

Calculation of the Equilibrium Moisture Content of Pellets and Olive Stones using the Henderson Mathematical Model

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ABSTRACT

Biomass which originates from forestry processes or is derived as a side-product from the production of olive oil are materials of biological origin used for different energy purposes, whether thermal or electrical. The present study is directed at explaining the Henderson mathematical model used for the calculation of EMC for pine tree pellets and olive stones, which is necessary for predicting adsorption states while stored in isolated environments.

Key Words: Pellets, Olive Stones, Equilibrium Moisture Content (EMC), Isotherms, Transport, Henderson Model

1. Introduction

Pellets are materials, produced from the wood accumulated through forestry processes, which lend themselves well to energy purposes, the functional relationship between the activity of water and EMC at a given temperature being represented through the adsorption isotherms of the product [1]. On the other hand, olive stones represent only 20% of the whole product taken from the land so there are repercussions due to the labor involved in picking the olives and their subsequent treatment in the olive press.

Use of the static gravimetric method to determine the adsorption curves describes the changes that occur in biomass which is exposed to established hydrothermal conditions, where the adsorption curve is described by a progressive increase until EMC is reached [4] [6].

The process of obtaining pellets requires a wood press where the lignin performs the function of binding, in this way increasing the density of the wood. This does not necessarily have to be obtained by tree-felling as it can also come from pruning and the left-overs from carpentry. Meanwhile, the collection of olive stones is made possible due to the production of olive oil.

The composition of pine wood radiata is 25% hemicellulose and 34% cellulose, while olive stones are composed of 35% and 28% respectively. The latter produces water during storage which is absorbed.

2.1 Experimental Procedures

The procedures for determining the EMC points include the saturated salt method, which consists of a thermal bath where samples inside sealed containers with included saturated salts are placed and kept at a constant humidity, without air circulation.

Saturated salts (LiCl, CH₃COOK, MgCl₂, K₂CO₃, Mg(NO₃)₂, SrCl₂, NaCl, KCl, BaCl, K₂SO₄): each salt introduced into a sealed container - a vacuum - with the four biomass samples being analyzed, produces a characteristic relative humidity.

This procedure is carried out at two temperatures - 15°C and 35°C - being that these temperatures are standardized for relative humidity and salts with the method titled COST90. Once results are obtained - as much with pellets as with olive stones - the sorption isotherms can be constructed, which provides a representation of the sorption rate of each material as according to their nature.

2.2 Mathematical Models

The mathematical models have one objective, which is to represent mathematically the experimental results obtained. These are used to determine the moisture content of hygroscopic materials, which are classified according to the type of analysis carried out.

There are two methods used to experimentally obtain EMC: 'dynamic' and 'static'. The first is based on the precise manipulation of weight under controlled conditions, where dynamic changes in the mass of the samples is a function of time. In the static model, the samples are exposed to a set of diverse chemical substances which possess the characteristic of ceding or removing humidity to or from the environments in which they are found, until such a time that a state of equilibrium is reached.

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

Equation 1 – GAB (Guggenheim–Anderson–de Boer).
Multi-layer kinetic model and mono-layer condensed

X_{eq}: Moisture produced by the product corresponds to the situation in which primary adsorption values are saturated by water molecules. C: Guggenheim constant; characteristics of the product corresponding to the heat of adsorption of the mono-layer. K: Correction factor corresponding to the heat of sorption of the multi-layer and the proportion of water in the element.

$$X_{eq} = \exp\left(\left(\frac{A}{T+C}\right) \exp\left(\frac{-B a_w}{100}\right)\right)$$

Equation 2 - Chung-Pfost equation.
Semi-empirical model.

Xeq: Content of moisture in equilibrium %.a_w: Water activity in element.T: Temperature (°K).A: Chung- pfost constant.C: Chung- pfost constant.

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

Equation 3 – Oswin equation.
Empirical model.

Xeq: Content of moisture in equilibrium %.a_w: Water activity in element.T: Temperature (°K).C₁: Oswin constant.C₂: Oswin constant.C₃: Oswin constant.

$$X_{eq} = \frac{1}{100} \left(\frac{-Ln(1 - a_w)}{c_1(T + C_3)} \right)^{1/c_2}$$

Equation 4 – Modified Henderson equation.
Empirical Model.

Xeq: Content of moisture in equilibrium %.a_w: Water activity in element.T: Temperature (°K).C₁: Henderson constant.C₂: Henderson constant.n: Henderson constant.

$$X_{eq} = K_1 a_w^{n_1} + K_2 a_w^{n_2}$$

Equation 5 – Peleg equation.
Empirical kinetic model; Isotherms sinoidal not sigmoidal.

Xeq: Content of moisture in equilibrium %.a_w: Water activity in element.T: Temperature (°K).K₁: Peleg constant.K₂: Peleg constant.

The mathematical models of Henderson and Chung-Pfost are the only ones in which the temperature in the analysis of the adsorption isotherms is taken into consideration [8], given that the relationship between moisture and temperature will be the determinant variable for evaluating the optimal conditions for conserving the characteristics of the product during transport.

3. Objectives

To detail the collation of the EMC points of the adsorption isotherms, at 15°C and 35°C, for pellets (HR% 5,5, Granulometría 6 mm y densidad 670 Kg/m³) and olive stones (HR 9,2%, Granulometría 0-3 mm densidad 720 kg/m³) through the saturated salts method.

4. Methods

In every test tube, homogenized samples were used; crushed and sieved to 100 ml, 10 g of pine pellets (5.5%).

In the saturated salts method, the adsorption curves were measured at 15 °C and 30 °C. For the construction of the isotherms, ten points of equilibrium for each isotherm were used, following the COST E8 method and corresponding to different salts. A decanter was used with room for three samples each prepared with a saturated salt at the bottom.

4.1 Statistical analysis

The time required for the collection of the isotherms in each container was 30 days. The weight was measured before and after. The equilibrium moisture content (EMC) is determined by the equation:

$$\text{EMC (\%)} = \frac{W_w - W_o}{W_w} \times 100$$

Equation 6 – Moisture equilibrium formula.

EMC (%) = equilibrium moisture content (%). W_w : Weight dry (g). W_o : Weight wet (g).

The hygroscopic equilibrium depends on the temperature and relative humidity. A series of points are determined by the anhydrous capacity of the salts. For each one, a thermal equilibrium value is taken for each biomass, resulting in the saturation of absorbtion.

4.2 Model adjustments

To make the model adjustments and to evaluate the estimated parameters of the regression coefficient and the standard error associated with the parameters: the residual error was evaluated using least squares regression; the relative average percentage (%E) was calculated to evaluate the grade of the adjustment.

$$\% E = \frac{100}{N} \sum_{n=1}^n \left(\frac{X_e - X_p}{X_e} \right)$$

Equation 7 - Formula for relative average error.

%E: Relative average error. X_e : experimental EMC (%). X_p : theoretical EMC. n: number of samples.

5. Results

Table 1. EMC of pellets of different biomasses; saturated salts method.

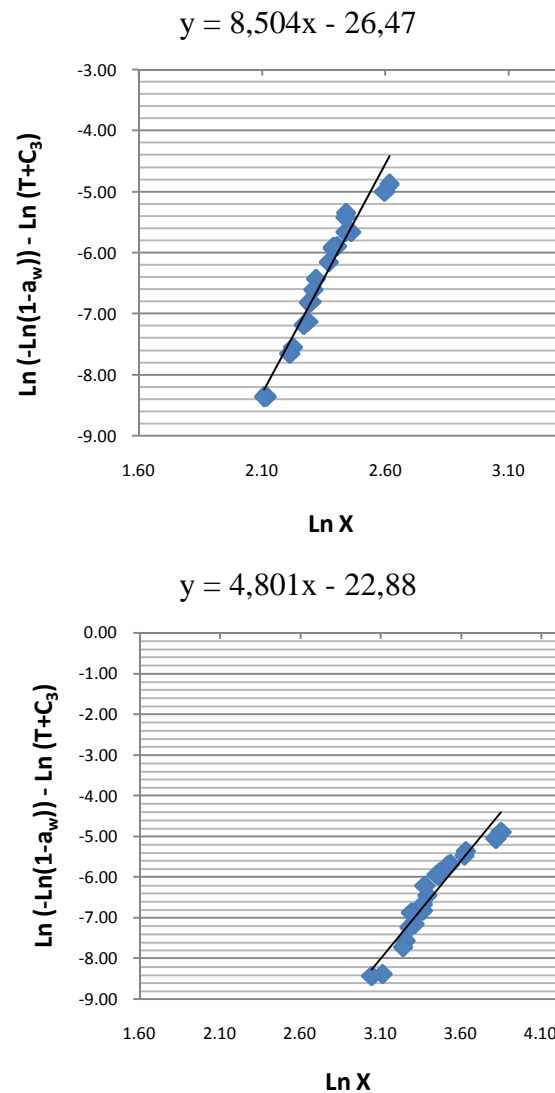
Salt	Pellets			Olive stones		
	a _w	15°C	35°C	a _w	15°C	35°C
Li CL	11,19%	7,65%	2,22%	11,17%	7,50%	2,15%
CH ₃ COOK	23,40%	8,50%	2,70%	21,37%	8,55%	2,68%
MgCl ₂	33,30%	9,30%	3,00%	32,00%	8,60%	2,95%
K ₂ CO ₃	43,15%	9,55%	3,18%	42,55%	9,40%	3,15%
Mg(NO ₃) ₂	55,87%	9,80%	3,45%	49,72%	9,70%	3,20%
SrCl ₂	74,13%	9,90%	3,50%	66,08%	9,77%	3,40%
Cl	75,53%	10,30%	3,75%	75,11%	10,00%	3,50%
KCl	82,79%	10,50%	3,80%	82,95%	10,40%	3,69%
BaCl	91,07%	10,75%	3,96%	89,40%	10,72%	3,90%
K ₂ SO ₄	97,89%	11,00%	4,80%	96,71%	10,90%	4,50%

In the analysis of the results shown in table 1, the EMC values for each temperature have been obtained.

$$\ln(-\ln(1-a_w)) - \ln(T+C_1) = C_2 \ln(X_{eq}) \times 100 + \ln(C_3)$$

Equation 8, Henderson linear equation.

Represented in the excise axis are the anhydrous values that are reached by salts responding to the Henderson formula. Meanwhile, the ordered axis represents the logarithmic values of the results of the experimental process. Through the least squares method [5], as represented in the table, the results were obtained which allow the table of adjustment for the Henderson formula for pellets and olive stones to be constructed.



Graphic 1. Henderson adjustment for pellets and olive stones.

The lines of adjustment were deduced from the values of the characteristics of the Henderson model, C_2 being a straight slope and C_2 calculated from the exponential of the natural complementary value of the line [10]. As seen in table 2, the Henderson formula fits better in developments with higher levels of anhydrides.

Table 2. Henderson constants for pellets and olive stones.

Biomass	C_2	C_1	R_2	E (%)
Pellets	8,50	3,17E-12	0,917	9,90 %
Olive stones	4,80	1,10E-10	0,955	8,58 %

As can be seen in graphic 1, the slope of the line for pellets is greater, which indicates higher levels of moisture absorbtion.

The discrimination between the actual values and those represented by the Henderson model has a variation that will be represented by the relative average error (E). The samples are under 10%, which corroborates the degree of reliable adjustment [3].

5.1 Modeling of moisture equilibrium points

Once the characteristic values for each biomass are obtained, an error index of points for moisture equilibrium states at each temperature can be simulated or predicted.

$$X_{eq} = \frac{1}{100} \left(\frac{\ln(1 - a_w)}{3,17E - 12(T + 450)} \right)^{1/8,50}$$

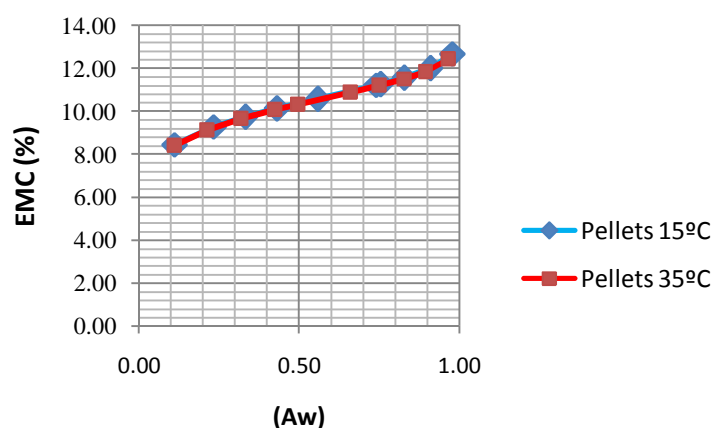
Equation 9 – Henderson equation – coefficients for pellets.

Table 3. Development of values of equilibrium points for pellets, 15 °C.

a_w	11,19%	23,40%	33,30%	43,15%	55,87%	74,13%	75,53%	82,79%	91,07%	97,89%
X_{eq}	8,42	9,26	9,72	10,11	10,56	11,20	11,26	11,56	12,00	12,67

Table 4. Development of values of equilibrium points for pellets, 35 °C.

a_w	11,14%	23,11%	33,03%	43,16%	54,47%	72,53%	75,41%	81,77%	90,69%	97,59%
X_{eq}	8,38	9,10	9,62	10,04	10,30	10,86	11,19	11,51	11,84	12,44



Graphic 2. Henderson modeling equation, 15 °C and 35 °C – pellets.

$$X_{eq} = \frac{1}{100} \left(\frac{\ln(1 - a_w)}{1,10E - 10(T + 450)} \right)^{1/4,80}$$

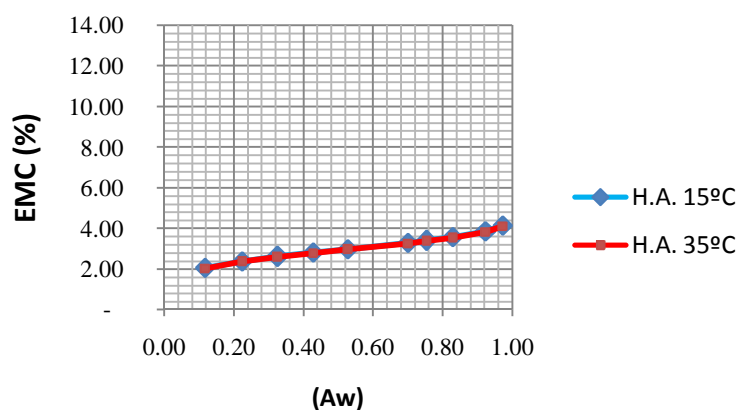
Equation 10 – Henderson equation – coefficients for olive stones.

Table 5. Development of values of equilibrium points for olive stones, 15 °C.

a _w	11,19%	23,40%	33,30%	43,15%	55,87%	74,13%	75,53%	82,79%	91,07%	97,89%
X _{eq}	2,03	2,41	2,62	2,81	3,04	3,37	3,40	3,56	3,81	4,20

Table 6. Development of values of equilibrium points for olive stones, 35 °C.

a _w	11,14%	23,11%	33,03%	43,16%	54,47%	72,53%	75,41%	81,77%	90,69%	97,59%
X _{eq}	2,02	2,34	2,58	2,78	2,91	3,19	3,37	3,54	3,72	4,06



Graphic 3. Henderson modeling equation, 15 °C and 35 °C – olive stones

Tables (3,4) and (5,6) belong to the modeling of the values of moisture points for pellets and olive stones at 15 °C and 35 °C, where the EMC is higher at lower temperatures. An increase in temperature decreases EMC for a_w [2] [3] [7]. Table 7 shows the difference for the same values of a_w at the temperatures referred to for each biomass.

Table 7. Difference between modeling values at 15 °C and 35 °C for pellets and olive stones.

a _w	11,14%	23,11%	33,03%	43,16%	54,47%	72,53%	75,41%	81,77%	90,69%	97,59%
Pellets	4,04%	15,32%	9,96%	6,81%	26,05%	34,03%	6,71%	4,53%	15,74%	23,77%
Olive stones	1,73%	7,01%	4,74%	3,35%	13,15%	17,94%	3,59%	2,47%	8,80%	13,84%

Conclusions:

The calculation of EMC is necessary for determining the characteristics of biomass before it is transported, given that the conditions must be favorable in order to avoid the effect of adsorption of moisture, which would reduce the quality of those characteristics. Thus, it is vital to determine the conditions of the environment in which it will be mobilized in order to optimize logistics systems, which will have a direct impact on product quality and cost.

The cellulose materials content in wood is greater than that of olive stones, which favors their higher sorption rate.

It can be observed experimentally (table 7) that the separation of sorption values for each point between the isotherms of the biomass, at 15°C and 35°C, is quite a lot less in the case of olive stones. In the same way, the maximum sorption limits of every type of biomass proportionally determine the average distance between the values of EMC points for water.

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