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Study of the Thermal Behavior of Almond Shells and Acorn Cups for Production of Fuel Briquettes

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Abstract:

Because of the importance of his field, its neutrality in terms of pollution, biomass sector is an attractive way for the promotion of renewable energies, the fight against deforestation and the protection of our environment. In Morocco, almond shells and acorn cups are still rejected as a solid waste, while they can be a source of renewable energy and provide a continuous supply of solid liquid and gas fuels, through a thermochemical conversion. The conversion of acorn cups and almond shells to energy by thermochemical conversion processes requires a fundamental understanding of their thermal properties. The purpose of this research is to investigate the thermal behavior of these wastes, its energy recovery by the production of fuel briquettes from roasted fine and to study combustion behavior of these briquettes. The results of thermogravimetry (TGA), derivate thermogravimetry (DTG) and differential thermal (DTA) analysis allowed us to determine the stages of thermal decomposition of acorns cups and almond shells and associated phenomena. Characterization of briquettes showed us that the particle size and residence time during roasting are the determinants factors of their quality.

Keywords: Renewable energy, fuel briquettes, almond shells, acorn cups.

1. Introduction

Morocco is now facing a difficult situation in terms of energy: increasing energy dependence, increasing the cost of energy in a global context of scarcity of fossil resources, and depletion of wood which is a key energy resource in Morocco, especially in rural areas (Stéphane & Morgane, 2010). Before the deficit of natural resources, it is essential to identify solutions to ensure sustainable access to cooking fuel while preserving our environment, so our resources and climate. The objective of this work is to promote alternative energies to reduce the demand for wood energy, such as biochar. The latter takes on a major importance since it allows value of unused agricultural residues or other types of renewable biomass by turning it into charcoal briquettes that can be used in the same way as charcoal (Ndiaye, A, Baur, J. 2006).

Indeed the use of agricultural waste as an energy source has received in the last decades a great importance because they have many economic and environmental benefits (Lee,S. et al ,2007). Many studies have been conducted on different waste for characterization of their properties and an energy valuation:

Jinje Park et al (2013), have studied the slow pyrolysis of rice straw in temperatures between 300 and

700 ° C and to characterize the yields and the detailed composition of biocharbon, bio-oil and non-condensable gases. The study of the thermal behavior of different date palm residues under inert and oxidative atmospheres was undertaken by El May, Y. et al. (2012). Agirre, I. et al. (2012) conducted experiments in high temperature pyrolysis of cuttings of fruit in a screw reactor for the production of the coal used as the reducing agent in the production of non-ferrous metals and in the process of recycling. Varol, E. et al (2007) studied the effects pyrolysis temperature of pistachio shells on the product yields and composition. For Ioannidou, O. et al (2007), their work is focused on the study of the potential of corn residues for energy, fuel materials and chemicals production.

Chou, C.S et al (2009) studied the optimal conditions for the preparation of fuel briquettes from rice straw by a piston-mold process conditions. This study demonstrated the feasibility of preparing solid fuels from biomass which is a renewable and neutral resource in terms of pollution.

In this context, our study concerns the energy recovery from agricultural waste namely almond shells and acorn cups by production of fuel briquettes. Our work focused on the study of the thermal behavior of this waste by means of ATG and DTA and on their heat treatment by roasting. The briquettes were prepared using the roasted particles and a binder. The study of the influence of various parameters (size, residence time) on the combustion behavior of the fuel briquettes was also undertaken.



2. Material and methods

2.1 Preparation of sample

The acorn is the fruit of the oak, it is an achene, containing one seed (rarely two seeds). It is wrapped on its base by a cup. The samples of acorns were collected from the forest of green oak located to El Hajeb, Morocco. Almond samples were from the region of Meknes in Morocco. After shelling acorns and almonds, the hulls obtained were dried in an oven for 12 hours at a temperature of 105 °C to decrease their moisture content and facilitate their grinding. After sieving, the samples with particle size between 200 microns and 1.6 mm were collected for the experimental tests.

2.2 Thermogravimetric analysis

Thermogravimetric analysis is widely used to study the thermal degradation characteristics of agricultural waste and other materials (Park, J.et al ,2013; Ôrfǎo, J.J.M. et al ,1999; Dorge.S et al ,2011; Virmond,E. et al ,2012; Titiloye ,J. O. et al ,2013). Ghaly and Ergudenler (1999) recommended the use of samples with small particles to ensure temperature uniformity of the sample. In this work we investigated the thermal behavior of agricultural waste in an oxidative atmosphere using an apparatus of the type Shimadzu TA-60. The TGA were conducted in air at a heating rate of 20 $^{\circ}$ C min-1 from room temperature to 900 $^{\circ}$ C. We chose a slow heating (<50 $^{\circ}$ C) to study the thermal behavior of samples under conditions where the transport process do not hide the study of the chemistry effects (Crønli M.G. et al, 2002).

2.3 Thermochemical traitement of samples:Roasting

The results of thermogravimetric analysis allowed us to determine the temperature of thermochemical processing allowing to maximize the yield in solid product while improving waste properties. We chose to heat treatment at a temperature below the decomposition of waste, to do this we used the roasting, in effect this conversion occurs at temperatures between 230 $^{\circ}$ C and 280 $^{\circ}$ C under inert atmosphere (Leroy, V, et al 2006). During torrefaction process density and the specific heating value of the product increase and there is a reduction in moisture content (Hakkou, M.et al 2006).

We took flasks where we put the various samples and weighed them before putting them in the steam room in 230°C for a definite duration. The flasks are closed to avoid any air inlet. At the end of the roasting, we weighed samples again to determine the weight losses. Table 1 shows the particle size and retention time of each sample.

holding time size
acorn cups (mm) almond shells (mm)

3.5

Table 1.The particle size and the holding time of samples,

2.4 Manufacture of fuel briquettes

30min 60min

Roasted fines (3.5mm) were ground and sieved using a sieve shaker of increasing openings (100 μ m at 1, 6 mm). To investigate the effect of particle size on the properties of the fuel briquettes, the latter were manufactured from a mixture of roasted fine with particle size 200 μ m or 600 microns and a binder (green clay+ wheat flour), followed by compaction by means of a hollow cylinder and of a hammer and drying at room temperature. Table 2 shows the components of the formed briquettes.

Table 2. The composition of briquettes,

roasted waste	Holding time	Particle size	Amount of binder
Acorn cups	30 min	200 μm	
	1h	600 μm	20 % of the green clay + 5 % of the
Almond shells	30 min	200 μm	wheat flour +Water according to the
	1h	600 μm	mixture

2.5 Testing and comparing briquettes combustion

This study consists in lighting in four melting pots in clay the made briquettes, every melting pot contains a type of briquettes (size grading 200 μ m or 600 μ m, thermal processing time 30 min ou1h) and observing their behavior of combustion. More specifically, we warmed a certain amount of water (25 ml) under the same



conditions by the same amount of mass briquettes made from roasted fine with particle size of $200\mu m$ and $600\mu m$ and we noted the temperature of the water as a function of time. These experiments have the interest to inform us about the speed of the consummation of briquettes and to show us the capacity of the fuel to raise the temperature of the water. These experiments were conducted in earthen pots outdoors.

3. Results and discussion

3.1 Thermogravimetric analysis

The TG,DTG and DTA curves of the two samples are shown in Fig. 1, Fig. 2. DTG and DTA curves exhibit three peaks which shows that thermal degradation under the oxidative atmosphere of the two samples passes through three main steps: The first corresponds to the evaporation of moisture, the second the devolatilization and final the oxidation of the coal. The first stage is an endothermic phenomenon (curve DTA) which extends of the ambient temperature to approximately a temperature of 127° C, in this region the loss of mass is minimal (<12, 5%) with a rate of (< 3.5% / min). Water loss and volatilization of lighter molecules may have contributed to the loss of mass at this stage.

The second step has an exothermic phenomenon curve (DTA) that occurs almost a temperature between 257 $^{\circ}$ C and 378 $^{\circ}$ C for acorn cups and between 282 and 398 $^{\circ}$ C for almond hulls. The third stage also exhibits an exothermic phenomenon occurring between a temperature of 397 $^{\circ}$ C and 522 $^{\circ}$ C for two wastes. We notice that the degradation of both waste as well as the rate of weight loss at the second region (\sim 50%, 9%. min-1) is greater than those of the third (\sim 17%, 4%. min-1). As suggested by M.Versan Kok V.Leroy and other (Versan Kok,M. et al, 2013; Feifli, F.F., C.A.Luengo ,2005), the first exothermic region is due to the combustion of volatiles light, the second region presents the combustion of the coal. It is noted that the maximum degradation is obtained at about 312.86 $^{\circ}$ C with a rate of 15.2%. min⁻¹ for the acorn cups and 339.39 $^{\circ}$ C at a rate of 13% for almond shells , this difference is probably due to a variety in the composition of the two waste, it may be that the cups containing more volatile and less ash material, this also shows that the cups are more reactive than the almonds shells .

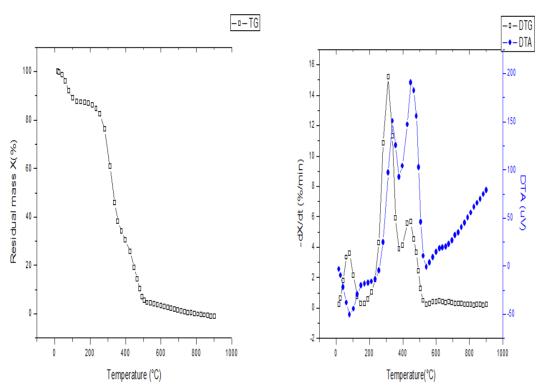


Figure 1.TG, DTG and DTA curves of acorn cups.



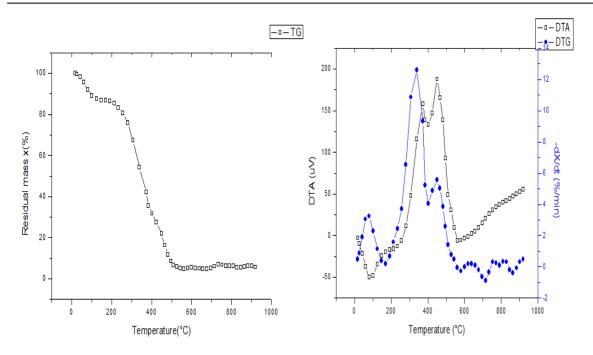


Figure 2.TG, DTG and DTA curves of almond shells.

3.2 Roasting

We found that the color of the roasted samples becoming darker or black with increasing temperature and duration of the roasting, this is due to the increase of carbon (NOCQUET, T., 2012).

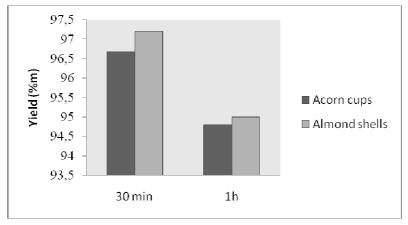


Figure 3. Solid yield after roasting

From Figure 3, we found that the loss of mass of the solid is greater with increasing roasting time. The overall yield of volatile species produced during the roasting process increases with the reaction time, the same way that the yield of solid decreases, which is consistent with the literature (Prins,M.J et al 2006; Deng,J. al 2009; Commandre,J. 2010). Under the same conditions (temperature, residence time) the mass loss of cups is greater than those of almond shells so the cups are more reactive than almond shells. The mass loss resulted from the release of volatile matters, some condensable and non-condensable gases (CO, CO2 ...) and water (Ballerini, D. 2011).

3.3 Testing and comparing briquettes combustion

According to the test of combustion we notice the presence of smoke released during the firing and light difficulty of firing compared with the charcoal. Briquettes made from roasted fine for 30 minutes release more smoke than that having undergone duration of roasting of 60 min. To test the cooking water we used briquettes made from fine roasted for 60 minutes because they emit less smoke during their combustion.

From figure 4 and 5, we found that the increase of the temperature of the water is faster for briquettes having a



size grading of 600 μm until approximately 48°C, then the tendency is knocked down for the benefit of those of size grading of 200 μm , this shows that the taking of fire of the briquettes of 600 μm is more quickly than those of 200 μm and that the fuels realized from the size grading of 200 μm ignite with difficulty but they preserve their energy because the reaction of the combustion is slow sight that particles are compacted well and stuck some of the others.

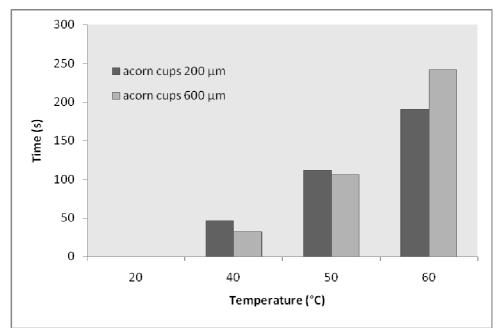


Figure 4. Water heating using the briquettes of acorn cups

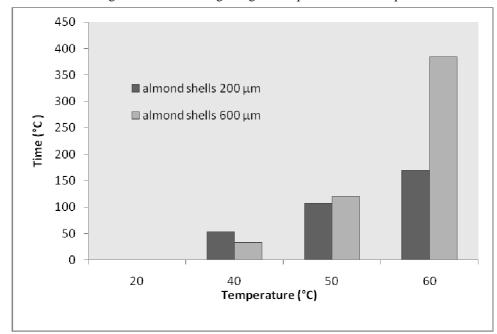


Figure 5. Water heating using the briquettes of almond shells

4. Conclusion

Thermogravimetric and differential thermal analysis in an oxidative atmosphere have shown that the thermal degradation of almond shells and acorn cups passes through three main stages: moisture evaporation which is an endothermic phenomenon; volatilization of the light molecules, exothermic phenomenon and the oxidation of



coal, exothermic phenomenon. The temperature of the start and the end of each step differs from the waste in other according to its composition and its reactivity.

According to the test of combustion of briquettes we concluded that the roasting time influences the quality of briquettes. A long duration allows a strong devolatilization, resulting briquettes emitting less smoke and that the particle size influences the behavior of combustion, more the size grading is big more is fast the consumption of briquettes.

This study confirmed that energy recovery from almond shells and acorn cups by the production of fuel briquettes using roasted fine, green clay and wheat flour (starch) as a binder is a promising avenue for the fight against deforestation and promotion of renewable energies.

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