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Mathematically simulated transportation of pellets and olive stones.

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Abstract
Production of biomass in the Canary Islands isat a very low level, necessitating imports from the Iberian Peninsulain order to keep up supplies - according to a report by IDAE (Institute for Energy Diversification and saving), the Canaries are the lowest consumers of energy through biomass in all of Spain. As a consequence, consumption of biomass in the Canary Islands is insignificant due to the lack of exploitation of local resources and geographical expense provisions which are down to the reliance on resources located on the peninsula. Therefore, the transport conditions depend on the environmental conditions and the sorption capacity of the biomass. The experimental equilibrium moisture content data were subsequently fitted by mathematical sorption models, which is necessary for determining the best conditions for transportation. Non-linear regression analysis was used to evaluate the models' parameters. The validation of the two selected models was carried out using statistical parameters, the mean relative percentage error (E %) and the coefficient of determination (R^2).

Keywords: Isotherms, Transport, biomasses, Henderson, Chung-Pfost, Oswing, GAB, Pilosof.

1. Introduction
Pellets and olive stones are hygroscopic materials, which tend to balance their humidity conditions with environments in which hygroscopic conditions exits [1]. Hence, where they are transported to is very important if their characteristics and properties are to be maintained.
Biomass moisture equilibrium describes changes in moisture caused by exposure to several hydrothermal conditions that increase until moisture equilibrium is reached. Calorific power depends on the humidity content, which increases as the humidity lowers. The calorific power value depends on the density and humidity - higher humidity reduces the calorific value [2].
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 of the material. The potential benefits of biomass use could have a great impact on the environment and reduce greenhouse emissions.
Wood is essentially composed of cellulose and hemicelluloses, which respectively represent 34% and 25% of the area where water storage occurs while waiting to be absorbed. In contrast olive stones are 28% cellulose and 35% hemicelluloses, which highlight their hygroscopic properties, identified by solubility tests [3].
The aim of this study is to determine the point at which moisture sorption takes place in the two most widely-produced biomass products in Spain, in order to specify the optimal transport conditions which will have the least impact on the characteristic qualities of biomass.

1.1 Mathematical models
Numerous mathematical models for the description of how moisture sorption occurs on hygroscopic materials are available. Some of these models are based on the theories of the mechanism of sorption; others are purely empirical or semi-empirical. There are two methods for obtaining the experimental limits of moisture sorption: ´Dynamic and Static`. The most suitable mathematical models were used for each method.

$$X_{eq}=\frac{KCga_w}{(1-Ka_w)(1-Ka_w+CgKa_w)}Xm \qquad (1)$$

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.

$$X_{eq} = \mathrm{E} - \mathrm{F}\ \mathrm{Ln}(-(\mathrm{T}+\mathrm{C})\ \mathrm{Ln}(\mathrm{a_w})) \qquad (2)$$

Chung-Pfost Equation.
Semi-empirical model.
Xeq: equilibrium moisture content. a_w: relativity humidity. T: temperature (ºC). E: Chung- pfost constant. F: Chung-pfostconstant. C: Chung-pfost constant.

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

Oswin Equation.
Empirical model.
Xeq: equilibrium moisture content. a_w: relativity humidity. T: temperature (ºC). C1: Oswing constant. C2: Oswing constant. C3: Oswing constant.

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

Henderson modified Equation.
Empirical model
Xeq: equilibrium moisture content. a_w: relativity humidity. T: temperature (ºC).K1: Henderson constant.K2: Henderson constant.

$$\mathrm{X_{eq}} = \mathrm{K1}\ \mathrm{a_w}^{\mathrm{n1}} + \mathrm{K2}\ \mathrm{a_w}^{\mathrm{n2}} \qquad (5)$$

Peleg. Equation.
Kineticmodel.
Xeq: equilibrium moisture content. a_w: relativity humidity. T: temperature (ºC).K1: Peleg constant. K2: Peleg constant.

$$\mathrm{q(t)} = \frac{\mathrm{Q\ x\ t}}{\mathrm{B+t}} \qquad (6)$$

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

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

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

Mathematical equations which is modeling by (Eq.2) (Eq.4)[13]were the only ones which were able to measure the temperature in the analysis of the sorption's isotherms [1,2,5,6].The relationship between humidity and temperature will be the main factor for determining and evaluating the transport conditions. Mathematical models (Eq.2) and (Eq.4) have been approved by the American Society of Agricultural Engineers for maize and paddy rice, and are the most commonly-used because of their generality and relative accuracy [4], in addition to being the only ones to accurately measure the temperature in the analysis of adsorption isotherms [5].

1.2 Experimental procedures
Describing methods for determining points of moisture equilibrium:

-Acid Salts Method: Static Process. This procedure takes account of moisture equilibrium points through the saturated salt method [6]. It consists of a water bath where the samples are placed in glass jars which are kept at a constant humidity and were a vacuum has been created inside (Li CL, CH_3COOK, $MgCl_2$, K_2CO_3, Mg $(NO_3)_2$, $SrCl_2$, NaCl, KCl, BaCl, K_2SO_4).Samples were weighed at two-day intervals using the analytical balance. The equilibrium was reached when the sample weight difference between three consecutive readings was equal to or less than the balance accuracy of 0.5 during a 24-hourinterval.
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 point of moisture content equilibrium in the material for relative humidity until the weight of the sample is in equilibrium (Eq.1) (Eq.2)(Eq.3) (Eq.4) (Eq.5).
-Climate Chamber Method: Dynamic process. This method is based on the use of a chamber with a 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).

2. Materials and methods

In order to obtain points of equilibrium for moisture adsorption isotherms of 15 and 35°C, two distinct biomasses were used:
-Pellets (HR5.5%, size4-6 mm and density 670 kg/ m^3),
-Olive stone (HR 9,2%, size0,3-5 mm and density720 kg/m^3),

2.1. Static analysis

The method used to determine sorption isotherms was determined gravimetrically, using the standard static gravimetric method - standardized in the European COST90 [8] project - to plot the sorption curves for hygroscopic material. The method is based on the use of saturated salt solutions to maintain a fixed relative humidity, which corresponds with the tissue's water activity - ten salts were selected to give different water activities [1-5]. The saturated salt solutions were placed inside glass jars with three samples in each one. The water activities of the salt solutions were measured at different temperatures. 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).

$$\text{EMC (\%)} = \frac{Ww-Wo}{Ww} x\ 100 \qquad (8)$$

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

2.2. Kinetic analysis

The climatic chamber method measures the samples when they are placed into a climate chamber, which is automatically controlled and maintains the desired temperature (15±0, 4 ºC)-(35±0, 4) – relative humidity can be varied within the range of 90 %RH-72% RH. The net bags are moved in turn by a hook attached to a balance for weighing without the need to open the chamber. The resolution of the balance is 0.001g .The relative humidity is altered in steps after the samples have reached equilibrium.

2.3. Biomasses environmental conditions

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; outside temperature between 5 and 35ºC.

2.4. Average error rate

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

$$\% E = \frac{100}{N} \sum_{n-1}^{n} \left(\frac{Xe - Xp}{Xe}\right) \quad (9)$$

Average error rate:

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

3. Results

3.1Static analysis, determining points of balance of moisture by adsorption curves

Difference in slopes between the sorption curves of biomass is showing in figure 1 , (Eq.4) [4,5] 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) [1,5] equations models are linear, while (Eq.1) is parabolic.

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

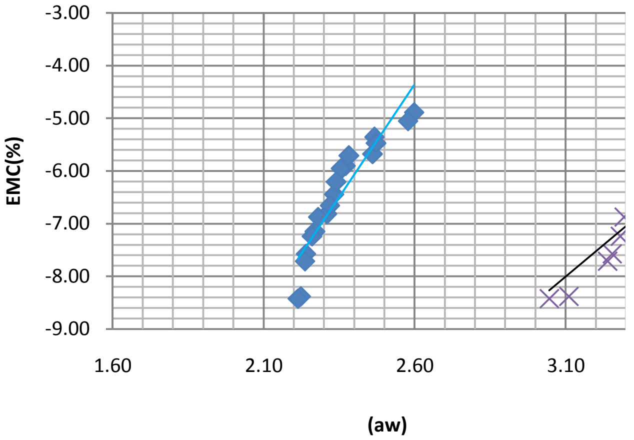

Figure 1.1: Henderson pellets and olive stone fit settings. (Eq.4) [4, 5,13].

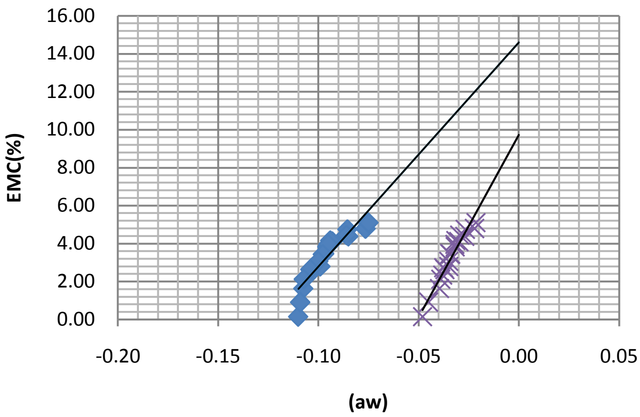

Figure 1.2**:**Chung-Pfost pellets and olive stone fit settings(Eq.2) [4-7].

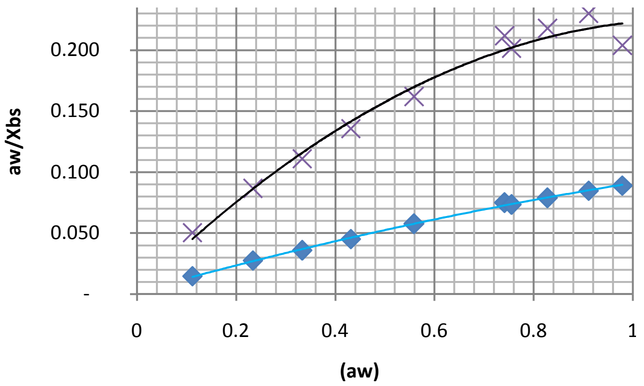

Figure 1.3: GAB 15ºC pellets and olive stone fit settings. (Eq.4) [4-6].

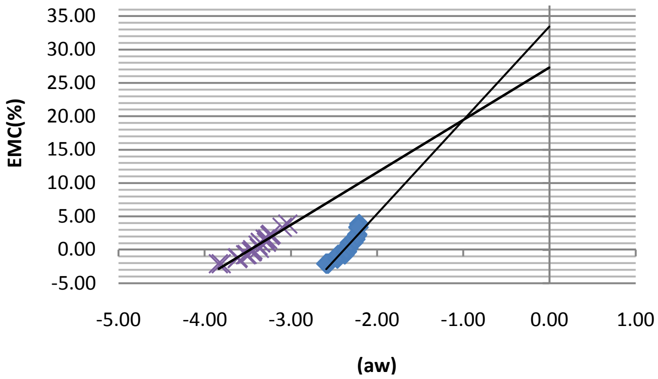

Figure 1.4: Oswing pellets and olive stone fit settings (Eq.2) [4, 5, 10].

Results of the non-linear regression analysis of the adsorption isotherms of pellets and olive stones obtained at 15 and 35°C is representing in table 1.

The values of constants of the models - that is (Eq.1) (Eq.2)(Eq.3) [5,6,7,13] show a fit to the adsorption data, along with their standard error and the correlation coefficient; the percent average for relative deviation of the percent average for the studied temperatures is given.

Table 1: Models parameters of pellets and olive stones.

Model		**Pellets**		**Olive Stone**	
		15 ºC	**35 ºC**	**15 ºC**	**35 ºC**
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%
Chung-Pfost	E	0,0089	0,0082	0,0052	0,0053
	F	0,126	0,1220	0,0510	0,0503
	R2	0,930	0,890	0,970	0,970
	E(%)	4,00%	3,64%	4,84%	6,22%
GAB	K	0,2100	0,2400	0,4500	0,4300
	C	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%

.

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. Representation water moisture sorption activity shown in Figures 2.1 and 2.4, 15ºC, shows the difference of each biomass and their sorption capacity limit.

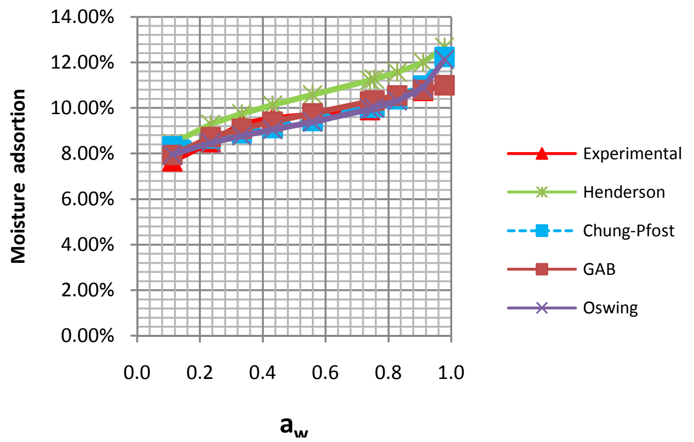

Figure 2.1: Sorption isotherms Pellets 15ºC [1,7,13].

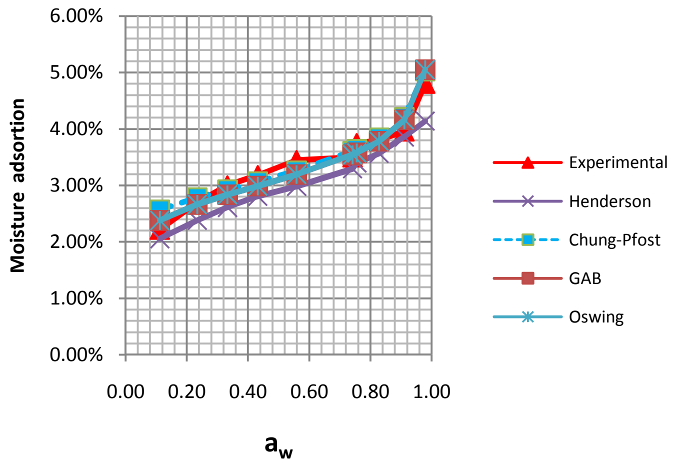

Figure 2.3: Sorption isotherms Olive stones 15ºC [5,6 ,13].

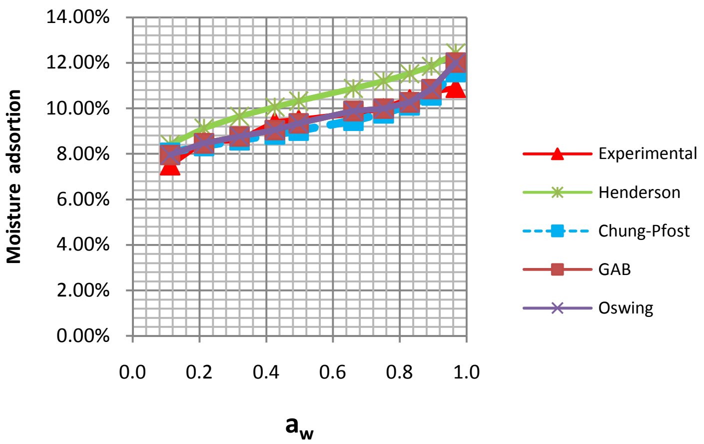

Figure 2.2: Sorption isotherms Pellets 35ºC [1,7,13].

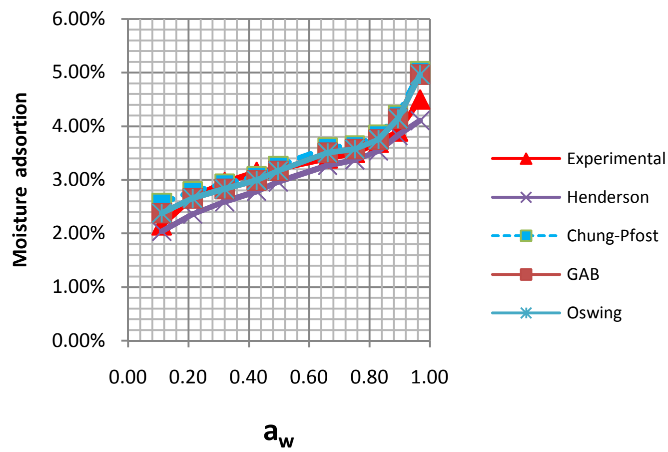

Figure 2.4: Sorption isotherms Olive stones 35ºC [5,6 ,13].

EMC (%) increases with the temperature [5]; as noted in figure 2, sorption curves for pellets have higher balance points. The procedure for investigating the effect of sorption on the resulting sorption curve and hygroscopic material behavior consisted of determining the development process and maximum value of the sample (Eq. 6) immediately after determination of the sorption curve at 15 and 35ºC.

3.2 Dynamic analysis, determination of adsorption kinetic model (Pilosof)

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

Sorption lines represent a measure of moisture biomass over time. The higher slope corresponds to pellets due to a 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 [3, 8, 15, 19].

The kinetics moisture biomasses content which is represented in table 2, (Eq. 6) [3, 8, 15,19], 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 -these are required to absorb half the maximum amount of moisture.

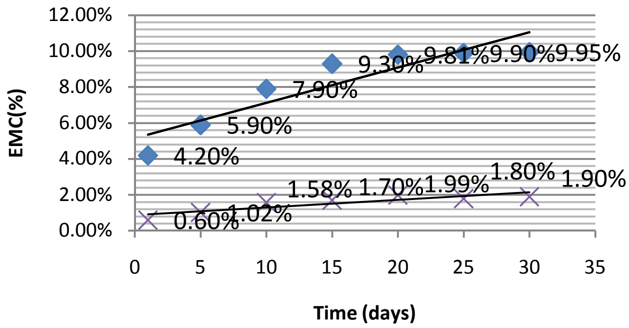

Figure 3.1: Daily weight increases - Pellets 35ºC -72%,

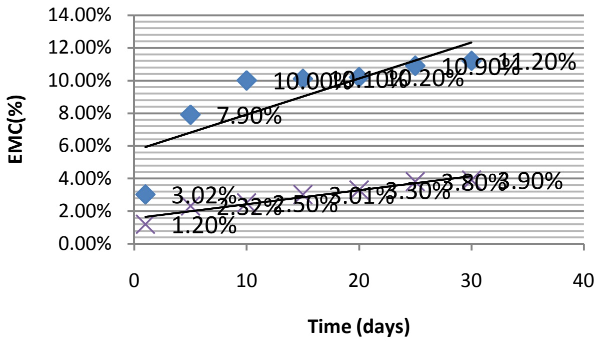

Figure 3.2: Daily weight increases - Pellets 35ºC -90%,

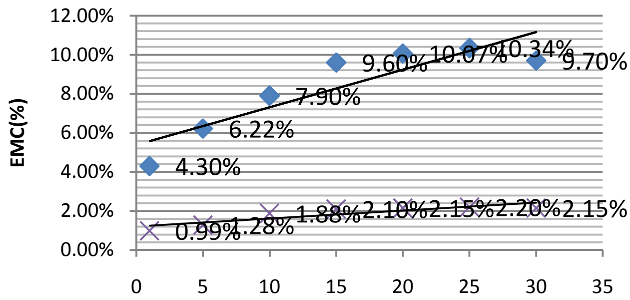

Figure 3.3: Daily weight increases - Olive Stones 5ºC -72%

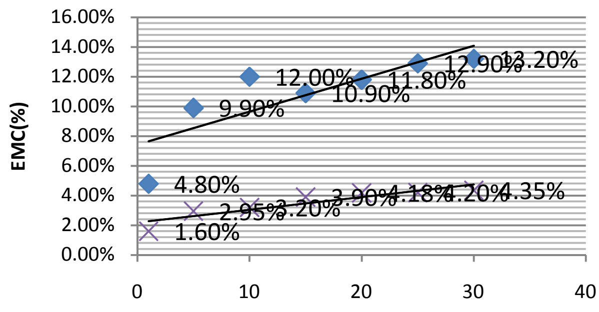

Figure 3.4: Daily weight increases- Olive Stones5ºC -90%

Table2: Parameters Pilosof Pellets and Olive Stones (72 y 90%), 15 y 35ºC.

35ºC	90%				72%			
	Q	*B*	*K*	*R2*	*Q*	*B*	*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
15ºC	90%				72%			
	Q	*B*	*K*	*R2*	*Q*	*B*	*K*	*R2*
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

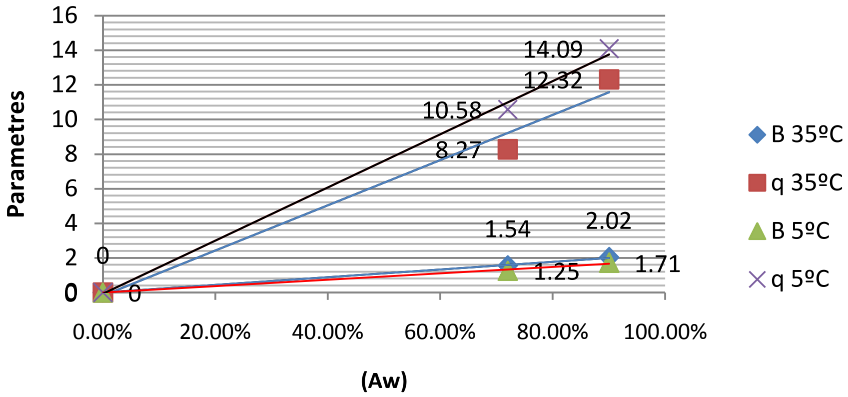

Figure 4.1: Pellets Pilosof variation Kinetics sorption's parameter over water activity.

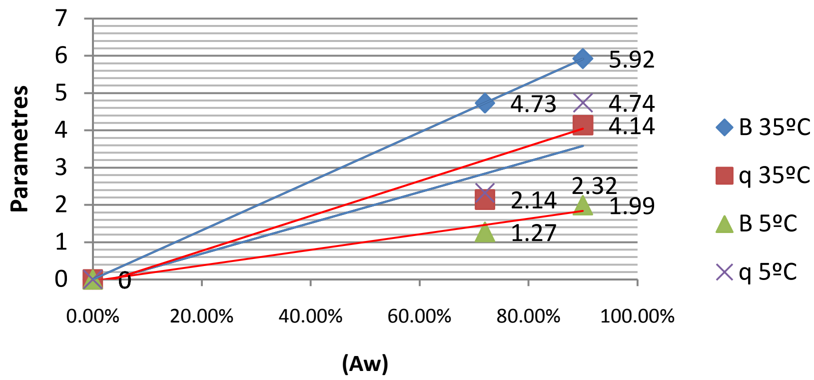

Figure 4.2: Olive stone Pilosof variation Kinetics sorption's parameter over water

Lineal representation of the parameters of biomass depending on relative humidity is shown figure 4, following parameters of Pilosof data. This operation permits the linear modification of moisture sorption for each biomass to be known: (4.1) Pellets,(4.2) Olive Stones [19, 21].

3.3. Fitting temperature and humidity container.

Outside temperature variation affects the relative humidity inside the compartment; this variation can be liberalized by least squares regression, it's represented in figure 5 -a pellet varies by 57- 75%, whereas olive stones by 65 -68%.

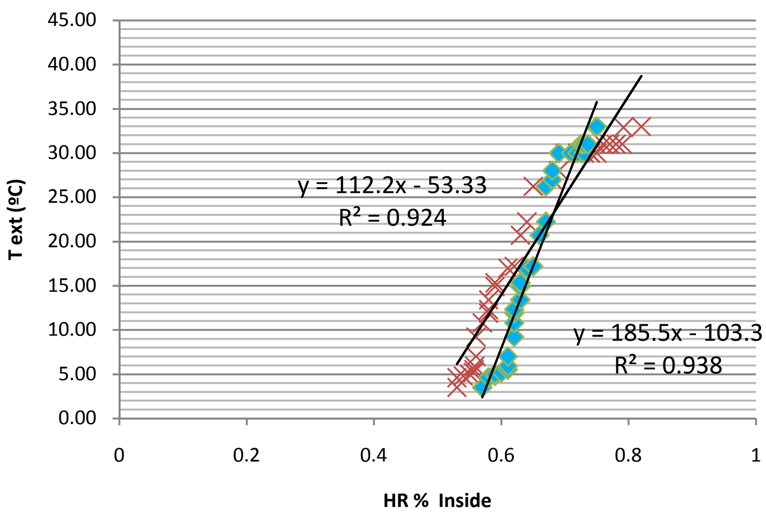

Figure 5: Relative humidity Fit setting versus Container outside temperature

3.4. Comparative relationship between statics and dynamics models.

A Comparison of correlations between the static and dynamic models is necessary in order 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 to containers and how this affects the biomasses stoked for transportation. Spain is a big producer of biomasses and therefore this research is highly relevant. Static models provide the limits of each of the moisture sorption and development curve sat different temperatures, which allow us to know how much moisture sorption, the dynamic model, on the other hand, will provide the amount of moisture sorption over time. To find out the best conditions for transport in containers, we compare the static and dynamic models in the figures 6 and 7 which represent the at the first figure is sorption's isotherms of biomass (pellets and olive stone) 15 and 35 ºC [3, 5, 6, 7] and is compared with the second one which represents the relative variation of humidity in a compartment, last figure gives the value the of Pilosof of parameters for determination of kinetic sorption over time[3, 8, 15,19]. The standard transport conditions for transport time to between 5 and 8 days.

4.1. Pellets condition:

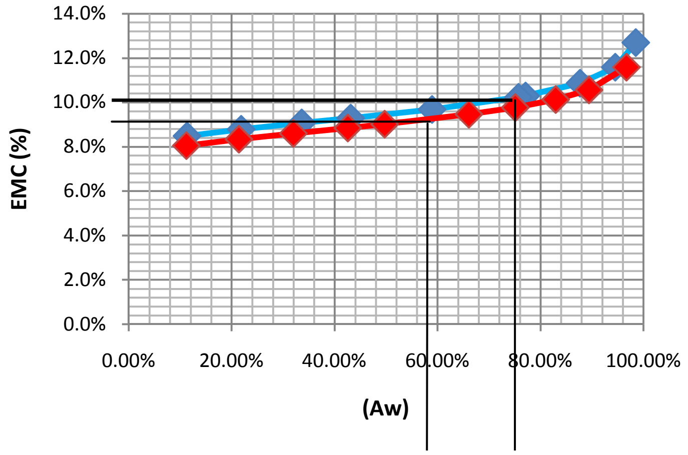

Figure 6.1: Sorption isotherms Chung-Pfost model Pellets 5 and 35ºC [4-7].

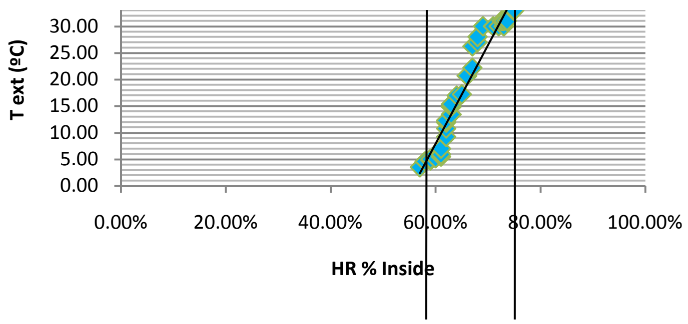

Figure 6.2 : Water activity into a container Pellets.

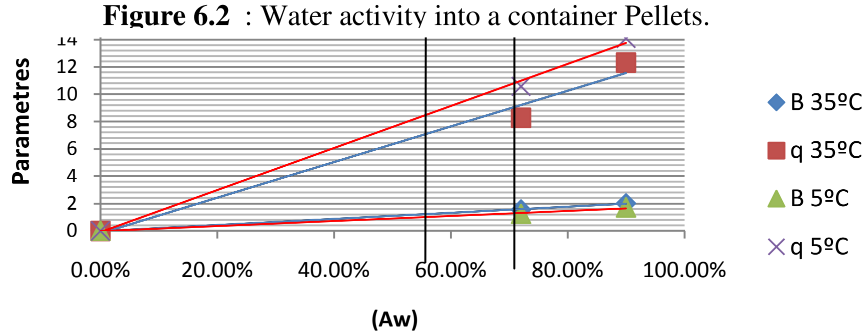

Figure 6.3 : Parametres Pilosof fit settings Pellets

Pellets Sorption T $_{ext.}$ =5ºC
HR*75%*
t= 5 days $q(t) = \frac{Q \times t}{B+t} = \frac{11{,}45 \times 5}{1{,}37+5}$ **= 9, 00%** t= 8 days $q(t) = \frac{Q \times t}{B+t} = \frac{11{,}45 \times 8}{1{,}37+8}$ **= 9, 80%**

Pellets Sorption T$_{ext.}$ =35ºC

HR*57%*
t= 5 days $q(t) = \frac{Q \times t}{B+t} = \frac{7{,}26 \times 5}{1{,}26+5}$ **= 5,80%** t= 8 days $q(t) = \frac{Q \times t}{B+t} = \frac{7{,}265 \times 8}{1{,}26+8}$ **= 6,30%.**

Transport compartment conditions for pellets are between 57% and 75%, which produces sorption in pellets of 9.3 and 10.4% [4-7], corresponding to the Pilosof [15,19] parameters 11.45 and 7.26(g H_2O/100gr), and 1.37 and 1.26 seconds time parameters.
Gravimetric method based on the use of saturated salt at 5 and 35 of wood pellets shows in figure 6.1, represents equilibrium water points over each temperature, limited by extreme imposed by figure 6.2 which represents the biomass humidity relative conditions into a maritime container according to the external temperature. Difference between extremely points is the 1,2% of moisture sorption as shown in figure 6.1.

4.2. Olive Stone conditions:

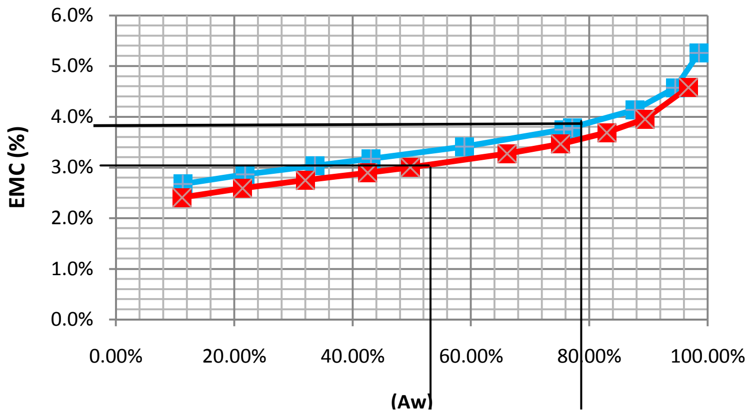

Figure 7.1: Sorption isotherms Chung-Pfost model Olive Stone 5 and 35ºC [4-7].

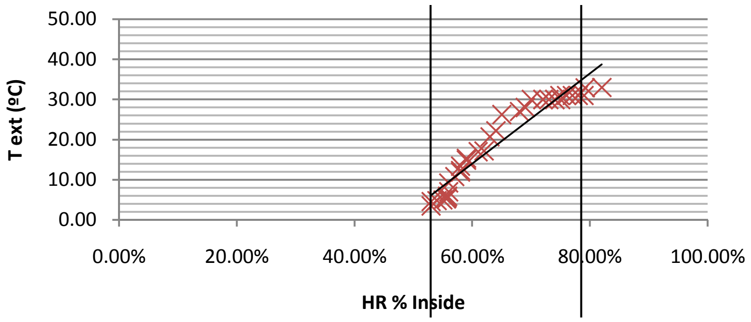

Figure 7.2 :Water activity in a container of Olive Stones.

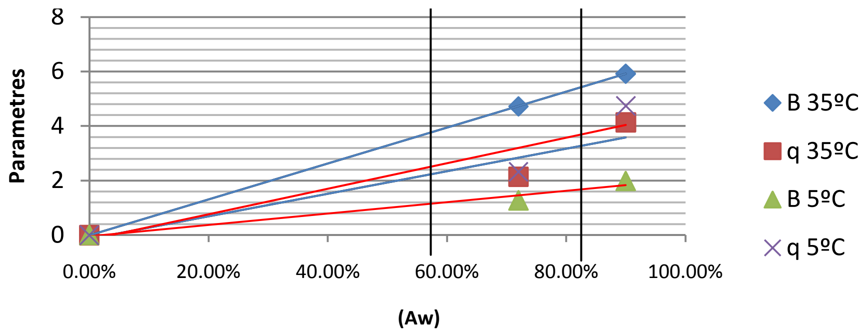

Figure 7.3 :Pilosof Parametresfit settings for Olive Stones [15, 19]

Olive Stones sorption $T_{ext.}$ =5ºC
HR*78%*
t= 5 days $q(t) = \frac{Q \times t}{B+t} = \frac{3{,}67 \times 5}{1{,}67+5} = \mathbf{2{,}70\%}$ t= 8 days $q(t) = \frac{Q \times t}{B+t} = \frac{3{,}67 \times 8}{1{,}67+8} = \mathbf{3{,}00\%}$

Olive Stones sorption $T_{ext.}$ =35ºC
HR*53%*
t= 5 days $q(t) = \frac{Q \times t}{B+t} = \frac{3{,}48 \times 5}{2{,}05+5} = \mathbf{1{,}20\%}$ t= 8 days $q(t) = \frac{Q \times t}{B+t} = \frac{3{,}48 \times 8}{2{,}05+8} = \mathbf{1{,}40\%}$

Optimal conditions in transport compartments for olive stones are between 53% and 79%, which produces sorption in pellets of 2,99 and 3,80 % [4-7], corresponding to the Pilosof parameters 3,67 and 3,48g H_2O / 100gr, and time parameters of 2,05 and 1,67 seconds.
By the same way that we did before, figure 7.1 represents equilibrium water points over each temperature for olive stone , limited by extreme imposed by figure 6.2 in this case the difference between extremely points is the 0,8 % of moisture sorption as shown in figure 7.1.

Conclusion:

1. The Relationship between sorption capacities obtained in the saturated salts method and slope development of relative humidity obtained by Pilosof parameters provide the parameters for calculating the sorption of each biomasses over time.
2. 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.
3. Difference between the upper and lower limits of each biomass sorption moisture is directly related to the values of maximum moisture sorption as seen in the graphs 6.1 and 7.1.
4. Olive stones are 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 which figure 8 shows. Therefore, calorific power of biomasses depends on the moisture content (10). 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 found [5].

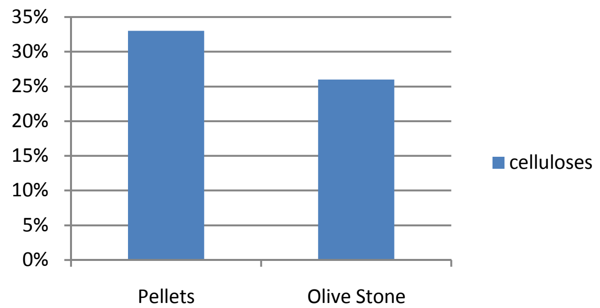

Figure8: Cellulose quantity -Pellets, Olive Stones.

Table4:Superior calorific power.

Biomass	SCP
Pellets	18.290kj/kg
Olive Stone	18.600 kj/kg

$$ICP = \frac{scp}{1+h} - 665\left(\frac{0{,}54+H}{1+h}\right) \quad (10)$$

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

5. The comparison of biomass sorption capacities between olive stones and pellets follows the static and dynamic models – the latter is more profitable to transport as it requires a less exigent system of transport.

6. Finally, the usefulness of the correlation between static and dynamic modeling for transportation scheduling of the most appropriate biomass product requires procedures that should be applied.
7. Recommendations for improving the transportation of biomass in shipping containers consist of the installation of an automatic system of humidity control, managed by an electronic control unit which regulates the humidity of the container environment. This will be scheduled in advance for each biomass, thereby looking to stabilize the status of air saturation at all times during transport.

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