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Equilibrium moisture content in charcoal exposed to different relative humidity conditions

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Abstract
Equilibrium moisture content is an important characteristic associated with hydrocarbon fuels, including biomass and charcoal. Its determination is essential since it negatively affects several properties, especially the caloric value and energy density. Thus, this research was conducted with the aim of determining the equilibrium moisture content of charcoal produced for industrial purposes from 6-year-old *Eucalyptus* and *Corymbia* species exposed to different relative humidity conditions at a temperature of 30 °C. Four samples of charcoal were collected from each of the four species of *Eucalyptus* and *Corymbia* used in the study. The equilibrium moisture content of the samples was always achieved by desorption. At the end of the experiment, the dry masses were obtained. Twelve simple and multiple linear models were used to estimate the equilibrium moisture of the samples. Overall average equilibrium moisture estimates were slightly higher in *Eucalyptus* species in all relative humidity conditions, except at 90%. Considering the scientific principle of parsimony, the simple linear model was selected for both *Corymbia* and *Eucalyptus* species. The difference between *Corymbia* and *Eucalyptus* equilibrium moisture of charcoal was higher at lower relative humidity conditions.

Keywords
Climatic chamber; Hygroscopicity; Bioreducer; Steel industry

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1. Introduction

Humidity is one of the factors that negatively affects the calorific value of traditional fuels, especially in lignocellulosic materials. Hygroscopicity is associated with the presence of hydroxyl functional groups (-OH), which have the ability to bind, by hydrogen bonds, to water present in the environment, causing an increase in adsorption or a reduction in desorption [8]. The equilibrium moisture content of lignocellulosic materials is associated with the availability of such functional groups, present in their polymers and structural macromolecules.

Carbonization, as well as drying and torrefaction, promotes the reduction of hydroxyl functional groups (-OH) available for bonding with water, which will cause a reduction in the equilibrium moisture content of carbonized materials [11 e 13]. The main thermal decomposition reactions are decarboxylation, decarbonylation, dehydrogenation and demethylation [9]. The carbonization temperature directly affects the availability of functional groups in charcoal [3 e 10], which will negatively affect its hygroscopicity.

Equilibrium moisture content is an important characteristic associated with hydrocarbon fuels, including biomass and charcoal. The moisture content reduces its mechanical strength, due to the expansion of water vapor when it is heated, excessive smoke release, ignition properties and low combustibility [2 e 5]. In addition, it negatively affects the calorific value of fuels, reducing their energy density substantially [1].

Hygroscopicity is a relevant characteristic due to its implication in the final use of charcoal. Therefore, research to understand its behavior during its use and exposure to different environments, both in production and in storage conditions, is necessary. The objective of this study was to determine the equilibrium moisture content of charcoal from 6 years old *Eucalyptus* and *Corymbia* species, produced for industrial purposes at different relative humidity

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conditions in a climate chamber.

2. Materials and Methods

The genetic materials come from experimental *Eucalyptus* and *Corymbia* plantations (latitude 28° 48', longitude 48° 54' and altitude 711 m), spaced 3.0 x 2.6 m (7.8 m^2), at six years of age, located in the Municipality of Paraopeba, State of Minas Gerais, Brazil. According to the Köppen classification, the climate of the region is Cwa, with an average annual rainfall of 1300 mm, an altitude of 750 m and an average temperature of 20.4 °C. The experiment was implemented at the company Vallourec, which is part of a network that makes up the "Potential Species Project" of the Cooperative Forest Improvement Program in the Institute of Research and Forest Studies (IPEF).

Four species of *Eucalyptus* (*E. amplifolia* Naudin, *E. longirostrata* (Blakely) L.A.S.Johnson & K.D.Hill, *E. major* (Maiden) Blakely, *E. urophylla* S. T. Blake) and *Corymbia* (*C citriodora* subesp. *citriodora* K. D. Hill & L. A. S. Johnson, *C. citriodora* subesp. *variegata* K. D. Hill & L. A. S. Johnson, *C. henryi* (S.T. Blake) K. D. Hill & L. A. S. Johnson, *Corymbia torelliana* (F.Muell.) K.D.Hill & L.A.S.Johnson) were used in this study. Wood samples, without bark, were taken from disks at the base and at 1.3m height in the trees. The wood was carbonized in an electric furnace (muffle) with the wood previously dried in an oven at 103±2°C. The initial temperature, heating rate, final carbonization temperature and residence time were 100°C, 100 °C h^{-1}, 450°C and 30 minutes, respectively [12]. Four charcoal samples were used per species. These samples had an average volume of 18.35 cm^3 and 16.58 cm^3, for *Corymbia* and *Eucalyptus* species, respectively.

The charcoal samples were conditioned at a temperature of 30℃ and relative humidity ranging from 90 to 40% with a 10% interval in a Hotpack climatic chamber. In each charcoal exposure condition, the mass of the samples was monitored on an analytical balance (0.0001g) until stabilization in a period of 24 hours between two weighings. Once the condition of hygroscopic equilibrium was reached, all samples were weighed. At the end of the experiment, the dry mass of the samples and their equilibrium moisture content, on a dry basis, were determined. The dry mass of the charcoal samples was obtained after drying in a calibrated oven at 103±2°C for a period of 2 hours.

In evaluating the experiment, linear regression analysis was adopted for *Corymbia* and *Eucalyptus*, in which the equilibrium moisture variation models were adjusted as a function of relative humidity. Twelve regression models were tested and the best model was selected based

Table 1. Regression models tested to estimate charcoal equilibrium moisture content.

Number	Model	Model Equation
1	Simple Linear	$Y_i = \beta_0 + \beta_1 X_i + \varepsilon_i$
2	Quadratic	$Y_i = \beta_0 + \beta_1 X_i + \beta_2 X_i^2 + \varepsilon_i$
3	Cubic	$Y_i = \beta_0 + \beta_1 X_i + \beta_2 X_i^2 + \beta_3 X_i^3 + \varepsilon_i$
4	Square Root	$Y_i = \beta_0 + \beta_1 \sqrt{X_i} + \beta_2 X_i + \varepsilon_i$
5	Potential	$Y_i = \beta_0 X_i^{\beta_1} + \varepsilon_i$
6	Exponential	$Y_i = \beta_0 \beta_1^{X_i} + \varepsilon_i$
7	Hyperbolic 1	$Y_i = \beta_0 + \frac{\beta_1}{X_i} + \varepsilon_i$
8	Hyperbolic 2	$Y_i = \frac{1}{\beta_0 + \beta_1 X_i} + \varepsilon_i$
9	Logarithm (e)	$Y_i = \beta_0 + \beta_1 ln(X_i) + \varepsilon_i$
10	Logarithm (10)	$Y_i = \beta_0 + \beta_1 log(X_i) + \varepsilon_i$
11	Reciprocal log	$log(Y_i) = \beta_0 + \frac{\beta_1}{X_i} + \varepsilon_i$
12	Cubic Root	$Y_i = \beta_0 + \beta_1 \sqrt{X_i} + \beta_2 X_i + \beta_3 X_i^{1,5} + \varepsilon_i$

The potential and exponential models were linearized to fit the equations as follows: potential – $\log(Y_i) = \log(\beta_0) + \beta_1 \log(X_i) + \varepsilon_i;$
exponential – $\log(Y_i) = \log(\beta_0) + \log(\beta_1) X_i + \varepsilon_i;$

on the regression significance (F test), significance of the regression coefficients (t test), both at a 5% level, by the adjusted coefficient of determination (adjusted R²), variation coefficient of the model and graphical analysis of residuals. In case of very similar the models based on the selection criteria mentioned above, the scientific criterion based on parsimony was adopted for the definitive selection. The models were adjusted using the Statistical Analysis System (SAEG) software version 5.0, REGREAMD1 package. For data analysis, simple and multiple regression models presented in Table 1 were tested to estimate the equilibrium moisture content of charcoal from each evaluated species.

3. Results and Discussion

The average equilibrium moistures estimates were slightly higher in *Eucalyptus* species in all relative humidity conditions, except at 90% (Table 2). It was observed an increase in the charcoal equilibrium moisture due to the increase in relative humidity in the climatic chamber. A similar trend was also observed by [6], who evaluated the hygroscopicity of charcoal produced at different final carbonization temperatures and two relative humidity conditions, and [4], which evaluated charcoal conditioned under different conditions of relative humidity and produced at different temperatures (340 to 460 ºC).

Table 3 presents the adjusted models, their adjusted coefficients of determination and coefficients of variation. It can be observed that all models presented good adjustments (R^2cor) and low coefficients of variation (CV<10%). The CV measures the relative dispersion of the data and therefore the lower the better the model. The quadratic model (2), for *Corymbia*, and the 2 and cubic (3), for *Eu-*

Table 2. Average equilibrium moisture content of Corymbia and Eucalyptus species.

Specie	Relative humidity (%)					
	40	50	60	70	80	90
CC	4.84	5.63	6.30	6.90	7.68	8,70
CCV	4.75	5.54	6.19	6.76	7.51	8.60
CH	4.89	5.66	6.29	6.78	7.58	8.50
CT	4.59	5.30	5.92	6.40	7.13	8.85
Average	4.77	5.53	6.18	6.71	7.47	8.66
EA	5.34	6.09	6.70	7.23	7.93	8.98
EL	5.39	6.16	6.79	7.30	7.99	8.51
EM	5.19	5.93	6.54	7.01	7.68	8.56
EU	5.28	5.99	6.56	6.97	7.62	8.20
Average	5.30	6.04	6.65	7.13	7.80	8.56

CC = *Corymbia citriodora* subesp. *citriodora*, CCV = *C. citriodora* subesp. *variegata*, CH = *C. henryi*, CT = *Corymbia torelliana*, EA = *Eucalyptus amplifolia*, EL = *E. longirostrata*, EM = *E. major*, EU = *E. urophylla*.

Table 3. Fitted models, adjusted coefficient of determination (R^2cor) and coefficient of variation (CV).

Model	Regression Coefficients - *Corymbia*				R^2cor	$CV(\%)$
	$\hat{\beta}_0$	$\hat{\beta}_1$	$\hat{\beta}_2$	$\hat{\beta}_3$		
1	1,7603	0,07373			0,953	4,27
2	3,5833	0,01348ns	0,0004635		0,961	3,90
3	-4,7443	0,43251	-0,006250	0,0000344	0,970	3,44
4	8,1341	-1,6366	0,1768		0,959	3,89
5	-0,4458	0,6978			0,952	2,33
6	0,4879	0,004924			0,962	2,08
7	10,7721	-254,254			0,870	7,14
8	0,2749	-0,1788			0,949	4,64
9	-12,0133	4,4872			0,922	5,51
10	-12,0133	+10,3322			0,922	5,51
11	1,0962	-17,3636			0,918	3,02
12	-95,4778	38,5581	-4,9621	0,21665	0,973	3,23
Model	**Regression Coefficients - *Eucalyptus***				R^2cor	$CV(\%)$
	$\hat{\beta}_0$	$\hat{\beta}_1$	$\hat{\beta}_2$	$\hat{\beta}_3$		
1	2,8150	0,06307			0,943	4,09
2	3,0512	0,05526	0,0000601ns		0,942	3,87
3	-1,4919	0,2839	-0,003603ns	0,00001879	0,946	3,76
4	3,3268	-0,1314ns	0,071344		0,942	3,87
5	-0,1945	0,5724			0,945	1,99
6	0,5732	0,004014			0,942	2,04
7	10,5848	-0,0002212			0,890	5,34
8	0,2380	-0001378			0,928	4,56
9	-9,1044	3,8715			0,928	4,31
10	-9,1044	8,9144			0,928	4,31
11	10,7186	-14,3300			0,923	2,35
12	-51,2795	21,0622	-2,6389	0,1143	0,943	3,86

ns = not significant at the 5% probability level by the “t” test.

calyptus, showed non-significant regression coefficients. The hyperbolic model 1 (7) was the one that presented the worst fit and the highest CV in both *Corymbia* and *Eucalyptus*.

Figure 1 shows the graphs of the best distributions of residues observed in Corymbia and Eucalyptus species. The simple linear (1), quadratic (2), cubic (3) and cubic root (12) models were the ones that presented the best residual distributions. Considering the scientific principle

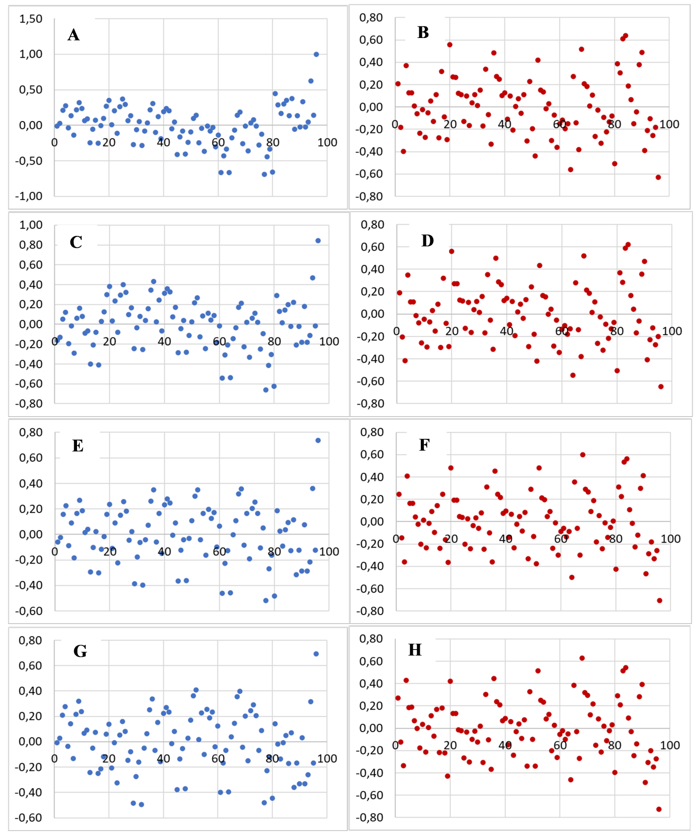

Figure 1. Graphs of the best distributions of residues observed in Corymbia (blue) and Eucalyptus (red) species. A and B simple model, C and D quadratic model, E and F cubic model and G and H cubic root model.

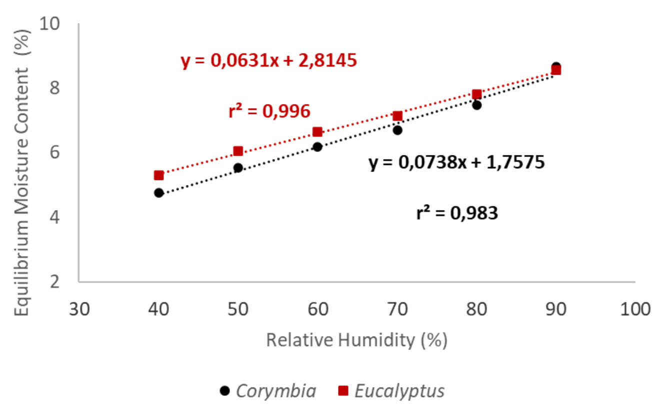

Figure 2. Observed difference in charcoal equilibrium moisture as a function of relative humidity.

based on parsimony, the selection of models seeks to find the one that involves the least possible parameters to be estimated and, also, the one that is closest to the true model [7]. Therefore, the simple linear model was chosen as the one that best represents the studied phenomenon.

Charcoal produced with *Eucalyptus* species showed higher equilibrium moisture, especially at lower relative humidities, and the difference between the charcoal equilibrium moisture estimates of *Corymbia* and *Eucalyptus* species tends to decrease with increasing relative humidity (Figure 2). The difference in equilibrium moisture between the genetic materials is still not very clear in the literature, but it must be associated with the chemical composition of the raw material, in addition to the charcoal production parameters (temperature, heating rate, pressure, etc.) [9].

4. Conclusion

Estimates of overall average equilibrium moisture content were slightly higher for *Eucalyptus* species in all conditions of relative humidity, except at 90%;

Considering the scientific principle based on parsimony, the simple linear model was selected for the *Corymbia* and *Eucalyptus* species;

The difference between the charcoal equilibrium moisture content estimates of *Corymbia* and *Eucalyptus* species was higher at lower relative humidity conditions.

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