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# Effect of materials mixture on the higher heating value: Case of biomass, biochar and municipal solid waste

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## ABSTRACT

The heating value describes the energy content of any fuel. In this study, this parameter was evaluated for different abundant materials in Morocco (two types of biochar, plastic, synthetic rubber, and cardboard as municipal solid waste (MSW), and various types of biomass). Before the evaluation of their higher heating value (HHV) by a calorimeter device, the thermal behavior of these materials was investigated using thermogravimetric (TGA) and Differential scanning calorimetry (DSC) analyses. The focus of this work is to evaluate the calorific value of each material alone in a first time, then to compare the experimental and theoretical HHV of their mixtures in a second time. The heating value of lignocellulosic materials was between 12.16 and 20.53 MJ/kg, 27.39 for biochar 1, 32.60 MJ/kg for biochar 2, 37.81 and 38.00 MJ/kg for plastic and synthetic rubber respectively and 13.81 MJ/kg for cardboard.

A significant difference was observed between the measured and estimated HHVs of mixtures.

Experimentally, results for a large variety of mixture between biomass/biochar and biomass/MSW have shown that the interaction between biomass and other compounds expressed a synergy of 2.37% for biochar 1 and 6.11% for biochar 2, 1.09% for cardboard, 5.09% for plastic and 5.01% for synthetic rubber.

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## 1. Introduction

Energy is a crucial element for industrial, economic and social development of all countries. Recently, shortage of fossil energy resources has been the most important worldwide concern (Yin, 2011). The energy demand is over 85% based on non renewable fuels (Srirangan et al., 2012) and raised from 9000 to 12,730 Mtoe between 1995 and 2013 (Goldemberg and Prado, 2013).

Coal is mainly used for energy production and has the largest reserves compared to oil, gas and other fossil energy sources and is expected to be in use for over 110 years (Connor, 2016).

However, global warming caused by greenhouse gas emissions (which must be reduced by 80–90% at 2050 (Meinshausen et al.,

2009)) threatens the environment balance and the climate stability (Sigar et al., 2008). As a result, it is necessary to find a renewable resource for decreasing the gaseous emissions from fossil fuels and provides the energy stock.

Among alternative resources, biomass energy is drawing global attentions contributing to about 14% of the world's total energy consumption (Alauddin et al., 2010; Saxena et al., 2009). In addition, it is an attractive clean and environmental friendly fuel as it significantly induces low amount of NO<sub>x</sub> and SO<sub>x</sub> emissions, reduces the net carbon emissions to the atmosphere and can be considered as an inexhaustible reserve due to the forest management. There is two ways for biomass conversion: thermochemical and biochemical processes. The thermochemical technology consists mainly of pyrolysis, gasification, liquefaction, combustion, carbonization or co-firing (Patel et al., 2016). The biochemical process involves the degradation of biomass under the action of bacteria, microorganisms and enzymes into gaseous or liquid fuels, such as biogas or bioethanol. Among these processes, hydrolysis and fermentation are very useful (Voloshin et al., 2016).

Nevertheless, the increasing of municipal solid wastes (MSW) requires the development of treatment technologies and

Abbreviations: AB, benzoic acid; C, carbon; DSC, differential scanning calorimetry; H, hydrogen; HHV, higher heating value; MSW, municipal solid waste; Mtoe, megaton of oil equivalent; N, nitrogen; Ni-Cr, Nickel-Chrome; O, oxygen; PE, polyethylene; PP, polypropylene; PVC, polyvinyl chloride; S, sulfur; TGA, thermogravimetric analysis; WTE, waste to energy.

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environmental protection strategies (He et al., 2010). Recently, there is a great interest was given to the treatment of MSW. Callejón-Ferre et al. have developed briquettes for recycling and reuse of plant wastes such as biomass, plastics and fertilizer and crop protection product containers from intensive cultivation into a stable non-toxic product (Callejón et al., 2010; Callejón-Ferre and López-Martínez, 2009).

Waste to energy (WTE) methods are promising solutions to harness energy from MSW and to reduce their environmental impact (Liu and Liu, 2005). WTE technologies can be biochemical (composting, anaerobic digestion process, etc.) or thermochemical (incineration, pyrolysis, gasification, etc.).

However, MSW is a complex mixture of different categories; food residue, plastics, paper, textiles, wood waste, etc, and depends on time and the region of waste origin (Luo et al., 2010; Xi et al., 2010; Zhou et al., 2014). The thermochemical conversion of MSW components to fuel has been discussed by a number of researchers (Arenas, 2012; Gregorio and Zaccariello, 2012; Sanli et al., 2014).

Before the treatment of any component, the knowledge of its thermal characteristics and chemical composition is essential. Several works report on the testing methods which include proximate and ultimate analysis, calorific value determination and ash fusion. Ultimate analysis is one of the important tests. It informs about the percentage of carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulfur (S). The concentrations of C, H and O allow to estimate the heating value while the amounts of N and S gives an idea of the environmental impact. While, the proximate analysis helps to determine the weight percentage of volatile matter, fixed carbon and ash contents. The product of this analysis helps to study the combustion phenomenon. For example, a high ash contents cause ignition and combustion problems. A low dissolved ash fusion can provide fouling and slagging problems. Moreover, the heating value increases with fixed carbon and volatile matter. The results of these two analyses are usually expressed on a dry weight basis after eliminating the moisture. The moisture content affects negatively the HV and can lead to combustion problems (Saidur et al., 2011).

Moreover, thermal characterization techniques such as differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) allow the determination of complementary and relevant properties. Indeed, DSC allows the determination of transition (melting, vaporization, etc.) or decomposition enthalpies (Shen et al., 2015). Also, thermogravimetric analysis describes the weight loss as a function of temperature, used to characterize volatile and moisture contents as well as to investigate the thermal behavior (Gašparović et al., 2012).

Heating value represents the quantity of energy produced when the fuel is burned, usually, determined experimentally by a bomb calorimeter (Riber et al., 2009; Zhou et al., 2015).

Higher heating value (HHV) can also be determined theoretically from the elemental analysis. Yin has developed an empirical correlation (Eq. (1)) for prediction of HHV by using linear regression method based on data of biomass samples taken from literature, especially on carbon and hydrogen contents (Yin, 2011).

$$\text{HHV (MJ/kg)} = 0.2949\text{C} + 0.8250\text{H} \quad (1)$$

Callejón-Ferre et al. have also proposed several HHV prediction equations (Eqs. (2) and (3)) from elemental analysis of crop residues produced in southeastern Spain (Callejón-Ferre et al., 2011).

$$\text{HHV (MJ/kg)} = -3.393 + 0.507\text{C} - 0.341\text{H} + 0.067\text{N} \quad (2)$$

$$\text{HHV (MJ/kg)} = 5.736 + 0.006\text{C}^2 \quad (3)$$

Shi et al. have collected 193 experimental data to develop an empirical model to estimate the HHV of MSW from Red Deer City

defined in Eq. (4), based on weight percentages on a dry basis of carbon, hydrogen and oxygen (Shi et al., 2016) as:

$$\text{HHV (MJ/kg)} = 0.350\text{C} + 1.01\text{H} - 0.0826\text{O} \quad (4)$$

HHV can also be estimated from the results of proximate and structural analysis. Akkaya has proposed a predictive model based on the components of proximate analyses from 444 data using adaptive neuro-fuzzy inference system (ANFIS) approach. The biomass HHV prediction performance was 0.8836 for a coefficient of regression  $R^2$  and 1.3006 for root mean square error RMSE (Akkaya, 2016). Alvarez et al. have developed two models (Eq. (5) and Eq. (6)) from twenty samples of olive, wine industries, forest and agro wastes (Álvarez et al., 2015). The first was based on lignin (L) and hemicellulose (H) quantity, while the second was based on lignin content.

$$\text{HHV (MJ/kg)} = 17.0704 + 0.0449\text{L} - 0.0202\text{H} \quad (5)$$

$$\text{HHV (MJ/kg)} = 16.1964 + 0.0555\text{L} \quad (6)$$

Callejón et al. have established 15 mathematical HHV prediction equations based on the structural analysis of the biomass. They concluded that the models based on structural analysis are less reliable than the mathematical models of the same species based on proximal and element analysis (Callejón-Ferre et al., 2014).

Several works have investigated biomass blends with Coal during combustion (Sung et al., 2016), pyrolysis (Goldfarb and Ceylan, 2015) and gasification (Chen et al., 2015; Zhang et al., 2016). For biomass and MSW blends, number of authors is attracted by thermal conversion of biomass and plastic mixture during gasification and pyrolysis. (Alvarez et al., 2014; Narobe et al., 2014; Oyedun et al., 2014a, 2014b; Özge Çepeliogullar, 2014; Sajdak et al., 2015; Sajdak and Muzyka, 2014; Sajdak and Słowik, 2014; Xue et al., 2015). However, there are few informations regarding theoretical HHV estimation for mixtures containing cardboard.

The aim of this work is to determine the impact of mixture between different materials (biochar, MSW and biomass) on HHV and also, interpret the thermal behavior of these materials.

## 2. Material and methods

### 2.1. Raw materials

The raw materials used in this work were chosen in view of their abundance in Morocco and their higher organic matter in order to develop densified materials with a high energetic power in the future. The feedstock included six kinds of biomass (sugar cane, eucalyptus sawdust, alfa (*macrochloa tenacissima*), kernel olive, wood sawdust, manure), three types of MSW (cardboard, plastic and synthetic rubber) and two types of biochar (simple biochar (biochar 1) and commercial activated biochar (biochar 2). Plastic sample used in this study is a heterogeneous mixture of polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC), while wood sawdust is from a traditional carpentry.

The samples were firstly dried at 105 °C for 24 h. Then, different mixtures were prepared using different percentages (25%/75%, 50%/50% and 75%/25%): biochar1/biomass, biochar2/biomass, plastic/biomass, synthetic rubber/biomass and cardboard/biomass.

### 2.2. Elemental analysis

Element analyses (C, H, N and S) were performed on a VARIO-ELEMENTAR analyzer. The elementary composition was determined through quantitative high temperature decomposition. For such determination, the samples are converted into gaseous compounds. The gas mixture is cleaned, separated into its components

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