.

Low O/C and H/C atomic ratios indicate a higher degree of carbonization and ensure high heating values, because energy contained in carbon-carbon bonds is greater than that of carbon-oxygen and carbon-hydrogen bonds [10], [11]. Conversely, high O/C and H/C atomic ratios indicate low heating values; this is typical of the fresh plant biomass [3]. The CPB has the lowest O/C and H/C ratios; therefore, its heating value is higher than the rest of the biomasses studied (Table I).

Table I. - Characterization of biomass samples.

	Biomass			
	Agricultural		Forestry	Invasive species
	Vineyard	Tomato plant	Canary pine needles	<i>Pennisetum setaceum</i>
Proximate analysis (wt.%)				
MC	12.1	12.7	10.5	11.8
AC	4.3	28.6	3.3	15.4
VM	77.2	59.2	75.9	72.8
FC*	18.5	12.2	20.8	11.8
VM/FC	4.18	4.85	3.65	6.17
Ultimate analysis (wt.%)				
C	45.4	33.1	49.0	38.9
H	6.0	4.9	6.1	5.1
N	1.3	3.0	1.2	0.6
S	ND	1.9	ND	ND
O**	43.1	28.5	40.4	40.0
O/C	0.71	0.65	0.62	0.77
H/C	1.59	1.76	1.49	1.56
Mineral content (%)				
Ca	62.42	48.96	50.36	14.43
K	17.05	18.62	4.96	31.33
Na	ND	ND	ND	ND
Mg	3.80	2.96	2.79	1.88
P	2.99	1.23	2.45	1.13
Cl	2.09	9.29	2.50	15.00
Fe	5.18	3.87	13.96	3.43
Si	1.35	1.75	3.59	28.52
Al	ND	ND	1.93	ND
S	1.70	10.91	3.27	2.57
Ti	0.36	0.46	0.54	0.24
Cr	0.76	0.27	2.01	0.50
Mn	1.14	0.78	3.37	0.34
Zn	1.16	0.12	1.96	ND
V	ND	0.11	ND	ND
Cu	ND	0.11	4.07	ND
Br	ND	0.18	ND	0.34
Rb	ND	0.04	ND	ND
Sr	ND	0.33	ND	0.30
Sc	ND	ND	0.35	ND
Ga	ND	ND	0.46	ND
Ni	ND	ND	1.44	ND
HHV (MJ kg ⁻¹) ^{a)}	18.4	13.9	20.0	15.1
HHV (MJ kg ⁻¹) ^{b)}	18.6	13.3	19.2	15.4
HHV (MJ kg ⁻¹) ^{c)}	18.3	13.3	19.2	15.6
LHV (MJ kg ⁻¹) ^{d)}	16.8	12.0	17.7	14.3
Density (kg m ⁻³)	1593.3	1745.6	1376.0	1517.5

*Calculated from the difference of moisture, ash and volatile matter.

**Calculated from the difference of C, H, N, S and ash.

^{a)} [1]

^{b)} [2] from proximate analysis.

^{c)} [2] from DTG curve.

^{d)} [3] using HHV^{b)}.

ND: Not Detected.

A biomass used for energy purposes should have a low ash content and, consequently, a low inorganic content. Moreover, the concentration and behaviour of elements such as Ca, K, Na, P, Cl, S, Si and heavy metals are mostly responsible for many technological and environmental problems during biomass processing [12]. Normally, high concentrations of Ca, Mg and P in biomass are advantageous for use as solid fuel; however, high contents of K, Na, Cl and some trace elements could be a problem. Specifically, it is known that the compounds NaO_2 and K_2O are particularly troublesome because they lower the melting temperature of biomass ash causing serious operational problems including corrosion, agglomeration, fouling and slagging [13]-[15]. The reaction of alkali metals with silica present in the ash produces a sticky, mobile liquid phase, which can lead to blockages of airways in the furnace and boiler plant. It should be noted that while the intrinsic silica content of a biomass source may be low, contamination with soil introduced during harvesting can increase the total silica content significantly, such that while the content of intrinsic silica in the material may not be a cause for concern, the increased total silica content may lead to operational difficulties [11]. On the other hand, the presence of chlorine is important, due to the potential formation of toxic compounds in the flue gases, while their combination with K may result in corrosion problems [16].

The inorganic content of the biomass tested is referred to ashes and is shown in Table I. The main cations contained in all biomasses are calcium and potassium, which could be mostly found in carbonate, silicate or oxalate salts [17]. Other elements were also found, such as magnesium, phosphorus, iron and several trace elements. The greater presence of alkaline earth metals (Ca, Mg) compared to alkali metals (K and Na) is advantageous; thus, the problems associated with the low melting temperature of biomass ash would be avoided. The presence of sodium was not detected in any of the samples; however, the PSB sample showed higher K content than Ca content; even so, its ash content was not excessively high when compared to the TPB sample. Furthermore, washing of alkali-rich biomass fuels prior to their use may reduce some technological and environmental problems. However, such future large-scale washing may create new environmental concerns related to the fate of alkali metals, Cl, S, P, and some hazardous trace elements leached from biomass [12]. Chlorine content was generally low in all biomasses, ranging from 2.09% (VB) to 15.00% (PSB). Plant species that have been green in its life could be aggressive for combustion in biomass boilers due to its high chlorine content (from chlorophyll).

Although the alkali metals present in biomass can cause operational problems (corrosion, agglomeration, etc.), it has been shown that in pyrolysis or gasification processes they can have a catalytic effect and can increase the yields of some products [18]. Interactions with inorganic elements present in biomass such as K, Na, Ca and Mg are frequently reported to influence the conversion. According to Collard and Blin [19], the interactions between constituents and the catalytic influence of the minerals naturally present in biomass can significantly modify the yields of some products. Besides, various inorganic compounds can be added to biomass samples to enhance

the yield of a certain product and reduce the number of the pyrolysis products [20], [21]. Therefore, the use of catalysts could enable a better optimization of the conversion and be a decisive option to make thermochemical processes more competitive.

In addition, biomass density and heating values have also an impact on the behaviour of thermochemical conversion processes. The heating value of a material is an indicator of its content in energy released when it burns in the air. Generally, biomass is characterized by HHV of 15-20 MJ kg^{-1} , which is much lower than that of coal varying from 22 to 35 MJ kg^{-1} [1], [22]. Biomasses with high HHV are attractive as power sources to produce clean energy, since they could replace fossil fuels. CPB contains a higher HHV than the rest of the biomasses, followed by the VB and the PSB; the TPB is the biomass with the lowest HHV. The difference between the HHV and LHV values is not considerable, so the removal of heat from vaporization does not greatly influence the results. The CPB is the biomass that has the highest heating value because it showed lower O/C and H/C atomic ratios; further, the VB has a higher heating value than the PSB, since its O/C ratio is lower than that observed for the PSB. CPB and VB would be the two most suitable biomasses to produce considerable amounts of energy.

Dense particles contribute to a longer burnout time; conversely, low-density particles have lower energy efficiency, also lead to high transport costs and reduce the storage capacity of both the biomass producer and the end-user [23]. The TPB is the biomass with the highest density, followed by the VB and the PSB. The CPB is the biomass with lowest density, so its energy performance would be lower than the previous ones. The density values are in the range of those found by Parascanu et al. [24] when they analyzed different Mexican biomasses (Castor bean peel, Castor bean stem, Agave bagasse, Coffee pulp, Opuntia stem and Pinus sawdust) by the same method (1346.3-1726.7 kg m^{-3}).

B. Selection of biomasses

The characteristics of the four biomass samples were analyzed to determine which of them is the most suitable for each of the thermochemical processes: combustion, pyrolysis and gasification.

Regarding the combustion process, the most important parameter to consider is the heating value (Jenkins et al., 1998), which is influenced by the carbon, hydrogen and oxygen content in the biomass. Low O/C and H/C atomic ratios indicate a higher degree of carbonization and ensure high heating values, since the energy contained in the carbon-carbon bonds are higher than that contained in the carbon-oxygen and carbon-hydrogen bonds. Furthermore, biomass should lead to low ash content [24]. From the energy point of view, the biomasses under study are not the most recommended for use in combustion processes, since they present low HHV due to the high O/C and H/C atomic ratios; however, from an environmental point of view, its use is more advantageous than coal in terms of polluting emissions since the sulfur content in biomasses is much lower (or even non-existent) than that of coals. Considering the

most appropriate characteristics for the combustion process, the biomasses may be ranked in descending order as follows: CPB>VB>PSB>TPB.

Regarding the pyrolysis process, feedstocks with low heating value, high volatile matter content and low ash content are recommended [25]. Considering the heating value, all the studied biomasses could be suitable for the pyrolysis process since they show relatively low HHV between 13.9-20.0 MJ/kg (Table I). According to García et al. [8], it is recommended that the biomass subjected to pyrolysis present a volatile matter content in the range of 65-85%, since it is the portion that can be transformed into gas; and that the ash content is less than 10%; biomasses with ash contents of more than 30% are inadmissible to use for heat generation. Therefore, the TPB is discarded as biomass for the pyrolysis process, due to its high ash content and its low volatile matter content. The CPB (3.32 wt.% AC and 75.91 wt.% VM) and the VB (4.25 wt.% AC and 77.25 wt.% VM) are the most recommended biomasses for the pyrolysis process, followed by the PSB (15.4 wt.% AC and 72.79 wt.% VM). Despite this, the product to be obtained during the pyrolytic process must be considered: gaseous, liquid (bio-oil) or solid (char) fraction. Generally, the most desired products in pyrolysis processes are pyrolysis oils or char, while the gaseous fraction is usually the focus of attention in gasification processes. Considering the most appropriate characteristics for the pyrolysis process, the biomasses may be ranked in descending order as follows: CPB>VB>PSB>TPB.

Gasification process includes two main steps: biomass pyrolysis leading to char formation and gasification of the char producing syngas; therefore, biomasses subjected to gasification ought to have characteristics similar to those required for pyrolytic processes (low heating value, high volatile material content and low ash content). In addition, they should have a high fixed carbon content [25]. Fixed carbon is an important parameter because, in most gasifiers, the conversion of fixed carbon to gases determines the rate of gasification and its performance. This conversion reaction, being the slowest, is used to determine the size of the gasifier [3]. Another important parameter to consider is the biomass water content due to water favors the formation of hydrogen. Moreover, its presence is desirable, since it allows to decrease and even cancel the amount of steam added to the oxidizing agent. However, an excess of humidity decreases the performance of the process, since the water that enters with the solid consumes energy when vaporizing. Although the limits depend on the type of gasifier, values between 10 wt.% and 30 wt.% are acceptable. All the biomasses used meet this requirement (Table I). According to the ash and volatile matter content, the CPB and the VB are the most suitable biomasses for the gasification process; according to the fixed carbon content, these two biomasses are exactly which present the highest values, 20.77 wt.% and 18.50 wt.% for the CPB and VB, respectively (Table I). Therefore, the CPB and the VB are the most suitable biomasses for the gasification process, followed by the PSB. Considering the most appropriate characteristics for the gasification process, the biomasses may be ranked in descending order as follows: CPB>VB>PSB>TPB, coinciding with those of the combustion and pyrolysis process. However, when the

biomass to be treated is mostly organic, it is advisable to use gasification, while if the presence of inorganic materials is important, it would be advisable to choose a pyrolysis process [26]. The three biomasses suitable for the pyrolysis and gasification processes have similar inorganic material contents (Table I); therefore, the behavior of the three biomasses in both thermochemical processes will be studied.

In brief, for the three thermochemical processes, the most suitable biomasses, according to their characteristic properties, in descending order is as follows: CPB>VB>PSB>TPB. This classification may be used as a guide for the selection of the most appropriate fraction for energy utilization; however, two significant parameters must be considered, i.e., the available quantity and the seasonal variation of biomass [27].

4. Conclusion

The energetic properties of several biomass residues (or sources) from the Canary Islands through thermochemical processes were studied in order to know their utilization potential as solid biofuels.

The quality of biomasses in descending order, according to their characteristic properties, is CPB>VB>PSB>TPB. CPB, PSB and VB represent a good quality biomass source with medium moisture, and low Cl and S content. However, the high ash content in TPB may represent a significant barrier to further utilization.

VB, CPB and PSB proved to be potential candidates for energy generation through thermochemical conversion.

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