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Fast characterization of biomass fuels by thermogravimetric analysis (TGA)

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HIGHLIGHTS

- A methodology for the full characterization of lignocellulosic biomass is proposed.
- Suitable TGA analysis allows an accurate determination of the proximate analysis.
- The DTG curve is used for the determination of the content of the natural polymers.
- Empirical correlations are obtained for predicting HHV and C, H and O contents.

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ABSTRACT

A methodology is proposed based on thermogravimetric analysis, deconvolution of the DTG signal and empirical correlations for characterizing biomass fuels for boilers and combustors. This methodology allows determining accurately and in a short time the main parameters required for industrial operation, as are the higher heating value (HHV), the contents of moisture, volatile matter, fixed carbon, ashes, carbon, hydrogen and oxygen, and the kinetic parameters of the thermal decomposition of the biomass. At the present time, these parameters are obtained by using specific equipment that are much more sophisticated and expensive than the methodology proposed. Twelve types of vegetable lignocellulosic biomasses have been used in the study, i.e., wastes from wood industry, food industry and agriculture. The comparison of the results obtained, based on the methodology developed in this paper, with those published in the literature evidence the validity of the methodology for a wide range of materials.

1. Introduction

Vegetable biomass is one of the oldest energy sources on which mankind supported development. Biomass was set aside in the XX century due to the increase in energy demand, especially in the developed countries, and to the availability and higher energy density of coal, natural gas, oil and their derivatives. Nevertheless, the limited availability of fossil resources and their location at given zones in the world create a great dependence on oil importing countries, which seriously affects energy supply and even the economy of the region. Furthermore, there is an increasing concern about the impact production processes, especially those for energy production, have on the environment, which makes unsustainable an energy system massively based on fossil fuels.

Bearing in mind the present scenario on which development and welfare are related to energy consumption, alternative energy production resources should be considered, especially those that are geographically well distributed, renewable and environmentally friendly by contributing to neutral CO_2 balance. Vegetable biomass fulfils these three conditions, and therefore increasing interest is being paid to this alternative and renewable source for energy and raw materials [1,2]. Thus, except in the extreme regions (polar icecaps and extremely dried zones), vegetal biomass grows around the world in different forms (herbaceous plants, bushes, trees, algae and so on). Furthermore, the development in agriculture techniques has greatly increased soil fertility, which has given way to the abandonment of agricultural land over the last 20–30 years. Sustainable use of this land for the production of crops for energy production is a reasonable option to decrease energy dependence and contribute to avoiding environmental deterioration.

The use of edible crops for energy production has arisen a great controversy for the last years due to the increase in the price of human food this practice causes [3], and therefore certain first generation biofuels (mainly oil and ethanol) have not reached the

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Nomenclature

ASRE average square relative error
c_i mass concentration of i component (wt.%)
E_i activation energy of i constituent (kJ mol^{-1})
k_i kinetic constant for the weight loss of each i constituent (s^{-1})
$k_{i,ref}$ kinetic constant for the weight loss of each i constituent at the reference temperature (s^{-1})
N number of experimental data
t time (min)
W, W_0, W_∞ weight of biomass sample at t time, at the beginning of pyrolysis and at the end of pyrolysis, respectively (mg)
W_i, $W_{0,i}$, $W_{\infty,i}$ weight of i constituent in the sample at t time, at the beginning and at the end (mg)
X conversion of the biomass sample by mass unit of pyrolysable mass
X_i, $X_{\infty,i}$ conversion of i constituent at t time and at the end

development expected. Nevertheless, this is not the case for lignocellulosic biomass, given that it cannot be digested by human beings and is composed of a wide range of materials, as are: wood, wood-derived products, energy crops, agricultural products, agricultural industry products, forest wastes, wood manufacturing wastes and so on [4].

The more developed technologies for obtaining energy or fuels from biomass are those based on thermochemical treatments, namely, pyrolysis, gasification and combustion. Although pyrolysis is a route of great interest from an industrial and ecological perspective [5] due to the high yield of bio-oil obtained [6,7], the high content of oxygen and the presence of phenolic oligomers are obstacles in which intensive research is being carried out in order to progress in the development of the biorefinery [8]. Gasification has been intensively developed over the last century and nowadays is considered a suitable technology for the treatment of crushed wood and agro-forestry residues [9,10], although tar formation is a problem to be solved prior to the use of syngas as a chemical raw material [11].

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 [12,13].

Nowadays the two most developed technologies for obtaining heat and energy from biomass are grate and fluidized combustors [14,15]. The spouted bed is an alternative technology for solid fuel combustion, given that it has great advantages for the treatment of coarse and wide size distribution particles (as is the case of biomass) [16], and the turbulence of the regime ensures high heat and mass transfer rates [17], with pressure drop being much smaller than in fluidized beds [18,19].

The combustion efficiency and emission levels in vegetable biomass combustion systems depend on the properties of the fuel, operating conditions and combustor design [20]. Given that biomass is in many cases seasonal, the viability of any combustion plant requires adapting the operating conditions to the characteristics of the feed, and therefore biomass characterization should be fast, reliable and detailed. Accordingly, the aim of this paper is the development of a methodology based on a simple, fast and low cost analysis, such as TGA, to estimate all the usual analytical parameters required for a solid fuel characterization: elemental analysis, proximate analysis, heating value, and hemicellulose/cellulose/lignin ratio [21,22], which are the parameters of greater significance affecting degradation kinetics. DTG curve deconvolution is proposed for calculating the content of hemicellulose, cellulose and lignin [23,24] and the application of non-linear regression methods for correlating the contents of moisture, fixed carbon, volatile compounds and ashes with the contents of C, H, O and higher heating value, HHV [25–27].

2. Materials and methods

In order to study the different types of biomasses liable to energy recovery by combustion and with the aim of validating the methodology proposed with a sufficiently high number of materials, twelve types of biomasses have been used in this study, including commercial pellets, wood industry wastes (sawdust of *Pinus insignis, Acacia dealbata* and *Eucalyptus plantatio*), food industry wastes (rice husk, nut shells and olive stones), forest wastes (*Cytisus multiflorus, Pterospartum tridentatum* and *Pteridium aquilinum*) and two types of herbaceous materials (*Miscanthus sinensis* and *Rumex tianschanicus*). All these materials have been characterized in detail, with the physical–chemical properties measured being as follows: moisture content (according to ISO 589 standard and also in a HR83 halogen moisture analyzer, Mettler Toledo), proximate analysis (in a TA Instruments TGA Q5000IR following ASTM D5142 standard), elemental analysis (LECO TruSpec CHN analyzer and TruSpec-S module for S determination, according to ASTM D5373 and ISO19579 standards) and HHV (Parr 1356 isoperibolic bomb calorimeter following ASTM D5865 standard). The physical–chemical characteristics of the biomasses used in this study are shown in Table 1.

The moisture content of the materials used ranges from 7.21 wt.% w.b. (wet basis) for *Cytisus multiflorus* to 12.44 wt.% w.b. for *Pteridium aquilinum*, which are the usual equilibrium values for the conditions of temperature and moisture in the storeroom. These values significantly increase when the biomass is wet or when the atmospheric conditions are not favourable for collection. All the biomasses have high volatile matter contents, with values ranging from 65.33 wt.% dry basis (d.b.) for rice husk to 94.36 wt.% d.b. for *Cytisus multiflorus*. Concerning the other two parameters measured in the proximate analysis, Table 1 shows that vegetable biomass samples coming from different plant types or even from different parts of the plant have significantly different fixed carbon and ash contents. The content of fixed carbon is high in these biomass types derived from hard tissues (trunk, seeds), with values above 27 wt.% d.b. for olive stone, whereas in the case of soft tissues (leaves, young branches, bushes, grasses) the content is as low as 3.81 wt.% d.b. for *Rumex*. The ash content also changes significantly from sample to sample, with the values being even lower than 1 wt.% (pellet, nut shell, olive stone), whereas the values in the rice husk are close to 25 wt.% d.b. Carbon content ranges from 31.6 to 48.63 wt.% d.b., and N and S contents are generally low (around 1 wt.% d.b. or lower). The higher heating value (HHV) also varies considerably, with values ranging from 13.76 MJ kg^{-1} for rice husk to 20.36 MJ kg^{-1} for olive stone.

The methodology developed in this paper for fast characterization of the biomass is based on TGA, in the same equipment used for proximate analysis (TGA Q5000IR, TA Instruments). Accordingly, a detailed experimental study has been carried out in order