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Utilization of Plaster Waste for Reducing the Fouling Caused by Direct Burning of Vegetable Biomass

Devanchirles M. A. da Silva[a], Nathália Maria P. da Rocha e Silva[b,c], Leonardo B. dos Santos[a,b], Leonie A. Sarubbo[a,b], Valdemir A. dos Santos[a,b]*

[a]Centre of Science and Technology, Catholic University of Pernambuco, Rua do Príncipe, n. 526, Boa Vista, Cep: 50050-900, Recife-Pernambuco, Brazil
[b]Advanced Institute of Technology and Innovation – IATI, Rua Carlos Porto Carreiro, n. 70, Boa Vista, CEP: 50070-090, Recife, Pernambuco, Brazil
[c]Northeast Biothecnoloby Network,, Federal Rural University of Pernambuco, Rua Dom Manoel de Medeiros, s/n, *Dois Irmãos,* CEP: 52171-900, Recife, Pernambuco, Brazil
valdemir.alexandre@hotmail.com

The formation of fouling in the walls of the combustion chambers has been a limiting factor for the use of solid biomass as fuel for direct burning in non-rudimentary furnaces. Despite its high lignin content, with high Calorific Power, the biomass composed of residues of floating species of the *Eichhornia crassipes* species has been subject to restrictions of use. To contribute with the technology of adaptation of solid biomass use in furnaces of superior technology, this paper presents the potential of plaster waste to be as a promising material to reduce fouling generated by direct combustion of vegetable biomass. Macrophyte pruning residues were used in this study for pellet´s preparation that were filled by gypsum residues. An addition of gypsum residues to vegetable biomass pellets keeps lower heating value and can reduce maintenance time of furnaces due to decrease in standard fouling content in tens of percent.

1. Introduction

Solid biomass is an abundant resource that can be produced in agriculture, forestry and aquatic systems. This biomass is mainly composed of cellulose, hemicellulose, lignin and smaller amounts of other extractable components. As well as minerals such as silica, calcium carbonate and water, pectins, glycoprotein proteins, fatty compounds (cutin, suberin and waxes), oxalates, tannins and resins also make up this biomass (Tanger et al., 2013). Agricultural products, including plant and animal substances, forest residues, industrial wastes and the biodegradable part of industrial and urban wastes are its main sources (Ozcan et al., 2014). The use of solid waste as a source of energy can be accomplished by direct burning (Rakatoarisoal et al., 2015) or by the production of a biogas (Cotana et al., 2015). In direct burning it is usually used its compacting or agglomeration (briquettes), providing a series of advantages. Among these advantages, when compared to the use of this biomass in the natural state, are the facilities of storage, handling and increase of density, with consequent improvement of calorific power. This form of briquetting for solid biomass allows the same to be used in different types of burners (Rezania et al., 2016).
As properly referenced by Crema et al. (2011), aquatic macrophytes are an important community in shallow-water ecosystems, possessing a high rate of primary production, participating in nutrient recycling and providing food for herbivores and detritivores. Floodplain lakes of the Brazilian region are rich in aquatic macrophytes, including the abundant free-floating water hyacinth Eichhornia crassipes (Mart.) Solms (Pontederiaceae) (Villamagna and Murphy, 2010).
Net calorific value (NCV) is the amount of usable heat energy released when a fuel is burned under conditions similar to those in which it is normally used. The biomass of the floating macrophytes of the species Eichhornia crassipes has a higher lignin content, which has a NCV of 2.51.107 J/kg and a lower cellulose content, with a NCV of 1.59.107 J/kg. This composition allows the classification of the biomass as an excellent biofuel due to the High Calorific Power (HCP) value attributed to lignins. However, other factors should be

considered, such as ash and silica (Tavares and Santos, 2013). These macrophytes are herbaceous plants, having non-woody stems, which becomes a limiting factor for direct combustion. They also have high ashes content, which makes their use in boilers limited, because it can cause damage due to formation of fouling originated during the thermal decomposition process of the calcium oxalate. Generally, a high ash content results in problems such as slag production (D'agua et al., 2015). The thermal decomposition of the calcium oxalate present in the macrophyte residues leads to the formation of calcium carbonate, which in turn decomposes into CaO and CO_2. Since CaO is a fouling substance, these macrophytes are indicated as direct burning biofuels only for rudimentary furnaces.
In this work, gypsum residues were mixed in the pellet's composition to reduce the risk of fouling during the direct burning of macrophytes of the species *Eichhornia crassipes*, which would allow their use as fuel for any type of thermal equipment.

2. Material and Methods

2.1 Macrophytes

The individuals of E. crassipes (Crema et al., 2012) were collected in natural freshwater habitats in Recife city, Pernambuco State, Brazil, where the species are abundant and also have surfactant properties (Brasileiro et al., 2015; Sarubbo et al., 2015) (Figure 1).

Figure 1: Free-floating water hyacinth Eichhornia crassipes (Mart.) Solms (Pontederiaceae)

2.2 Preparation of The Residues of Macrophytes

Macrophyte pruning residues were obtained from a constructed wetland (Rakatoarisoal et al., 2015) for the treatment of oily water. The residues were left to dry under the sun for about 2 days. Then they were ground and kept in an oven at 50ºC until constant weight. From these residues briquettes were made, without and with the addition of residues of hydrated gypsum, to monitor the calorific power and the masses of the fouling left in the walls of the chambers where these briquettes were burned, as will be described next.

2.3 Thermal Decomposition of Hydrated Plaster

In a reactional medium containing gypsum ore ($CaSO_4.2H_2O$) or hydrated gypsum residue, which has the same molecular constitution, when temperatures reach 60 to 160 °C, around the atmospheric pressure, a thermal dehydration reaction begins (Paulik et al., 1992). This loss can vary from 0.0 to 0.5 water molecules, given rise to a semi-hydrate called gypsum plaster ($CaSO_4.0.5H_2O$), depending on the reaction time. When the medium reaches a temperature around 200 ºC, this material loses almost all its water of hydration and a calcium sulfate is obtained with little or no hydration capacity ($CaSO_4.\varepsilon H_2O$), receiving the denomination of soluble Anhydrite III, of instable character. The value of ε is in the range of 0.06 to 0.11 mol of water per mol of Anhydrite. When it reaches about 400ºC, the Anhydrite III becomes Anhydrite II ($\varepsilon \cong 0$). The latter form is of slow hydration and since the transformation process from phase III to phase II is exothermic, the transformation is very rapid and non-reversible to rehydrate half of the anhydrite and at 800°C the product is considered to be of difficult rehydration. During the decomposition of the hydrated gypsum residue, or gypsum ore, the formation of a pseudo-liquid state is observed, which is why gypsum furnaces have a bulkhead to prevent material leakage (Melo, 2012). The formation of this liquefied state of the gypsum mass can be used to agglutinate CaO or MgO molecules, avoiding the formation of fouling (CaO or MgO) in the final reaction step, which can migrate to the walls of the combustion chamber that delimit the reaction medium.

2.4 Thermal Decomposition of Calcium Oxalate

Calcium oxalate monohydrate, responsible for fouling on the walls of the combustion chambers, is thermally decomposed according to these three steps (Rak et al., 1995):
Step 1: $CaC_2O_4.H_2O \rightarrow CaC_2O_4 + H_2O$ (96.8 ^oC and 186.4 ^oC)
Step 2: $CaC_2O_4 \rightarrow CaCO_3 + CO$ (380.4 ^oC and 491.9 ^oC)
Step 3: $CaCO_3 \rightarrow CaO + CO_2$ (579.9 ^oC and 734.9 ^oC)
The laboratory experiments allow to identify the temperatures corresponding to the beginning and end of each thermal event, besides the maximum temperature represented by the Derivative Thermogravimetric (DTG*)* peak. Based on the Thermogravimetric Analysis (TGA) data, it is possible to recognize the decomposition bands and even calculate the mass variations due to losses of water, CO and CO_2.

2.5 Production and Burning of Briquettes

According to D'Agual et al. (2015), the macrophyte biomass is viable for the manufacture of briquettes and for its later use as solid fuel. These authors observed that for the formation of briquettes no heating and binders were necessary because this biomass had a sufficient moisture content in relation to other materials. Thus, the high yield of green matter, its periodicity and abundance outperform other biomasses used commercially, proving to be a viable alternative energy for Ibero-American countries.
To prepare the pellets, the residue of the macrophytes were dried to a moisture content of 13.0 % wt on a wet basis, determined using a thermobalance (Figure 2). The biomass was weighed and the pellets were made with macrophyte residues and 0.0, 2.0, 4.0, 6.0 and 8.0 % wt gypsum plaster residues. These percentages were calculated as a function of an average value of 1.51 % wt of the calcium content commonly found in floating macrophytes of the *Eichhornia crassipes* species, according to Tabuti et al. (1998). The strategy to verify the pellet's NCV with about 4 times more gypsum than the one corresponding to the calcium present in the macrophytes biomass was to observe the reduction of the quality of the biofuel with the percentage of gypsum added to the briquettes.

Figure 2: Determination of the pallet's moisture produced from residues of macrophytes and residues of hydrated gypsum

2.6 Experimental Planning
The experiments were carried out according to a single factor experimental design, for which the content of gypsum residues in the briquettes was chosen. The response variable was the ICP of the briquette as a function of gypsum content. To obtain ICP mean values of the macrophyte and gypsum residue briquettes, a

Parr® calorimeter was used. Experimental tests of burning and visual detection of residues were performed with the help of a mini blowtorch in a laboratory chapel (Figure 3). For this, the briquettes were placed inside an aluminum capsule and calcined using the blowtorch. Comparative images of the visual aspects of the residues provided qualitative material for comparison between fouling conditions on the walls of the biomass combustion chamber.

Figure 3: Experiments of pellet's burning with the aid of a blowtorch for visual identification of fouling levels as a function of the content of gypsum waste

3. Results and Discussion

Box plot graphical methods were used as a statistical tool to describe the results obtained (Carter et al., 2009). The graph of Figure 4 illustrates the influence of the hydrated gypsum content on the calorific value of the pruning residue briquettes of macrophytes of the *Eichhornia crassipes* species. A decrease in the calorific value is observed in the graph with the increase of the gypsum content in the composition of the briquettes. It is also observed that a maximum percentage of 4.0 % wt can be used as dosage of residue of gypsum hydrate. In this case, the pellet's macrophytes can be used as solid fuel with a NCV similar to that of wood, as determined by Telmo and Lousada (2011), of the order of $1.38 \cdot 10^7$ J/kg.

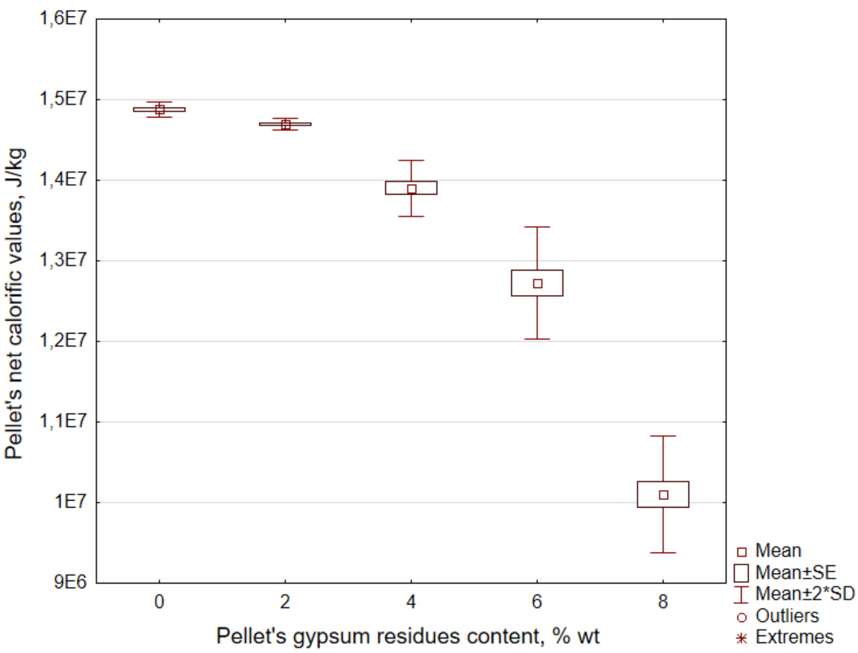

Figure 4: Net calorific value of Pellet's macrophytes as a function of the content of hydrated gypsum residues

Residues resulting from fouling left in the crucibles where the pellets were burned, with different percentages of hydrated gypsum, had their fouling contents evaluated and placed on a box plot graph (Figure 5). In this figure the data used in the had their values normalized as a function of the visual difficulties to differentiate the amount of mass retained in each fouling.

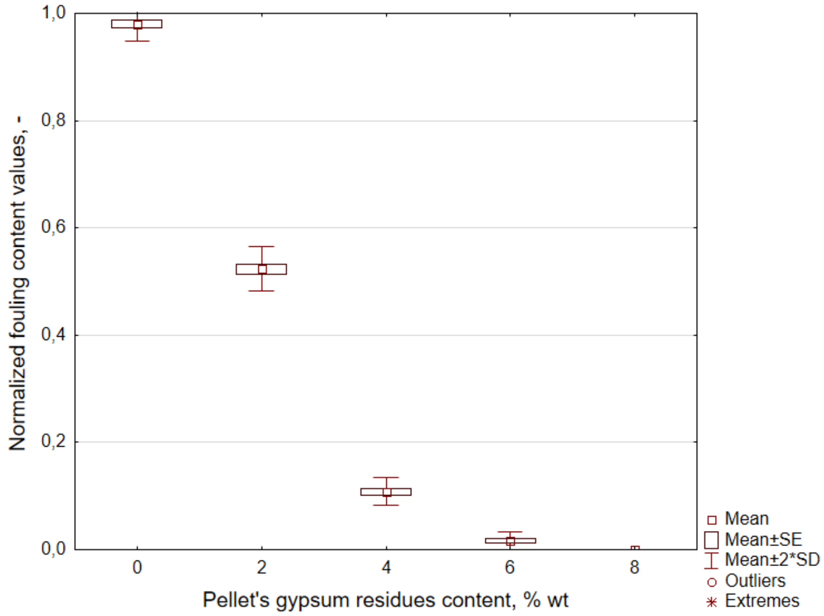

Figure 5: Normalized fouling content produced by the pallet's burning as a function of the percentage of hydrated gypsum

4. Conclusion

The floating macrophytes of the Eichhornia crassipes species have long been known to be true pests in lakes and rivers for reducing survival conditions of aquatic fauna. This work presented an attractive alternative for the use of pruning residues of these macrophytes, associated with residues of hydrated gypsum, as solid biofuel of ICP and free of incrustations, reducing the maintenance time of furnaces used for their combustion.

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