Study of Solar Drying Process and Moisture Desorption Isotherm of Moroccan *zygophyllum gaetulum* by Forced Convection

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ABSTRACT

Water desorption isotherms of *Zygophyllum gaetulum* were investigated at three temperatures 30, 40 and 50°C, by the dynamic gravimetric method. Experimental data are used to determine the best models for predicting the desorption equilibrium moisture content of *Z. gaetulum* for known values of temperature and water activity. The second part of this study deals with the drying kinetics of *Zygophyllum gaetulum* in a convective solar drying. The experimental results are used to determine the characteristic drying curve. Moisture transfer from *Z. gaetulum* was described by applying the Fick’s diffusion model. The effective diffusivity values changed from 7.89 \times 10^{-11} \text{ m}^2\text{s}^{-1} to 2.42 \times 10^{-10} \text{ m}^2\text{s}^{-1} within the given temperature range. An Arrhenius relation with an activation energy value of 56.72 \text{kJ.mol}^{-1} expressed the effect of temperature on the diffusivity.

Keywords: Desorption isotherms, Drying kinetics, Effective diffusivity, Forced convection, *Zygophyllum gaetulum*.

I. INTRODUCTION

The medicinal and aromatic plants have a great importance for both the pharmaceutical industry and the traditional medicine in Arab Maghreb countries [1]. The *Z. gaetulum* belongs to the family of Zygophyllaceae with branching and having small sheets made up of two fleshy leaflets, round, being used as water reserve. The fruit with the shape of reserved funnel with four lobes dilated with its summit. The *Z. gaetulum* pushes resolutely in the ergs. In Moroccan traditional pharmacopoeia, The *Z. gaetulum* is indicated for its antidiabetic properties. A recent study highlighted its hypoglycemia activity [2].

An important factor in the quality loss of dried medicinal and aromatic plants during storage is the water activity (a\(_w\)) which influences the biochemical reactions and stability of dried products. Some of these reactions are lipid oxidation, caking, agglomeration and degradation of vitamins and lycopene [3]. A large number of models have been proposed in the literature for the sorption isotherms [4]. It is usual for each investigator to report which model best fits the experimental data. It is therefore necessary to understand the moisture sorption characteristics of dried *Z. gaetulum*.

The stability of a dehydrated medicinal plant is influenced by its water activity. This stability is mainly a consequence of the relationship between the equilibrium moisture content and its corresponding water activity. Therefore sorption isotherms are essential tools in dehydration processes for selection of the proper operating conditions on the dryer, and packaging and storage requirements for a desired product shelf-life of dry products.

The second part of this study deals with the drying kinetics of *Z. gaetulum* in a convective solar dryer. The drying kinetics are then normalized according to Van Meel concept to find out the characteristic drying curve (CDC) necessary for calculation of the drying rate equation.

This study was mainly concerned with the:

- determination of the equilibrium moisture isotherms of desorption for *Z. gaetulum* at 30, 40 and 50 °C;
- fitting of the drying curves with ten mathematical models and determination of the characteristic drying curve (CDC) of *Z. gaetulum*;
- computation of the moisture effective diffusivity and the activation energy of *Z. gaetulum*.

II. MATERIALS AND METHODS

Sorption isotherms

*Zygophyllum gaetulum* used the sorption experiments, were grown in the region of Errachidia and got from the local market in April 2008. The study was conducted in the Laboratory of Solar Energy and
Medicinal Plants, Cadi Ayyad University of Marrakech (Morocco).

Sorption isotherms were determined by using the dynamic gravimetric method (Figure.1). Six saturated salt solutions were prepared under the recommendation of COST 90 project [5-6] by dissolving an appropriate quantity of salt in distilled water. The six salts were chosen, to have a large range of water activity (0.05-1). Table 1 shows the standard values of water activities, given for the six salts as a function of temperature [7].

Table 1: Equilibrium moisture contents of Z. gaetulum obtained at different temperatures.

<table>
<thead>
<tr>
<th>a_w</th>
<th>Desorption</th>
<th>a_w</th>
<th>Desorption</th>
<th>a_w</th>
<th>Desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 °C</td>
<td>0.0738</td>
<td>8.2386</td>
<td>0.0626</td>
<td>6.8182</td>
<td>0.0572</td>
</tr>
<tr>
<td>40 °C</td>
<td>0.3238</td>
<td>12.8205</td>
<td>0.3159</td>
<td>12.8205</td>
<td>0.3054</td>
</tr>
<tr>
<td>50 °C</td>
<td>0.4317</td>
<td>17.7778</td>
<td>0.4230</td>
<td>15.5556</td>
<td>0.4091</td>
</tr>
<tr>
<td>0.7275</td>
<td>80.0000</td>
<td>0.7100</td>
<td>77.5599</td>
<td>0.6904</td>
<td>42.0479</td>
</tr>
<tr>
<td>0.8362</td>
<td>87.0968</td>
<td>0.8232</td>
<td>79.7386</td>
<td>0.8120</td>
<td>62.3277</td>
</tr>
<tr>
<td>0.8980</td>
<td>95.0000</td>
<td>0.8910</td>
<td>94.4218</td>
<td>0.8823</td>
<td>93.3131</td>
</tr>
</tbody>
</table>

Duplicated samples each of 0.4180±0.0001 g for desorption were weighed and placed into the glass jars. This procedure continued until the weight was constant. The equilibrium moisture content of each sample was determined in a drying oven at 105°C for 24h. The hygroscopic equilibrium of Z.gaetulum was reached in 18 days for desorption.

Drying kinetics

The experimental set up, shown in Figure 2, mainly consists of an indirect forced convection solar dryer with a solar air collector, an auxiliary heater, a circulation fan and a drying cabinet. It was described in detail in references [8].

Experiments were performed to determine the effect of different drying air conditions on the drying kinetics. Three drying air temperatures (50, 60 and 70°C) and two drying air flow rates (0.028 and 0.056 m³.s⁻¹) were selected to examine the influence of temperature and air flow rate on the drying kinetics of Z. gaetulum.

The mass of the product used in drying experiments was (20.00 ± 0.01) g per tray. In the drying experiments, the 2nd and 10th shelves were not selected for efficient utilization of the drying air. However, the samples were uniformly spread evenly on a drying tray that was then placed on the first shelf of the drying cabinet. The heated air enters the drying cabinet below the trays and flows upwards through the samples. In order to dry the product sufficiently, it was important to keep the drying air temperature constant. In solar drying processes, the drying air temperature can vary based on the magnitude of the solar radiation. However, the auxiliary heater was used for controlling the drying air temperature. The amounts of daily solar radiation were measured with a Kip–Zonen solarmeter. Temperature measurements and recordings at different points in the solar dryer were made by Cr-Alumel thermocouples (0.2 mm diameter) connected to a data logger enabling ±0.1°C accuracy, and the outlet temperatures were measured with thermometers. The relative humidities were measured by capacitance sensors. These values were determined by probes Humicolor ±2% [9]. A digital weighing apparatus (±0.001 g) measures the mass loss of the product during the drying process. During each drying experiment, the weight of the product on the tray was measured by removing it from the drying cabinet for approximately 15–20s. These measurements were undertaken each 10 min at the beginning of the experiment and at 40 min intervals at the end. The initial and final moisture contents of each sample were determined by a drying oven whose temperature was fixed at 105°C for 24h.

III. RESULTS AND DISCUSSION

Sorption isotherms

Experimental results

The experimental results of the equilibrium moisture content at 30, 40 and 50°C at six water activities are given in Table 1. As shown in this table, a significant temperature effect on the desorption for the full range of water activities was observed for this product.
Figure 3 illustrates the effect of temperature shift on the desorption isotherms of *Z. gaetulum*. At a constant water activity, an increase in temperature leads to a decrease in the amount of sorbed water indicating that the material becomes less hygroscopic.

An increase of temperature causes an increase of water activity for the same moisture content. Similar results have been reported in the literature [9-10-11].

![Figure 3: Desorption isotherms of *Z. gaetulum*.](image)

**Modelling**

Literature reported many models predicting the relation between the equilibrium moisture content in the product, water vapour pressure and temperature. The GAB model is often used to describe the sorption isotherms in biological products. In this study it was found to fit the best our sorption isotherms. The results are given in Figure 4.

![Figure 4: Desorption isotherms of *Z. gaetulum* described by GAB model](image)

**Drying kinetics**

The experimental curves describing the evolution the drying rate as a function of time and water content are presented respectively in Figures 5 and 6. The curves obtained present the three classically described drying periods.

- **Period of temperature setting (period 0):** The temperature of *Z. gaetulum* rises up to a value corresponding to the temperature of draining air. The evaporated flow water increases and the water activity on the surface of the plant is equal to 1.

- **Constant drying rate period (period I):** This period corresponds to a linear decrease of the moisture content of the plant. Quantity of interstitial water available being sufficient since the water migration of the interior of the plant towards the periphery regularly replaces evaporated water. For this drying period, one can compare the drying rate of *Z. gaetulum* to that of an interstitial water surface, i.e. independent of the nature of the dried body, but depends only on the aerothermal conditions. The energy brought by the draining air is used to evaporate the quantity of water. The drying rate becomes maximum because the water activity of *Z. gaetulum* on the surface is always equal to 1.

- **Falling drying rate period (period II):** From a certain moisture content of the plant called critical moisture content, the water activity on the surface of the product starts to decrease and consequently the drying rate. The drying rate is not limited any more by the aerothermal conditions, but rather by the characteristics of the product to be dried like the internal migration of water, the structure of the product. The transition from period I to period II is not very clear in the case of *Z. gaetulum*. This returns the determination of the critical moisture content in this rather difficult point.

In many studies [12-13-14], it was noted that drying kinetics of the most biological products revealed no constant drying rate period. The falling rate period as mentioned in figure 6 is characterized by a two-stage phenomenon.

![Figure 5: Drying curves of *Z. gaetulum* at different temperatures](image)
Characteristic drying curve (CDC)

The purpose of CDC consists in normalizing the drying kinetics in a theoretical model from experimental data. By using Van Meel’s concept of characteristic drying curve, it is possible to represent the drying rate period of a given product, obtained under different conditions by a single normalized drying rate curve. Van Meel [15] assumed constant critical moisture content and suggested a modification of the coordinates to arrange all experimental drying rates in a single basic curve as follows:

In abscissa: \( X \rightarrow X' = \frac{X - X_{eq}}{X_{cr} - X_{eq}} \)

In ordinate: \( -\frac{dX}{dt} \rightarrow f = \frac{-\left(\frac{dX}{dt}\right)}{-\left(\frac{dX}{dt}\right)_{cr}} \)

Since the constant rate period is not usually well distinguished, many authors modified the Van Meel concept [16] for products with no constant rate period. They used simply the initial moisture content \( X_0 \) and the equilibrium moisture content \( X_{eq} \) derived from desorption data to obtain dimensionless moisture content and initial drying rate \( -\left(\frac{dX}{dt}\right)_0 \) to normalize the drying rate as follows:

In abscissa: \( X \rightarrow X' = \frac{X - X_{eq}}{X_0 - X_{eq}} \quad 0 \leq X' \leq 1 \)

In ordinate: \( -\frac{dX}{dt} \rightarrow f = \frac{-\left(\frac{dX}{dt}\right)}{-\left(\frac{dX}{dt}\right)_0} \quad 0 \leq f \leq 1 \)

The application of this new transformation to the whole set of experimental drying curves led to figure 7. This curve allows to conclude that, all drying curves obtained with the dimensionless moisture content \( X' \) and dimensionless drying rate \( f \), for different temperatures (50-70°C), fall into a tight band, indicating that the effect of variation in temperature is small over the range tested. Mrquardt-Levenberg non-linear optimization method, using the computer program ‘Curve Expert 3.1’ was used to find the best equation for the characteristic drying curve. A polynomial model was found to fit the best the dimensionless experimental data:

\[
\begin{align*}
    f &= 1.8337 \left( X' \right) - 2.3403 \left( X' \right)^2 + 1.5005 \left( X' \right)^3 \\
    \text{Standard error: } S_e &= 0.062 \\
    \text{Correlation coefficient: } r &= 0.99
\end{align*}
\]

The solar drying curves obtained were fitted with 11 different thin-layer drying models (Table 2). The correlation coefficient (r) and the reduced chi-square (\( \chi^2 \)) were the statistical parameters used for selecting the best equation to describe the thin-layer drying curves of Z. gaetulum. The reduced chi-square can be calculated as follows: \( \chi^2 = \frac{\sum_{i=1}^{N} \left( X_{exp,i} - X_{pre,i} \right)^2}{N-n} \). Where \( X_{exp,i} \) is the ith experimental moisture ratio, \( X_{pre,i} \) the ith predicted moisture ratio, N the number of observations, and n the number of constants in models.

In this study, the coefficients of each model, the most suitable model for drying of Z. gaetulum, the
relationship between the drying air temperature and the coefficients of the best suitable model were also determined.

Table 2: Selected mathematical models applied to the drying curves

<table>
<thead>
<tr>
<th>Model name</th>
<th>Model equation</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Newton</td>
<td>( X^* = \exp(-kt) )</td>
<td>[17]</td>
</tr>
<tr>
<td>Page</td>
<td>( X^* = \exp(-k^2t) )</td>
<td>[18]</td>
</tr>
<tr>
<td>Henderson and Pabis</td>
<td>( X^* = a \exp(-kt) )</td>
<td>[19]</td>
</tr>
<tr>
<td>Logarithmic</td>
<td>( X^* = a \exp(-kt) + c )</td>
<td>[20]</td>
</tr>
<tr>
<td>Two term</td>
<td>( X^* = a \exp(-kt) + b \exp(-k_1t) )</td>
<td>[21]</td>
</tr>
<tr>
<td>Two term exponential</td>
<td>( X^* = a \exp(-kt) + (1-a) \exp(-k_2t) )</td>
<td>[22]</td>
</tr>
<tr>
<td>Wang and Singh</td>
<td>( X^* = 1 + at + bt^2 )</td>
<td>[23]</td>
</tr>
<tr>
<td>Approximation of diffusion</td>
<td>( X^* = a \exp(-kt) + (1-a) \exp(-k_2t) )</td>
<td>[24]</td>
</tr>
<tr>
<td>Verma et al.</td>
<td>( X^* = a \exp(-kt) + (1-a) \exp(-gt) )</td>
<td>[25]</td>
</tr>
<tr>
<td>Midilli-Kucuk</td>
<td>( X^* = a \exp(-kt^n) + bt )</td>
<td>[26]</td>
</tr>
</tbody>
</table>

The drying data as moisture ratio \( X^* \) versus drying time were fitted to 11 thin layer drying models. The drying models coefficients were computed and presented in Table 3.

Table 3: Models constants and statistical results obtained from selected drying models

<table>
<thead>
<tr>
<th>Model</th>
<th>( \theta (\degree C) )</th>
<th>Coefficients</th>
<th>( r )</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Newton</td>
<td>50</td>
<td>k=0.0054</td>
<td>0.9962</td>
<td>6.1912 ( 10^4 )</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>k=0.0054</td>
<td>0.9980</td>
<td>2.4186 ( 10^4 )</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>k=0.0108</td>
<td>0.9688</td>
<td>5.6932 ( 10^3 )</td>
</tr>
<tr>
<td>Page</td>
<td>50</td>
<td>n=1.1227</td>
<td>0.9985</td>
<td>2.7000 ( 10^4 )</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>n=0.9923</td>
<td>0.9980</td>
<td>2.7226 ( 10^4 )</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>n=1.4581</td>
<td>0.9883</td>
<td>2.5222 ( 10^3 )</td>
</tr>
<tr>
<td>Henderson and Pabis</td>
<td>a=1.0121, k=0.0055</td>
<td>0.9965</td>
<td>6.1099 ( 10^4 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>a=1.0057, k=0.0054</td>
<td>0.9981</td>
<td>2.5284 ( 10^4 )</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>a=1.0474, k=0.0116</td>
<td>0.9727</td>
<td>5.4610 ( 10^3 )</td>
</tr>
<tr>
<td>Logarithmic</td>
<td>50</td>
<td>a=1.2686, k=0.0037, c=-0.2772</td>
<td>0.9994</td>
<td>1.0540 ( 10^4 )</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>a=0.9054, k=0.0067, c=0.1118</td>
<td>0.9989</td>
<td>1.3482 ( 10^4 )</td>
</tr>
</tbody>
</table>

The drying data as moisture ratio \( X^* \) versus drying time were fitted to 11 thin layer drying models. The drying models coefficients were computed and presented in Table 3.
The Midilli-Kucuk equation was found to be the appropriate model describing the drying curves of *Z. gaetulum* with an *r* of 0.9998 and *X* of 5.9846 10⁻⁵. The coefficients of the accepted model for thin layer convective drying of the product were determined as below:

\[ X^* = a \exp(-kt^n) + bt \]

\[ a = -0.3577 + 0.0511 \theta - 4.810^4 \theta^2 \]  
\[ k = 0.1007 - 0.0032 \theta + 2.610^5 \theta^2 \]  
\[ n = -11.5467 + 0.4122 \theta - 0.0032 \theta^2 \]  
\[ b = 0.0176 - 6.8510^4 \theta + 6.510^6 \theta^2 \]

The four expressions (Eqs. 2-5) predicted well the moisture ratio *X* at three drying temperatures 50, 60 and 70°C for *Z. gaetulum* with an *r* of 1 and Sr of 0.

These results can be proved consequently from figure 8 which plotted Midilli-Kucuk predicted moisture ratios versus drying time at 50, 60 and 70°C. Also from this figure, it can be concluded that the predicted moisture ratio decreased with the increasing in the drying air temperature and consequently the drying time decreased.

![Figure 8: Experimental and predicted moisture ratios obtained using Midilli-Kucuk model](image)

**Effective diffusivity and activation energy**

The experimental results obtained have shown that internal mass transfer resistance due to presence of falling rate period controls the drying time. The drying data in the falling rate period are usually analysed by Fick’s diffusion equation. The solution of this equation developed by Crank [27], and the form of Eq. (9) can be applicable for slab geometry by assuming uniform initial moisture distribution, constant diffusivity and negligible shrinkage [28]:

\[ X^* = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left( -\frac{(2n+1)^2 \pi^2 D_{eff} t}{4L^2} \right) \]  

(6)

Where *D* <sub>eff</sub> is the effective diffusivity (m<sup>2</sup>.s<sup>-1</sup>); *L* is the half thickness of the slab in samples (L=2 mm); and *n* is a positive integer constant. In practice, only the first term of Eq. (6) is used yielding:

\[ X^* = \frac{8}{\pi^2} \exp \left( -\frac{\pi^2 D_{eff} t}{4L^2} \right) \]  

(7)

Effective diffusivity is also typically calculated by using slope of Eq. (7), namely, when natural logarithm of *X* versus time was plotted, straight line with a slope was obtained:

\[ \text{Slope} = \frac{\pi^2 D_{eff}}{4L^2} \]  

(8)

The correlation between the drying conditions and the determined values of the effective diffusivity can be expressed by using an Arrhenius type equation [18] such as:

\[ D_{eff} = D_0 \exp \left( -\frac{E_a}{RT} \right) \]  

(9)

Where *D*<sub>0</sub> is the pre-exponential factor of the Arrhenius equation (m<sup>2</sup>.s<sup>-1</sup>), *E*<sub>a</sub> is the activation energy of the moisture diffusion (kJ.mol<sup>-1</sup>), *T* is the air absolute temperature (K) and *R* is the universal gas constant (J.mol<sup>-1</sup>.K<sup>-1</sup>).

The slope of Eq. (7) is the measure of the diffusivity, figure 9 shows the plot of ln(*X*<sup>*</sup>) versus drying time for the studied range of temperatures. The values of *D*<sub>eff</sub> are presented in Table 4. It is apparent at constant drying air flow rate that *D*<sub>eff</sub> increases with the increase of drying air temperature. Similarly, at constant drying air temperature, *D*<sub>eff</sub> increases with the increase of drying air flow rate. The effective diffusivities of *Z. gaetulum* varied in the range of 7.89 10⁻¹¹ to 2.42 10⁻¹⁰ m<sup>2</sup>.s<sup>-1</sup>.
Table 4: Values of effective diffusivity of Z. gaetulum

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Drying air flow (m$^3$.s$^{-1}$)</th>
<th>$\theta$ (°C)</th>
<th>Effective diffusivity (m$^2$.s$^{-1}$)</th>
<th>$r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.028</td>
<td>50</td>
<td>7.90 $10^{-11}$</td>
<td>0.9948</td>
</tr>
<tr>
<td>2</td>
<td>0.028</td>
<td>60</td>
<td>7.42 $10^{-11}$</td>
<td>0.9974</td>
</tr>
<tr>
<td>3</td>
<td>0.028</td>
<td>70</td>
<td>2.43 $10^{-10}$</td>
<td>0.9443</td>
</tr>
<tr>
<td>4</td>
<td>0.056</td>
<td>50</td>
<td>7.12 $10^{-11}$</td>
<td>0.9884</td>
</tr>
<tr>
<td>5</td>
<td>0.056</td>
<td>60</td>
<td>1.54 $10^{-10}$</td>
<td>0.9549</td>
</tr>
<tr>
<td>6</td>
<td>0.056</td>
<td>70</td>
<td>2.73 $10^{-10}$</td>
<td>0.9955</td>
</tr>
</tbody>
</table>

Figure 9a: Plot of ln($X^*$) vs time for different drying air conditions

Figure 9b: Plot of ln($X^*$) vs time for different drying air conditions

The activation energy ($E_a$) was calculated from the slope of the plot of ln($D_{eff}$) versus reciprocal of the absolute temperature as presented in figure 10. The activation energy of Z. gaetulum was found to be 56.72 kJ.mol$^{-1}$.

**IV. CONCLUSION**

The sorption isotherms of the Z. gaetulum at 30, 40 and 50°C were determined. The GAB model is retained for the description of the experimental desorption data with a relative error not exceeding 3%. It has also been noted that the temperature has an important effect on the sorption equilibrium. The experimental results show that the sorption isotherms of Z. gaetulum have a sigmoid type (V) form.

The concept of characteristic drying curve was checked in order to obtain an overall expression of the drying kinetics. By using an appropriate change of variable, the drying rate equation was determined empirically. The CDC is suitable to control and predict the drying process independently of the chosen parameters.

The goodness of fit of the observed values with ten thin-layer drying equations was evaluated. The Midilli-Kucuk equation was the best model to fit the experimental drying curves and was recommended as the thin layer model for Z. gaetulum. The drying parameters in this model were quantified as a function of the drying air temperature.

The effective diffusivity values changed from 7.89 $10^{-11}$ to 2.42 $10^{-10}$ m$^2$.s$^{-1}$ within the given temperature range and increased as temperature increases. An Arrhenius relation with an activation energy value of 56.72 kJ.mol$^{-1}$ expressed the effect of temperature on the effective diffusivity.

**REFERENCES**


