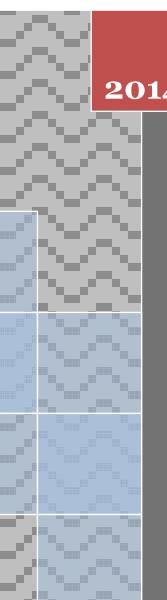


Volume 10 Issue 24





FULL PAPER BTAIJ, 10(24), 2014 [16507-16517]

Mathematically simulated transportation of biomass

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ABSTRACT

A transport biomass region with little local production capacity necessarily requires appropriate specials conditions to maintain their characteristics for energy production.

The aim of this paper is to study the two biomass with higher production in Spain and the testing of static gravimetric procedures saturated salt and procedures climatic chamber (15, 35°C) models GAB, Henderson will be used, Chung Oswing Pfost to determine the parameters for static methods to be cooperate with dynamic parameters, therefore predict the best conditions to be transport into the containers.

Inversion points in the isotherms for all temperatures between 0.58 and 0.66 a_w identified, increasing temperature difference, the humidity values of the monolayer (Xm) obtained with the model of GAB vary between 8.8 % for pellets and 2.5 % for olive stone.

KEYWORDS

Isotherms; Transport; Biomasse; Henderson; Chung-Pfost; Oswing; GAB; Pilosof.

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(2)

(5)

INTRODUCTION

Pellets and olive stones are hygroscopic materials, which tend to balance their humidity conditions with environments in which hygroscopic conditions exits^[1], so where they are transported is very important if their characteristics and properties are to be maintainined.

Biomass equilibrium moisture describes moisture changes caused by exposure to several hydrothermal conditions that increase until moisture equilibrium is reached. Calorific power depends on the humidity content, which gets higher as the humidity decreases. The calorific power value depends of the density and humidity, higher humidity reduce the calorific value^[2].

Unlike pellets, wood chips are produced directly from a drum chipper, which is the most basic method of biomass production from wood. The process of producing pellets, meanwhile, requires a pellet press, which increases the density. In fact, potential biomass energy wasted from burning wood has a great impact on the environmental.

The Canary Island's energy potential from biomass is currently one of the lowest in Spain according to a report of IDAE (Institute for Energy Diversification and saving), As a consequence biomass consumption is not significant, due to the lack of exploitation of local resources and geographical expense provisions regarding use of the peninsula.

Wood is essentially composed of cellulose and hemicelluloses which represents 34% and 25% of where water storage occurs while waiting to be absorbed. In contrast olive stones are 28% cellulose and 35% hemicelluloses which highlights their hygroscopic properties, identified by solubility tests^[3].

The aim of this study is to determine the moisture sorption's point of the 2 most widely-produced biomasses products in Spain in order to specify the optimal transport conditions which will have the least impact on the characteristic qualities of biomass.

Mathematical models

The mathematical models used for determining the moisture content of hygroscopic materials are classified according to different models methods. There are two methods for obtaining experimental limits moisture sorption, Dynamic method and the Static, and the most suitable mathematical models were used for each method.

$$X_{eq} = \frac{K Cg a_{w}}{(1 - Ka_{w}) (1 - Ka_{w} + Cg Ka_{w})} Xm$$
(1)

GAB (Guggenheim-Anderson-de Boer).

Kinetic model based on the multilayer and a condensed film (monolayer).

Xeq: moisture of the product corresponding to the situation in which the primary points of adsorption are saturated by water molecules. C: constant Guggenheim, characteristic of the product and the monolayer heat-related adsorption. K: is a correction factor related to the heat of sorption of multicapa. aw, proportion of water in the element.

$$X_{eq} = E - F Ln(-(T + C) Ln(a_w))$$

Chung-Pfost Equation.

Semi-empirical model.

Xeq: equilibrium moisture content. a_w: relativity humidity. T: temperature (°C). E: Chung- pfost constant. F: Chung-pfost constant. C: Chung-pfost constant.

$$X_{eq} = A_{OS} + B_{OS}T \left(\frac{a_W}{1 - a_W}\right)^{C/os}$$
(3)

Oswin Equation.

Empirical model.

Xeq: equilibrium moisture content. a_w: relativity humidity. T: temperature (°C). C1: Oswing constant. C2: Oswing constant. C3: Oswing constant.

$$X_{eq} = \frac{1}{100} \left(\frac{Ln(1-a_w)}{K(T+C)} \right)^{1/n}$$
(4)

Henderson modified Equation.

Empirical model

Xeq: equilibrium moisture content. a_w : relativity humidity. T: temperature (°C). K1: Henderson constant. K2: Henderson constant.

$$X_{eq} = K1 a_w^{n1} + K2 a_w^{n2}$$

Peleg. Equation. Kinetic model.

Xeq: equilibrium moisture content. a_w: relativity humidity. T: temperature (°C). K1: Peleg constant. K2: Peleg constant.

$$q(t) = \frac{Q \times t}{B + t}$$
(6)

Pilosof. Equation.

Kinetic model.

q (t): Weight modification. T: time. Q: Moisture sorption equilibrium capacity. B: Time to get the moisture equilibrium.

$$M(t) = Mo \left[1 - e^{\frac{t}{T_0}} \right]$$
(7)

Exponential equation.

Kinetic model

M (t): Weight modification. T: time. Mo: Moisture sorption equilibrium capacity. To: Time to get the moisture equilibrium.

Equations mathematical models (Eq.2), (Eq.4)^[13] were the only one which measures the temperature in the analysis of sorption's isotherms^{[1] [2] [5] [6]}. The relationship between humidity and temperature will be the mainly variable to evaluate the transport conditions and for more information about characteristics. Mathematical models (Eq.2), (Eq.4) have been approved by the American Society of Agricultural Engineers for maize and paddy rice, the most commonly-used because of their generality and relative accuracy^[4] in addition to being the only ones to measure the temperature in the analysis of adsorption isotherms^[5].

Experimental procedures

Describing methods for determination points of moisture equilibrium:

-Method <u>acid salts</u>, Statist Process, this procedures for the determination of moisture of equilibrium points are saturated salt method^[6], which consists of a water bath where the samples are placed in air-tight receptacles at a constant humilities, without air circulation inside which are salts (Li CL, CH₃COOK, MgCl₂, K₂CO₃, Mg (NO₃)₂, SrCl₂, NaCl, KCl, BaCl, K₂SO₄) and samples of chips, Pellets and olive stones are placed in a few samples up to the point that the variation of the same weight does not exceed the limit of 0.5 within a 24 hours interval.

The static method is based on the use of under conditions of control and precision in the weight change, where the increase in moisture adsorption occurs in biomasses exposed to a constant relative humidity for a specified period, evaluating the changes as a function of time^{[1] [5]}. The samples are exposed to specifics levels of humidity, which gives the equilibrium moisture content equilibrium of the material for relative humidity until the weight of the sample is in equilibrium (Eq.1) (Eq.2)(Eq.3) (Eq.4) (Eq.5).

-Method <u>climate chamber</u>, Dynamic process, the first method is based on the use a chamber with controlled temperature and atmosphere achieving apparent equilibrium conditions where dynamic changes in mass versus time is less than 0.005% / min. These equilibrium conditions have been considered appropriate^{[19] [20]}. (Eq.6) (Eq.7).

MATERIALS AND METHODS.

To obtain points of equilibrium for moisture adsorption isotherms of 15 and 35°C, use two biomasses used: -Pellets (HR 5.5%, size 4-6 mm and density 670 kg / m3), -Olive stone (HR 9,2%, size 0,3-5 mm and density 720 kg /m3),

Static analysis

They are used in each specimen of homogenized samples, ground and sieved to 100 ml, 10g pine pellets (5.5%), 8 g Olive Stone (9,2%).

The method used to determine the equilibrium points was based on the procedure proposed by COST $90^{[8]}$ to plot the sorption curves for hygroscopic material. This method consists of placing a series of samples in air-tight receptacles, containing a saturated solution of a certain type of salt and in turn immersed in a constant-temperature bath^{[1][2][4][5]}. Using in air-tight receptacles with provision for three samples prepared with each saturated salt at the bottom and fitted with a vacuum pump at the top, it is pre-tested to get the state anhydride in a closed desiccators. Once equilibrium is reached the difference between the samples can be seen in sample weight before and after exposure to the saturated salt^{[5][6]}.

The time required for obtaining isotherms moisture equilibrium was 30 days. The weight was analyzed at the beginning and end and was determined (8).

EMC (%) =
$$\frac{Ww-Wo}{Ww} \times 100$$

(8)

equilibrium moisture content.

EMC (%)= Adsorption weight (%). W_w : Anhydrides weight (g). W_o : Wet weight (g).

Kinetic analysis

The climatic chamber method, measures the samples when they are placed in to a climate chamber which is automatically controlled and maintains the desired temperature $(15\pm0,4 \text{ °C})$ - $(35\pm0,4)$,relative humidity can be varied within the range of 90 %RH-72% RH. The net bags are moved in turns by a hook attached to a balance for weighing without opening the chamber. The resolution of the balance is 0.001g. The relative humidity is altered in steps after the samples have reached the equilibrium.

Biomass stock will provide us with temperature variation on the outside of the compartments in which it is stored, as a result of the relative humidity inside. The experimental compartment is made of galvanized steel 2 mm thick with a temperature sensor, between 5 and 35°C outside temperature.

Average error rate

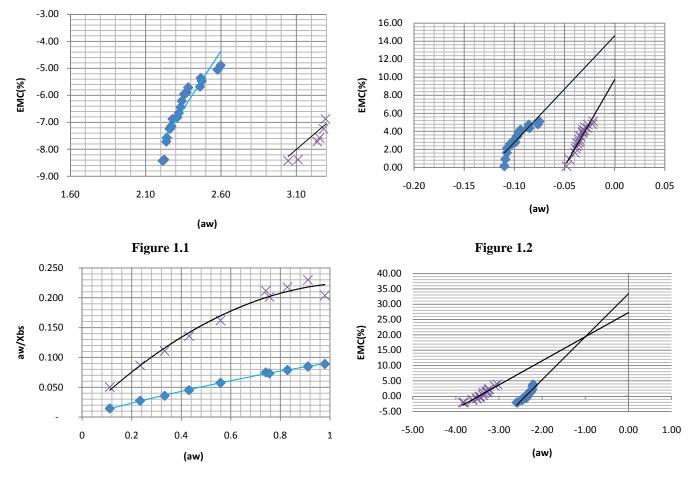
To determine models and the evaluation of the parameters the regression coefficient and standard error associated with the parameters were estimated, the residual error was assessed using least squares, we calculated the average relative error percentage (9) to assess the degree of adjustment.

% E =
$$\frac{100}{N} \sum_{n=1}^{n} (\frac{Xe-Xp}{Xe})$$

Average error rate

%E: average error rate, Xe: moisture experimental equilibrium content (%), Xp: moisture theoretical content, n: number.

RESULTS



Static analysis, determining points of balance of moisture by adsorption curves





Figure 1 : (1.1) Graphical Henderson pellets and olive stone fit settings (4), (1.2) Graphical Chung-Pfost pellets and olive stone fit settings (2), (1.3) Graphical GAB 15°C pellets and olive stone fit settings(4), (1.4) Graphical Oswing pellets and olive stone fit settings (2).

Figures 1 shows the difference in slopes between the sorption curves of biomass, (Eq.4) model fitting difference between pellets and olive stones is a remarkable by process to obtain the water activity "by least squares regression" which is an inverse logarithmic expression, whereas (Eq.2) and (Eq.3) water activity is directly. Mathematical expressions done by (Eq.4) (Eq.3) (Eq.2) equations models are linear, while (Eq.1) is parabolic.

Finally the equation model (Eq1) water activity model is not confronted with the biomass sorption unlike other models where the, relationship between water activity and water activity sorption in shown in parabolic curves.

(9)

		Pellets		Olive Stone	
Model		15 °C	35 °C	15 °C	35 °C
Herdenson	C2	8,64	8,57	4,66	4,98
	C1	2,35E-12	2,643E-12	1,89E-10	6,09E-11
	R2	0,900	0,930	0,960	0,960
	E(%)	9,92%	10,55%	9,49%	7,04%
	Е	0,0089	0,0082	0,0052	0,0053
	F	0,126	0,1220	0,0510	0,0503
Chung-Pfost	R2	0,930	0,890	0,970	0,970
	E(%)	4,00%	3,64%	4,84%	6,22%
GAB	К	0,2100	0,2400	0,4500	0,4300
	С	296,45	279,84	327,66	312,02
	Xm	8,820	8,550	2,510	2,500
	R2	0,999	0,999	0,993	0,995
	E(%)	1,59%	1,61%	4,92%	4,50%
Oswnig	C2	0,069	0,074	0,126	0,128
	C1	0,093	0,092	0,031	0,031
	R2	0,928	0,092	0,972	0,972
	E(%)	3,50%	3,10%	5,20%	4,30%

TABLE 1 : Models parameters of pellets and olive stones

TABLE 1, the results of the non linear regression analysis of adsorption isotherms of pellets and olive stone obtained at 15 and 35°C.

The values of constants of the four models, that is (Eq.1) (Eq.2) (Eq.3), show a fit to adsorption data along with their standard error and the correlation coefficient, and the percent average relative deviation of the percent average for the studied temperatures is given.

These results indicate that all the models are acceptable for predicting the equilibrium moisture content. However, (Eq. 1) gives the best fit for adsorption and desorption isotherms for the three temperatures, with the lowest standard error and the highest coefficient of correlation.

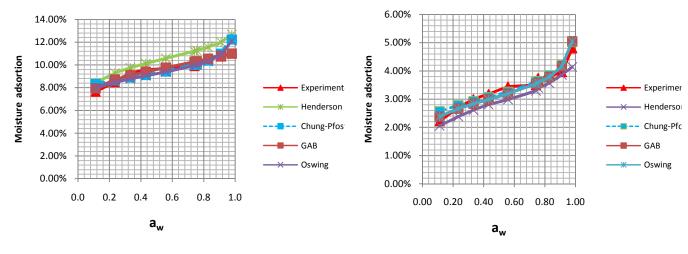
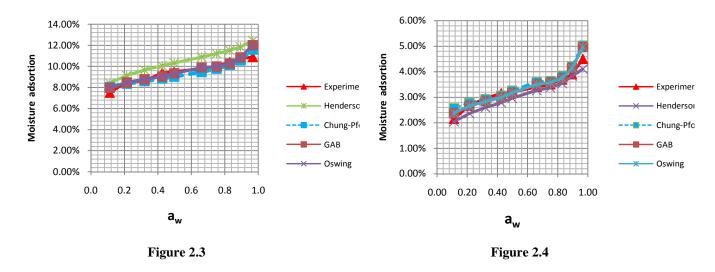


Figure 2.1

Figure 2.2





EMC (%) increases with the temperature,^[5] as noted in the graphs 2, sorption curves for pellets have higher balance points.

The procedure for investigating of the effect of the sorption on the resulting sorption curve and the hygroscopic behavior of the material was to determine the development process and maximum value of the sample (Eq. 6) immediately after the determination of the sorption curve at 15 and 35°C.

Dynamic analysis, determination of adsorption kinetic model (Pilosof)

Weight samples increasing to limit sorption equilibrium limit this process, which happen under relative humidity and constant temperature conditions, will last about 30 days. The obtained result will permit us to obtain Pilosof model parameters 72, 90 % HR.

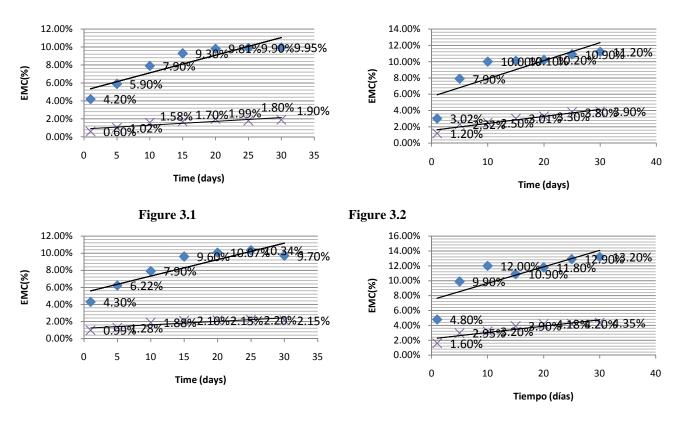


Figure 3.3

Figure 3.4

Figure 3 : Daily weight increases-pellets and olive stones, (3.1) Daily weight Pellets increases 35°C -72%, (3.2) Daily weight increases Pellets 35°C -90%, (3.3) Daily weight Increases Olive Stones 5°C -72%, (3.4) Daily weight Increases Olive Stones 5°C -90%

Sorption lines represent a measure of moisture biomass over time. The higher slope corresponds to pellets due to correlation between sorption limits. Figures 3.1 and 3.3 represent the conditions at 72 % where the slope is less than 90% in both cases.

TABLE 2, represents the kinetics moisture biomasses content (Eq. 6), Q is the amount of moisture absorbed in time, K is the moisture absorbing capacity or the maximum amount of moisture that can be absorbed under specified conditions in the same units, required to absorb half the maximum amount of moisture.

35°C		90%	/0			729	/0	
	Q	В	K	<i>R2</i>	Q	В	K	R2
Pellets	14,09	1,71	8,25	0,82	10,58	1,25	8,46	0,89
Olive Stone	4,74	1,99	2,38	0,92	2,32	1,27	1,83	0,90
15°C		90%	/0			729	%	
	<u>0</u>	<u>B</u>	<u>K</u>	<u>R2</u>	<u>0</u>	<u>B</u>	<u>K</u>	<u>R2</u>
Pellets	12,32	2,02	6,08	0,81	8,27	1,54	5,36	0,90
Olive Stone	4,14	5,92	0,70	0,96	2,14	4,73	0,45	0,91

TABLE 2 : Parameters pilosof, pellets and olive stone (72 y 90%), 15 y 35°C.

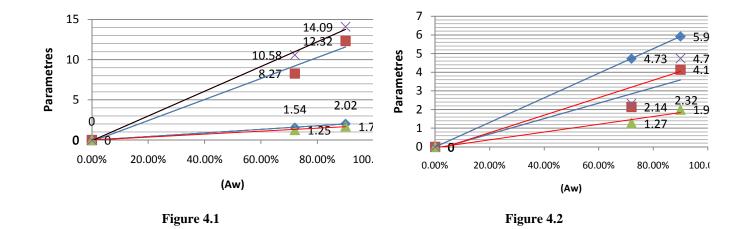


Figure 4 : Lineal representation of the parameters of biomass depending on relative humidity, following parameter Pilosof data. This operation permits the linear modification of moisture sorption for each biomass to be known.(4.1) Pellets,(4.2)Olive Stone.

Fitting temperature and humidity container

Graph 5, shows how outside temperature variation affects the relative humidity inside the compartment; this variation can be liberalized by least squares regression, a pellet varies by 57-75% whereas olive stones by 65 -68%.

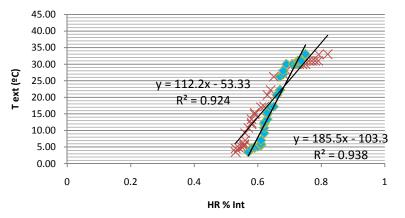


Figure 5 : Relative humidity Fit setting versus Container outside temperature

DISCUSSION AND CONCLUSION.

A Comparison of correlations between the static and dynamic models in order is necessary to determine the characteristics of the biomass before it is transported, and to predict the moisture sorption rate during transport. So as to ensure the logistical conditions, we will optimize production systems, which will impact directly on the quality of the product and therefore the cost.

The aim of this work is to determine the environmental humidity relative's to containers and how affects to biomasses stoked to be transported, Spain is a producer of biomasses and therefore this research is highly relevant.

Static models provide the limits of each of the moisture sorption and development curves at different temperatures, which allow us to know how much moisture sorption, there will be however to predict the specific amount adsorbed over a certain time would require a dynamic model.

To find out the best conditions for transport in containers we compare the static and dynamic model by a in the followings graphs.

-Graph 4.1 represents the comparative sorption's isotherms of biomass 15 and 35 °C.

-Graph 4.2 represents the relative variation of humidity in a compartment. The last one gives the value the of Pilosof parameters for determination of kinetic sorption over time. The standard transport conditions for transport time to between 5 and 8 days.

Pellets condition:

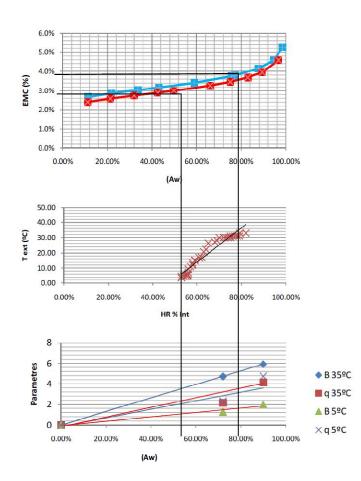


Figure 6 : (High) Sorption isotherms Chung-Pfost model Pellets 5 y 35°C, (Middle) Water activity into a container Pellets, (Below) Parametres Pilosof fit settings Pellets.

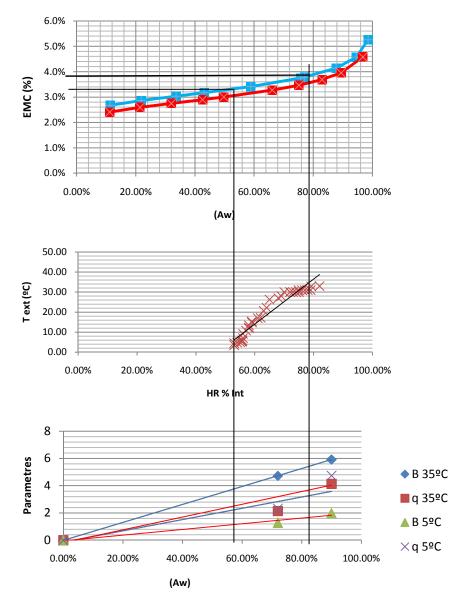
Pellets Sorption T _{ext}. =5°C HR 75%

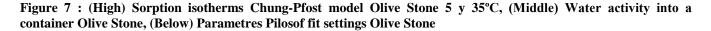
$$\underline{t=5 \text{ days}} q(t) = \frac{Q \times t}{B+t} = \frac{11,45 \times 5}{1,37+5} = 9,00\% \ \underline{t=8 \text{ days}} q(t) = \frac{Q \times t}{B+t} = \frac{11,45 \times 8}{1,37+8} = 9,80\%$$

Pellets Sorption T _{ext}. =35°C HR 57% $\underline{t=5 \text{ days}} q(t) = \frac{Q \times t}{B+t} = \frac{7,26 \times 5}{1,26+5} = 5,80\% \ \underline{t=8 \text{ days}} q(t) = \frac{Q \times t}{B+t} = \frac{7,265 \times 8}{1,26+8} = 6,30\%.$

Transport compartments conditions for pellets are between 57% and 75%, which produces the sorption's pellets of 9.3 and 10.4%, corresponding to the Pilosof parameters 11.45 and 7.26 (gr H2O/100gr) and 1.37 time parameters and 1.26 seconds.

Olive stone conditions





Olive Stone sorption T _{ext}. =5°C HR 78%

$$\underline{t=5 \text{ days}} q(t) = \frac{Q \times t}{B+t} = \frac{3.67 \times 5}{1.67+5} = 2,70\% \ \underline{t=8 \text{ days}} q(t) = \frac{Q \times t}{B+t} = \frac{3.67 \times 8}{1.67+8} = 3,00\%$$

Olive Stone sorption T _{ext}. =35°C HR 53%

 $\underline{t=5 \text{ days}} q(t) = \frac{Q \times t}{B+t} = \frac{3.48 \times 5}{2.05+5} = 1,20\% \ \underline{t=8 \text{ days}} q(t) = \frac{Q \times t}{B+t} = \frac{3.48 \times 8}{2.05+8} = 1,40\%$

(10)

Transport compartments conditions for Olive stone are between 53% and 79%, which produces the sorption's pellets of 2,99 and 3,80%, corresponding to the Pilosof parameters 3,67 and 3,48 (gr H2O/100gr) and 2,05 time parameters and 1,67 seconds.

CONCLUSION

The Relationship between sorption capacity obtained in the tests of saturated salts, and slope development relative humidity obtained by Pilosof parameters, provide the parameters for calculating the sorption of each biomasses over the time.

Sorption values for pellets at 3 and 6 days are higher than for olive stones. The Pilosof parameters also increase over the same time period therefore the values of sorption isotherms are higher for olive stones over distance.

The hygroscopicity capacity is stored in the cellulose and hemicelluloses cells which generate links with the water molecules of the medium in which they are^[5].

Olives are stone double the density of pellets, the percentage difference in the composition of cellulose is proportional to the limits of sorption between pellets and olive stones. So calorific power biomasses depends the moisture humidity content (10).

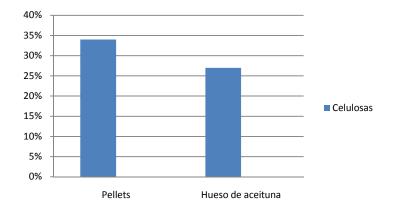


Figure 8 : Celluloses quantity, pellets, olive stone

TABLE 4 : Superior calorific power

Biomass	SCP			
Pellets	19.490 kj/kg			
Olive Stone	17.900 kj/kg			

$$ICP = \frac{scp}{1+h} - 665 \left(\frac{0.54+H}{1+h}\right)$$

Inferior calorific power, PCS: superior calorific power, h: % Moisture

The comparison of biomass sorption capacities follows the static and dynamics models between Olive stone and pellets, pellets are more profitable to transport that requires a less exigent system of transport.

Finally the usefulness of the correlation between static and dynamic modeling for the transportation scheduling of the most appropriate biomass product, so the requires procedures that should be applied.

Recommendations for improving the transportation of biomass in shipping containers consist of the installation of an automatic humidity system of control, managed by an electronic control unit, which regulates the humidity of the container environment. This centre will be scheduled in advance for each biomass, thereby looking to stabilize the status of air saturation at all the times during transport.

ACKNOWLEDGEMENTS

Sedam Managment, Oliver Gonzalez Arias, Miguel Afonso.

Salvador García Llanos, Departamento de Termodinámica, Universidad Las Palmas de Gran Canarias. Laboratorio de contol analítico de fuentes ambientales, Universidad de Las Palmas de Gran Canaria. Gonzalo Pierna-Vieja, Instituto Tecnológico de Canarias.

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