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Experimental Study of the Drying Kinetics of the Coconut Shells (Nucifera) of Cameroon

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ABSTRACT

Water diffusion of two species of coconut shells (CS) nucifera from Cameroon, in the case of drying, was experimentally studied. The experiment was done with the aid of an oven, by the method of gravimetric batch control of the mass of the test samples with the temperatures varied from 70° to 180° Celsius. The shells of mature coconuts from two species were conserved in the laboratory at a temperature ranging between 20° and 23° Celsius for two months before being mechanically cleaned. This study allows not only the determination of the water content of the shells, but also the identification of the drying model. It is thus from the ten model tests, and the statistical analysis shows that the Midilli model best predicted this drying phenomenon. The coefficient of effective diffusion was determined at different temperatures which permitted the evaluation of the activation energy per the Arrhenius equation.

Keywords: Coconut Shells; Drying Model; Drying Kinetics; Effective Diffusivity; Activation Energy

1. Introduction

Coconuts are a harvest largely cultivated in many regions of the planet to the point where coconut tree is considered in certain countries as the tree of life. The worldwide production is estimated at more than 54 million tons. Even though Cameroon is not amongst the top ten worldwide producers, it is not far away that coconut is a part of the daily food habits of these populations. This product is consumed in many forms: coconut milk, coconut flour, coconut juice, and dried coconut almonds. Although the by-products of the coconuts tree are for the most part thrown away into our environment, thus causing pollution, the populations look non-stop for ways to use them. It is thus the fibers of the trunk and the CS that are exploited in the elaboration of composites [1]; the CS is used in the elaboration of active carbon [2], in decoration, in kitchen utensils and in art objects. Outside of this, a non-negligible quantity of the CS is thrown away into our immediate environment. In order to optimize the potential that represents these plants for the worldwide population, along with protecting our environment, some works are oriented on the utilization of those shells. CSs are used as charge in the composites [3] and also in concrete [4]. Other works are based on the utilization of the CS as a stabilizing agent of cheap lateritic soil [5]. Recent studies have determined certain mechanical and physiochemical characteristics of the CS [6]. The utilization of CS in composites implies the phenomena of water diffusion which are currently unknown. The study of the model of drying kinetics of coconut almond has already been done for the food need [7].

In the present work, the attention is brought to the experimental study of the model of the drying kinetics of the CS (nucifera) at different temperatures including the estimate of the water content of CS. All the abbreviations of the quantities used in this text are given in **Table 1**.

2. Materials and Procedure

2.1. Materials

The coconuts used in this study come from the southern, littoral, and southwestern regions of Cameroon. Two

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Table 1. Nomenclature of quantities.

Nomenclature			
W(%)	Water content	$MR_{pre,i}$	Prédicted moisture ratio
m_0	Initial mass (kg)	$MR_{\exp,i}$	Experimental moisture ratio
m_{eq}	Mass at equilibrum (kg)	D_{eff}	effective diffusivity(m^2/s)
MR	Moisture ratio	t	Drying time
$m(t)$	Masse at instant t (kg)	R_i	Interior radius (mm)
a, b, c, k_0,	k_1, k, g, h: Models constants	R_e	R_e Exterior radius (mm)
n	Positive integer, essential coefficient of the models	r^2	Coefficient of determination
RMSE	root mean square errors	D_0	Pre-exponential factor of the Arrhenius equation (m^2/s)
SSE	Mean of the squares errors	R	Constant of perfect gas (kJ/mol·K)
N	Number of Observations	T	Drying temperature (˚C)
P	Nomber of onstants	T_{abs}	Absolute temperature (˚K)

varieties of coconut are concerned and they are distinguished by the form of their nut: one has an oblong form (species 1) and another has a round form (species 2). CS were separated from nuts and remained at the laboratory in approximate ambient moisture of 60% and at a temperature varying between 20˚ and 23˚C, for two months. They were cut and cleaned to eliminate the fibers and white matter that covered the inside of the shell. The cutting and the cleaning were done manually with the help of a workbench vise, a manual saw, and sandpaper. The test samples intended for the tests have geometry comparable to a portion of sphere as shown in **Figure 1**; they were cut in the southernmost direction of nut. For each of the test samples, we estimated the interior radius, marked R_i, and the exterior radius, marked R_e by the geometric traces. For each isothermal and for each species, 8 samples were tested for a total of 80 test samples.

2.2. Procedure

The undertaken experiments made it possible to determine the water content and the kinetics of drying of these CS using the method by stoving following the prescription of standard NF P 94-050. A drying oven of mark memmert model UN 160 with a precision of 5˚C was used to maintain samples to the following isotherms: 70˚C; 100˚C; 130˚C; 160˚C and 180˚C. A numerical balance of 0.01 g of precision was used to measure the masses. For each trial at each of the temperatures above, the oven was regulated until the desired isotherm was reached before the test samples were introduced. The test samples were weighed to determine their humid mass m_0 before being placed in the oven. The hour at which the samples were introduced into the oven was noted, and after a determined duration in the oven, the test sample is taken out and weighed in a lapse of time in order to minimize the incertitude of measure: the humid mass of the sample $m(t)$ was noted after duration of "*t*" in the oven. The experiment was repeated until the mass of the test sample no longer varied: the equilibrium mass m_{eq} of the sample was recorded.

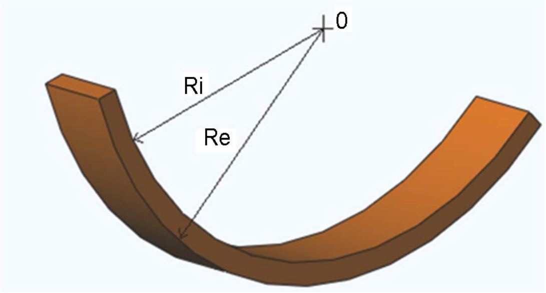

Figure 1. The geometry of the samples.

2.3. Theoretic Considerations

2.3.1. Mathematical Model of the Phenomenon of Diffusion

The water content W compared to the dry matter of the test samples is calculated from the humid mass m_0 and the equilibrium mass m_{eq} in the following formula (1). The moisture ratio (MR) which is the dimensionless equivalent of humidity can be calculated following the formula (2).

$$W(\%) = \frac{m_0 - m_{eq}}{m_{eq}} \times 100 \quad (1)$$

$$MR = \frac{m(t) - m_{eq}}{m_0 - m_{eq}} \quad (2)$$

where $m(t)$ represents the humid mass at the instant (t). **Table 2** below presents the mathematical models characteristic of the drying kinetics of plant products used to test those of the CS.

The program Matlab (2009) was used to identify the parameters of the different models from a non-linear regression. The effectiveness of a model was evaluated via statistical criteria such as coefficient of determination r^2, square root of error (SSE), root mean square error

Table 2. Mathematical models used in the drying kinetics of the CSs.

N°	Model names	Model	References
1	Newton et Lawis	MR = exp(−kt)	[8-14]
2	Page	MR = exp(−kt^n)	[8,10,13,15-18]
3	Henderson et Pabis	MR = aexp(−kt)	[9,10,12,14,19,20]
4	Logarithmic	MR = aexp(−kt)+bt	[8-10,12,14]
5	Two term	MR = aexp(−k$_0$t)+bexp(−k$_1$t)	[13,18,21]
6	Midilli	MR = aexp(−kt^n)+bt	[22-24]
7	Verma *et al*.	MR = aexp(−kt)+(1−a)exp(−gt)	[24,25]
8	Modified Henderson and Pabis	MR = aexp(−kt)+bexp(−gt) +cexp(−ht)	[23,24]
9	Peleg	MR = 1−[t/(a+bt)]	[26]
10	Aghbashlo	MR = exp[−kt/(1+at)]	[27]

(RMSE. In fact, a model is better if the higher r^2 is close to 1 and the lowest value of and with RMSE and SSE. Equations (3) and (4) give the expressions of those parameters.

$$RMSE = \left[\frac{1}{N}\sum_{i=1}^{N}\left(MR_{pre,i} - M\mathrm{R}_{\exp,i}\right)^2\right]^{1/2} \quad (3)$$

$$SSE = \frac{1}{N-P}\left[\sum_{i=1}^{N}\left(MR_{pre,i} - M\mathrm{R}_{\exp,i}\right)^2\right] \quad (4)$$

where $MR_{pre,i}$ and $MR_{\exp,i}$ are the moisture ratios of the predicted and experimental respectively for the i^{th} observation. N is the number of observations and P is the number of constants.

2.3.2. Estimation of the Effective Diffusivity

Fick's Equation (5) determines the diffusion of mass across the plant products [28]. In recognizing that the coefficient of effective diffusivity depends neither on the concentration, nor the position, it yields:

$$\frac{\partial M}{\partial t} = D_{eff}\nabla^2 M \quad (5)$$

where D_{eff} is the coefficient of effective diffusisity and M is the levels of humidity. The analytical solution to Equation (5), for a radial diffusion in a hollow sphere ($R_i \le r \le R_e$) was developed by Carslaw and Jaeger in 1959 [28]. The solution of Carslaw and Jaeger (6) applies in cases where the internal surface at $r = R_i$ and at the external $r = R_e$ are maintained at concentrations C_1 and C_2 respectively so that $C_1 = C_2$. This way, the coefficient of effective diffusivity is constant.

$$MR = \frac{6}{\pi^2\left(R_i^2 + R_iR_e + R_e^2\right)} \cdot \sum_{n=1}^{\infty}\left\{\left(\frac{R_e\cos n\pi - R_e}{n}\right)^2 \exp\left[\frac{-D_{eff}n^2\pi^2 t}{\left(R_e - R_i\right)^2}\right]\right\} \quad (6)$$

where D_{eff} is the coefficient of effective diffusivity (m^2/s) and "n" is positive integer. In limiting to the first term of this series, the Equation (7) becomes

$$MR = \frac{6}{\pi\left(R_i^2 + R_iR_e + R_e^2\right)}\left(R_i + R_e\right)^2 \exp\left[\frac{-D_{eff}\pi^2 t}{\left(R_e - R_i\right)^2}\right] \quad (7)$$

The natural logarithm of Equation (7) gives Equation (8) which permits to determine experimentally the coefficient of effective diffusivity D_{eff}.

$$LnMR = Ln\left[\frac{6\left(R_i + R_e\right)^2}{\pi^2\left(R_i^2 + R_iR_e + R_e^2\right)}\right] + \frac{-D_{eff}\pi^2}{\left(R_e - R_i\right)^2}t \quad (8)$$

The slope of the linear regression of Ln(MR) in function of time (t) permit to calculate D_{eff} in the following Equation (9).

$$slope = \frac{D_{eff}\pi^2}{\left(R_e - R_i\right)^2} \quad (9)$$

2.3.3. Computation of the Activation Energy

The activation energy is necessary for the activation of the phenomenon of diffusion studied. It is calculated from the Arrhenius equation [29] which results from the dependence of the coefficient of effective diffusivity to the absolute temperature (10). The natural logarithm of the Equation (10) gives the Equation (11) which allows the determination of the activation energy E_a using the slope of the line Ln(D_{eff}) in function of (1/Tabs).

$$D_{eff} = D_0 \exp\left(-\frac{E_a}{RT_{abs}}\right) \quad (10)$$

$$Ln(D_{eff}) = Ln(D_0) - \left(\frac{E_a}{R}\right)\cdot\frac{1}{T_{abs}} \quad (11)$$

In Equation (11), D_0 (m^2/s) is the pre-exponential factor of the Arrhenius equation; E_a is the activation energy (kJ/mol); R is the constant of perfect gas (kJ/molK).

3. Results and Discussion

3.1. Water Content

The humid mass m_0 and the equilibrium mass m_{eq} allowed the calculation of the water content of each of the samples tested using Equation (1). The **Table 3** shows the median values and the standard deviations obtained from 20 samples tested per species.

Table 3. Values in water content of the CS.

	CS Species 1	CS Species 2
Mean	15.02%	15.48%
Standard deviation	0.82 %	0.81%

3.2. Analysis of the Drying Kinetics

With an initial moisture content of 15.5 ± 2% (d.b), test samples was dried in the oven to a final moisture content of around 1% d.b. at drying temperature 70˚C; 100˚C; 130˚C; 160˚C; 180˚C. **Figure 2** shows the evolution of the moisture ratio (MR) in function of time, for different temperatures and for the two species of CS and the durations of drying are those necessary to reach a water content estimated at 1%.

It is noted that the drying kinetics of the two species of CS is not very different. It clearly appears that the drying temperature has an influence on the drying kinetics. The **Figure 3** shows the duration of drying as a function of the temperature. It is clear that between 70˚C and 130˚C, the duration of drying decreases rapidly, while between 130˚C and 180˚C this decreasing is slow. The fall of duration of drying which one observes around 100˚C is certainly due to a water departure by vaporization coupled with the destruction of the hydrogen bond between the shell and the molecules of water. Similarly T. Madhiyanon *et al*. (2009) [7], by studying the models of fluidized bed drying for thin-layer chopped coconut, they observed that the rate of moisture reduction was greater at a higher temperature, in response to influence of drying temperature on the ability to diffuse moisture.

The evolution of the moisture ratio (MR) obtained experimentally from the two species at different temperatures was tested by 10 mathematical models presented in **Table 1**; in the goal of identify the model that best predicted the drying kinetics. The statistical criteria r^2; RMSE and SSE were used to evaluate these models. It is clear that the Midilli, Logarithmic, and Modified Henderson models are more distinguished than the others and for the samples tested and at all the temperatures, with and $r^2 > 0.997$ and very weak values of RSME and SSE inferior. More particular, the Midilli model with and $r^2 > 0.998$; RMSE and SSE inferior to 10^{-2}, proves to be the best model for the prediction of the drying kinetics of the CS. As per the illustration, **Table 4** presents the values of these criteria for specie 2 at 100˚C. **Figure 4** shows a good concordance of the experimental results with this model.

To have a complete model, an interest in the variation of the parameters of the Midilli model in function of temperature must be taken. **Figure 5** presents the given experimental of the Midilli parameters in function of temperature. It is evident that only the parameter "n" is susceptible to the temperature and its evolution seems to be linear as shown in **Figure 6**.

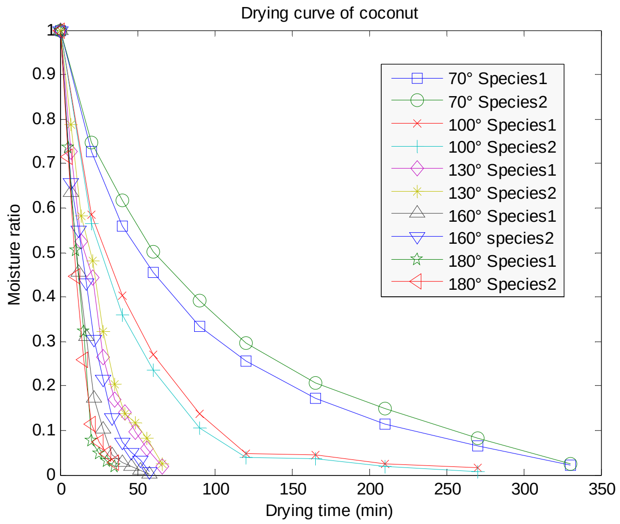

Figure 2. Experimental curves of the drying kinetics of the CS of species 1 and 2 at different temperatures.

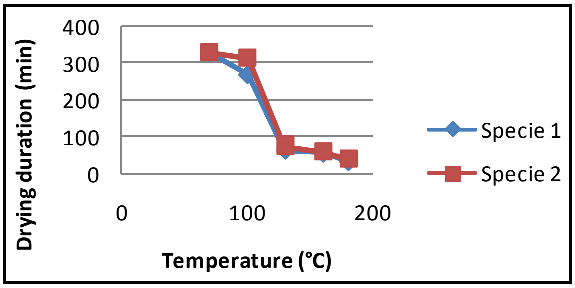

Figure 3. Influence of the temperature on the drying kinetics of the CSs.

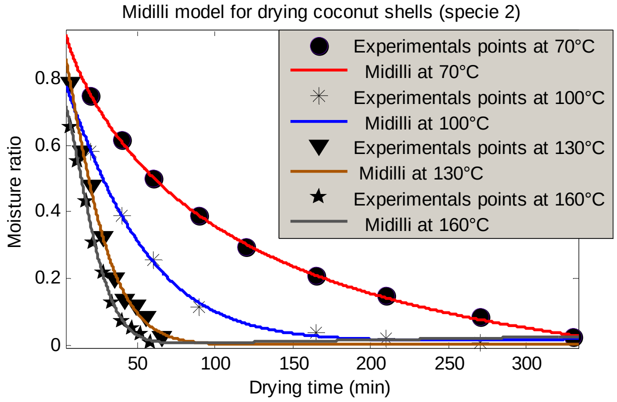

Figure 4. Modeling of the given experimental of species 1 and 2 per Midilli.

A complete expression of the modeling of the drying kinetics of the CS, in accounting for the dependence of the parameter "n" to the temperature, can be given by the Equation (12).

$$MR = 0.8789\exp\left(-0.01571t^{0.007438T_{abs}-1.714}\right) - 4.457\times10^{-6}t \qquad (12)$$

Table 4. Statistical criteria of the different models of specie 2 at 100˚C.

Models Name	SSE	r^2	RMSE
Midilli	0.0004	0.9988	0.0109
Logarithmic	0.0004	0.9984	0.0106
Modified Henderson	0.0006	0.9980	0.0242
henderson	0.0006	0.9978	0.0111
Verma *et al.*	0.0006	0.9978	0.0125
Page	0.0007	0.9976	0.0118
Aghbashlo	0.0010	0.9966	0.0139
Two term	0.0014	0.9950	0.0219
Newton or Lawis	0.0024	0.9917	0.0199
Peleg	0.0035	0.9877	0.0265

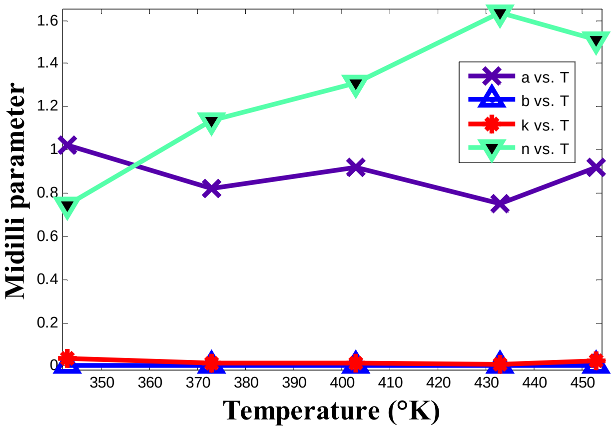

Figure 5. Variation of the Midilli parameters in function of temperature.

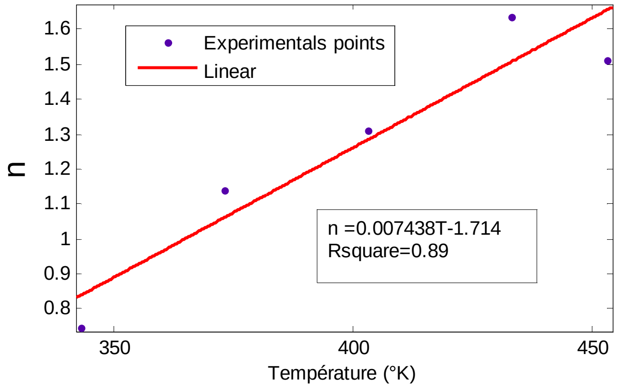

Figure 6. Linear regression of the parameter n in function of T.

where “*t*” is the time in seconds and T_{abs} is the absolute temperature

3.3. Effective Diffusivity

The mathematical model of the drying kinetics (12) has a linear part which is negligible in front of the exponential part. Fick’s Law expressed by Equation (8) can therefore be adopted for the estimation of the effective diffusivity. This coefficient is simply obtained from the slope of Equation (9), once the slope of the line Ln (MR) in function of time “t” is known. The values of D_{eff} for the two species of shell are recorded in **Table 5**. It clearly seems that the effective diffusivity D_{eff} increases considerably with the temperature. Furthermore, D_{eff} does not differ much from one species to another.

Table 6 presents a way of comparing the effective diffusivity of different plants. It is apparent that those of the CS appears among highest but remains close to that of the flax and the bamboo used in the composites.

3.4. Activation Energy

The value of the activation energy noted E_a was determined by exploiting the Arrhenius equation. Indeed, the curve which connects the experimental points of Ln(D_{eff}) and the inverse of the absolute temperature 1/Tabs (**Figure 7**) is almost linear. The slope of the linear regression line of these experimental points permits to deduce E_a from Equation (11), which is 31.69 and 34.46 kJ/mol for species 1 and 2 respectively. The intercept at the origin of this line permits to deduce the pre-exponential factor D_0 of the Arrhenius equation which is 4.7025×10^{-7} and 1.4306×10^{-7} for species 1 and 2 respectively.

Table 7 presents the comparing of the activation energy of some plant products. It is clear from this table that the activation energy of the diffusion of water across the CS is amongst the median values but remain close to some wood like Sapin.

4. Conclusion

The CS of the two species, having initial water retention of 15.5 ± 2%, sized relative to a portion of a hollow sphere, is dried in an oven at temperatures ranging between 70˚C and 180˚C, in the goal of studying their drying kinetics. It was clear that the drying kinetics of the two species was almost identical. Of the 10 model tests, 4 had well simulated the given experiment with a correlation coefficient $r^2 > 0.998$. Amongst these 4 models, the Midilli model was the most precise with an $r^2 > 0.999$ and very small values of RMSE and of SSE. The coefficient of effective diffusivity obtained from the Arrhenius equation varies from 1.46×10^{-8} to 16.10×10^{-8} in m^2/s for the species 1 and from 1.34×10^{-8} to 24.50×10^{-8} in m^2/s for species 2, in the temperature range going from 70˚C to 180˚C. The activation energy was found and was 31.69 and 34.46 kJ/mol for species 1 and 2, respectively. Within sight of the results obtained, it appears that the CS is a material prone to the phenomenon of diffusion of

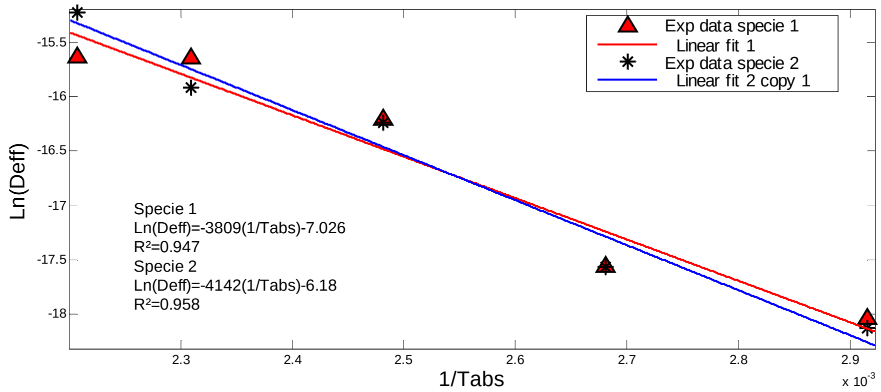

Figure 7. Relation between D_{eff} and $1/T_{abs}$.

Table 5. Values of the coefficients of diffusion of the two species of coconut shells.

Temperature	**70˚C**		**100˚C**		**130˚C**	
Species	Species 1	Species 2	Species 1	Species 2	Species 1	Species 2
	D_{eff} (× 10^{-8} m²/s)					
Test Samples	1.46	1.30	2.43	2.75	7.95	7.95
	1.46	1.30	2.27	3.40	9.89	9.24
	1.46	1.46	2.34	2.43	8.43	9.24
	1.46	1.30	2.36	2.43	10.22	8.92
Median	**1.46**	**1.34**	**2.35**	**2.76**	**9.13**	**8.84**
Standard Deviation	**0.00E+00**	**8.11E-10**	**1.15E-09**	**4.59E-09**	**1.10E-08**	**6.14E-09**

Temperature	**160˚C**		**180˚C**	
Species	Species 1	Species 2	Species 1	Species 2
	D_{eff} (× 10^{-8} m²/s)			
Test Samples	14.28	12.00	20.44	17.85
	15.57	14.28	2.43	19.96
	18.17	14.28	21.58	25.80
	16.06	8.60	19.96	34.40
Median	**16.00**	**12.30**	**16.10**	**24.50**
Standard Deviation	**1.62E-08**	**2.68E-08**	**9.14E-08**	**7.41E-08**

Table 6. Values of coefficients of effective diffusivity of some plants.

Products	**T (˚C)**	**D_{eff} (m²/s)**	**References**
Species 1 CS **Species 2 CS**	70 - 180	**1.46×10^{-8} - 16.10×10^{-8}** **1.34×10^{-8} - 24.50×10^{-8}**	Present work
Bunched coconut almonds	50 - 70	0.17×10^{-9} - 0.55×10^{-9}	[30]
Corn	55 - 75	0.09×10^{-9} - 0.17×10^{-9}	[16]
Okra	50 - 70	4.27×10^{-10} - 1.30×10^{-9}	[31]
Olive leaves	40 - 60	2.95×10^{-10} - 3.60×10^{-9}	[32]
Aloe Vera	30 - 70	5.64×10^{-10} - 18.1×10^{-10}	[33]
Black tea	80 - 120	1.141×10^{-11} - 2.985×10^{-11}	[13]
Lippia leaves	40 - 60	7.1×10^{-10} - 21×10^{-10}	[34]
Pumpkin	55 - 65	1.359×10^{-10} - 5.301×10^{-10}	[35]
Cantaloupe	30 - 55	0.053×10^{-9} - 0.111×10^{-9}	[36]
Green Beans	30 - 50	1.776×10^{-10} - 2.707×10^{-10}	[37]
Sweet Potato	50 - 90	1.26×10^{-9} - 8.80×10^{-9}	[38]
Ripe Banana	25 - 45	8.5×10^{-10} - 2.43×10^{-9}	[39]
Raphia leaves fiber	30 - 70	3.34×10^{-14} - 2.32×10^{-13}	[40]
Mushroom	50 - 60	1.55×10^{-9} - 4.02×10^{-9}	[41]
Bamboo		4.153×10^{-10} - 22.83×10^{-10}	[42]
Carrot	30 - 100	2.74×10^{-9} - 4.64×10^{-9}	[43]

Table 7. Activation energy of some plants.

Product	E_a (kJ/molK)	References
Species 1 CS **Species 2 CS**	**31.69** **34.46**	Case studies
Mature T coconut almond	25.94	[7]
Immature bunched coconut almond	65.16	[18]
Sitka tree	29.5	[44]
Pumpkin	27.8361 - 37.8437	[35]
Wheat	37.01	[11]
Black tea	406.028	[13]
Carrot	22.430	[45]
Aloe vera	24.4	[46]
Olive leaf	52.15 - 83.6	[32]
Okra	51.26	[31]
Green beans	23.97 - 47.26	[37]
Raphia leaves fiber	49 - 71	[34]
Potato	12.87 - 14. 35	[47]
Peanut shells	21.2	[48]
Corn	29.56	[16]

water during drying. It would be significant to study the influence of drying on mechanical properties of CS.

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