Study of mathematical models applied to sorption isotherms of Argentinean black bean varieties

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Abstract

Moisture sorption isotherms of five commercial black bean varieties harvested in the province of Salta, Argentina, were measured. Statistical methodology was applied to compare their sorption characteristics and it was observed that the five varieties could be considered as belonging to a same group.

Different equations proposed in the literature were studied and it was found that the best adjustments were provided by the Oswin and the White and Eiring equations. The estimated isotherm equations are given.

Adjusting the equations to sorption data found in literature, the White and Eiring equation provided a reasonable adjustment for all of them.

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1. Introduction

Black bean (Phaseolus vulgaris L.) represents one of the most important commodity produced in and exported from the Northwestern province of Salta, Argentina (Castillo, 2002). In black beans, as in cereal grains in general, molds are predominant spoilage flora during storage and they can also result in various kinds of damage, including a decrease in germination, discoloration, production of mycotoxins, heating, mustiness and total decay. By far, the most common procedure used to preserve quality in stored grains and seeds is reducing the water activity ($a_w$) to a level low enough to inhibit microbial growth. Because the control parameter used is the moisture content (m.c.), in order to establish humidity limits to inhibit microbial growth and mycotoxins production during storage, knowledge of water sorption isotherms of grains and seeds is essential to prevent the damage during storage and to diminish economical losses (Boente, González, Martínez, Pollio, & Resnik, 1994, 1996). In addition, it is useful to establish differences or similarities in water sorption characteristics of the black bean varieties harvested in Argentina in order to optimize their storage.

The first aim of this paper is to determine similar groups with five commercial varieties of Argentinean black bean using statistical methodology. The second aim is to model the relationship between $a_w$ and m.c. adjusting different equations proposed in the literature and selecting the best adjustments according to the goodness of fit criteria used. Finally, in order to find equations that provide a reasonable adjustment, not only for Argentinean varieties of black beans but also for different kinds of beans worldwide grown, data from the literature is analyzed.

2. Materials and methods

2.1. Water sorption characteristics

The samples used in this research correspond to five commercial varieties of black bean coming from
experimental fields in the localities of Cerrillos, Metán and Pichanal, in Salta province, Argentina. The variet-
ties, sown and harvested at the same time, were Camilo,
NAG 12, TUC 500, JEO 1 and JEO 2 and will be de-
noted as Varieties 1 to 5, respectively.

Samples were received with approximately 0.11 g
H₂O/g dry basis and stored at 5 °C until the analysis was
carried out. Water sorption characteristics were deter-
mained gravimetrically at 25 °C (Boente et al., 1996). The
isopiestic method was used and the range of water ac-
tivity considered was 0.60–0.93 which is the most im-
portant for microbial growth.

Approximately 2 g samples were stored over constant
relative humidity solutions in desiccators at 25 ±1 °C and
weighted periodically until equilibrium was attained
(20–40 days). The saturated salt solutions used in this
research were NaBr, NaCl, KCl, BaCl₂ and KNO₃
whose aw values are reported by Kitic, Favetto, Chirife,
and Resnik (1986) and Chirife, Favetto, Ferro Fontán,
and Resnik (1983).

In order to inhibit fungal growth, especially at high
aw, all grains were dipped in a mercury chloride solution
at 0.1%. Immediately, the grains were dried under an air
stream at ambient temperature in order to restore their
initial moisture (Pollio, González, & Resnik, 1987).
Once equilibrium was attained, moisture contents were
determined by drying in a vacuum oven at 60 ±1 °C for
28 h (Castillo, 2002). All measurements were done at
least in triplicate.

2.2. Statistical methodology

In order to compare water sorption isotherms, a two
way analysis of variance model was used (Scheffé, 1959).
The two factors were the five varieties and the aw at five
levels (aw₁ = 0.577 (NaBr), aw₂ = 0.752 (NaCl), aw₃ =
0.842 (KCl), aw₄ = 0.903 (BaCl₂), aw₅ = 0.927 (KNO₃)).
The model can be written as

\[ Y_{ijk} = \mu + \alpha_i + \beta_j + \gamma_{ij} + e_{ijk} \quad 1 \leq k \leq K_{ij}, \quad 1 \leq i \leq I, \]
\[ 1 \leq j \leq J, \]

where \( Y_{ijk} \) is the observed m.c., \( e_{ijk} \) the measurement
error, \( K_{ij} \) the number of replicates for variety \( i \) at the \( j \)th
aw level, \( I \) the number of varieties (\( I = 5 \)) and \( J \) the
number of aw levels (\( J = 5 \)) at which observations were
made. \( \mu \) is the true common mean, \( \alpha_i \) the true ith variety
effect, \( \beta_j \) the true jth aw level effect and \( \gamma_{ij} \) the interaction
effect between the ith variety and the jth aw level.

Assumptions underlying the model (1) (symmetry,
homocedasticity, normality) must be verified before the
adjustment (Boente et al., 1996) and if necessary, the
observed values can be transformed in order to obtain
for the predicted residuals \( \hat{e}_{ijk} \), a better behavior.

In this paper, differences between varieties were
studied, so the aim is to test the assumption \( H_{ls}: \)
\[ \alpha_i = 0 \leq i \leq 5. \]  Previously, the existence of interaction
should be tested (\( H_{ls}: \gamma_{ij} = 0 \leq i \leq 5, \ 0 \leq j \leq 5 \) because
in case m.c. and aw interact, the analysis must be per-
formed at each aw level.

Different equations for water sorption isotherms were
proposed in the literature. Due to the number of aw
levels considered and the number of replications only
equations with three or less parameters were studied. We
have studied the goodness of fit of 19 equations selected
for corn varieties by Boente et al. (1996).

The selected equations are described below. In all of
them \( M \) denotes the m.c. (dry basis).

Bradley equation:
\[ M = a + b \ln(-\ln aw) \]

Caurie equation:
\[ M = \exp(a + ba_w) \]

Chen equation:
\[ M = a + b \ln(-\ln aw + c) \]

Henderson equation:
\[ M = \exp(a + b \ln(-\ln(1 - aw))] \]

Hailwood and Horrobin equation:
\[ M = 1 / [a + ba_w + c / a_w] \]

which is equivalent to the GAB equation at constant
temperature.

Halsey equation:
\[ M = \exp[a + b \ln(-\ln aw)] \]

Harkins and Jura equation:
\[ M = \sqrt{1 / (a + b \ln a_w)} \]

Kühn equation:
\[ M = a + b(1 / \ln a_w) \]

Linear equation:
\[ M = a + ba_w \]

Mizrahi equation:
\[ M = a[a_w / (1 - a_w)] + b[1 / (1 - a_w)] \]

Oswin equation:
\[ M = \exp(a + b \ln(a_w / (1 - a_w))] \]

Smith equation:
\[ M = a + b \ln(1 - a_w) \]

Dole equation:
\[ M = a[a_w / (1 - a_w)] \]
Freundlich equation:

\[ M = \exp(a + b \ln a_w) \]  

(15)

Chirife et al. equation:

\[ M = \exp[a + b \ln(c - \ln a_w)] \]  

(16)

White and Eiring equation:

\[ M = 1/(a + ba_w) \]  

(17)

Haynes equation:

\[ M = a + \sqrt{(b + c \ln a_w)} \]  

(18)

Young and Nelson equation:

\[ M = a + b a_w + c a_w^2 \]  

(20)

\( a, b \) and \( c \) are parameters to be estimated.

Other equations proposed in the literature were considered but they were equal or equivalent to those above listed (Aguerre, Suárez, & Viollaz, 1989; Viollaz & Rovedo, 1999; Basunia & Abe, 1999; Menkov, 2000; San Martín, Mate, Fernández, & Virseda, 2001; Kouhila, Belghit, Daguenet, & Boutaleb, 2001; Sandoval & Barreiro, 2002).

Denoting \( e = M_{\text{observed}} - M_{\text{estimated}} \) the deviation between the observed m.c. and its estimated value, two criteria are generally used to evaluate the goodness of fit of each model:

The mean square of the deviations (Boente et al., 1996)

\[ S = \sum_{i=1}^{n} e_i^2 / n \]  

(21)

The mean relative percentage deviation in modulus (Boquet, Chirife, & Iglesias, 1978)

\[ P = \sum_{i=1}^{n} |e_i| / M_i \times 100 / n \]  

(22)

In each case, \( n \) is the number of observations available for each variety. In general, for the \( i \)th variety

\[ n = \sum_{j=1}^{s} K_{ij} \]

\( P \) should be used only when the residuals scale changes linearly with the m.c.

The statistical analysis was performed using SAS and Statistix packages (SAS Institute, 1999; Statistix version 1.0, 1996).

3. Results and discussion

The experimental results of the equilibrium moisture content of black bean seeds at each \( a_w \) at 25 °C are given in Table 1 for adsorption. The equilibrium moisture content at each \( a_w \) represents the mean value over the replications.

At high water activity levels (0.903 and 0.927) some samples showed visually fungal contamination. These samples were discarded, so it was necessary to apply an unbalanced analysis of variance model, as the one presented in Eq. (1).

After testing the assumptions underlying model (1) and transforming the data in order to improve the behavior of the predicted residuals, the hypothesis of null interactions was rejected. So a one way analysis of variance model was applied at each \( a_w \) level.

The normality assumption, tested by means of the Shapiro–Wilks statistic (Conover, 1980), was not rejected in any case, but at an \( a_w \) level of 0.752 the \( p \)-value was rather low (0.05 < \( p < 0.10 \)), and some outliers were observed. However, although the deletion of these outliers increased the \( p \)-value, it did not affect the results significantly.

With respect to the assumption that the error variance is constant, it was not rejected by the Bartlett’s test, in any case (\( p \)-values > 0.05).

Table 1

<table>
<thead>
<tr>
<th>Variety</th>
<th>( a_w )</th>
<th>Moisture content (g H2O/100 g db)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Camilo</td>
<td>0.577</td>
<td>10.64</td>
<td>0.13</td>
</tr>
<tr>
<td>JEO 1</td>
<td>0.577</td>
<td>10.61</td>
<td>0.17</td>
</tr>
<tr>
<td>JEO 2</td>
<td>0.577</td>
<td>10.56</td>
<td>0.12</td>
</tr>
<tr>
<td>NAG 12</td>
<td>0.577</td>
<td>10.91</td>
<td>0.18</td>
</tr>
<tr>
<td>TUC 500</td>
<td>0.577</td>
<td>10.76</td>
<td>0.02</td>
</tr>
<tr>
<td>Camilo</td>
<td>0.752</td>
<td>17.63</td>
<td>0.60</td>
</tr>
<tr>
<td>JEO 1</td>
<td>0.752</td>
<td>17.65</td>
<td>0.12</td>
</tr>
<tr>
<td>JEO 2</td>
<td>0.752</td>
<td>17.28</td>
<td>0.22</td>
</tr>
<tr>
<td>NAG 12</td>
<td>0.752</td>
<td>17.90</td>
<td>0.11</td>
</tr>
<tr>
<td>TUC 500</td>
<td>0.752</td>
<td>17.80</td>
<td>0.08</td>
</tr>
<tr>
<td>Camilo</td>
<td>0.842</td>
<td>24.11</td>
<td>0.03</td>
</tr>
<tr>
<td>JEO 1</td>
<td>0.842</td>
<td>24.27</td>
<td>0.42</td>
</tr>
<tr>
<td>JEO 2</td>
<td>0.842</td>
<td>24.45</td>
<td>0.13</td>
</tr>
<tr>
<td>NAG 12</td>
<td>0.842</td>
<td>24.62</td>
<td>0.47</td>
</tr>
<tr>
<td>TUC 500</td>
<td>0.842</td>
<td>24.40</td>
<td>0.11</td>
</tr>
<tr>
<td>Camilo</td>
<td>0.903</td>
<td>34.41</td>
<td>0.47</td>
</tr>
<tr>
<td>JEO 1</td>
<td>0.903</td>
<td>33.94</td>
<td>0.38</td>
</tr>
<tr>
<td>JEO 2</td>
<td>0.903</td>
<td>33.81</td>
<td>0.86</td>
</tr>
<tr>
<td>NAG 12</td>
<td>0.903</td>
<td>33.54</td>
<td>1.05</td>
</tr>
<tr>
<td>TUC 500</td>
<td>0.903</td>
<td>33.55</td>
<td>1.53</td>
</tr>
<tr>
<td>Camilo</td>
<td>0.927</td>
<td>40.79</td>
<td>0.90</td>
</tr>
<tr>
<td>JEO 1</td>
<td>0.927</td>
<td>42.84</td>
<td>0.96</td>
</tr>
<tr>
<td>JEO 2</td>
<td>0.927</td>
<td>41.79</td>
<td>0.77</td>
</tr>
<tr>
<td>NAG 12</td>
<td>0.927</td>
<td>42.84</td>
<td>1.06</td>
</tr>
<tr>
<td>TUC 500</td>
<td>0.927</td>
<td>41.59</td>
<td>0.71</td>
</tr>
</tbody>
</table>
In Table 2, the analysis of variance results for each \(a_w\) level are presented. It can be observed that there were no significant differences between varieties (\(p\)-values > 0.05).

Different equations were adjusted relating the dry basis m.c. and \(a_w\) values. The parameters were estimated by fitting a non linear model for each variety.

In order to decide which goodness of fit criteria should be used to select the best adjustment, the behavior of the absolute values of the residual versus the m.c. was analyzed. As a trend was present, the \(P\) criterion was used. As an example, in Fig. 1, the absolute values of the standardized residuals versus m.c. are shown for the Oswin equation (12) adjustment of Variety 2. The standardized residuals are obtained subtracting the residuals’ mean from the original residuals and dividing this difference by the residuals’ standard deviation.

It is interesting to point out that this behavior of the residuals is different from the one observed in the case of corn (Boente et al., 1996). So we recommend this analysis be performed for each material in order to select the appropriate goodness of fit criterium.

Using \(P\) as goodness of fit criterium, the best adjustments were provided by the Oswin (12), Hailwood and Horrobin (6), and White and Eiring (17) equations. However, the third parameter in the Hailwood and Horrobin equation (6), equivalent to GAB at constant temperature was not significant, so the adjustment it provides is equivalent to the White and Eiring (17) adjustment. It is generally accepted that values of \(P\) below 5% indicate a very good fit (Lomauro, Bakshi, & Labuza, 1985). In Table 3, the values of \(P\) corresponding to the selected equations are presented, and it can be observed that they are far below that limit.

As the analysis of variance results led to the conclusion that all varieties may be considered as belonging to a unique group, we adjust the selected equations to all the data in order to obtain general equations for black beans. The estimated equations are the following:

**Oswin equation:**
\[
M = \exp\left[-2.428 + 0.610 \ln\left(a_w/(1 - a_w)\right)\right]
\]  
(23)

**White and Eiring equation:**
\[
M = 1/(20.701 - 19.732a_w)
\]  
(24)

The numbers between parenthesis are the standard deviations of the estimated parameters. The values of the goodness of fit criterium \(P\) were 1.75 for the Oswin equation and 2.11 for the White and Eiring equation, indicating a very good fit.

Trying to obtain a model appropriate for beans in general, not only for black beans, data from the literature (Gane, 1950; Weston & Morris, 1954; Dexter, Andersen, Pfahler, & Benne, 1955; Jordao & Stolf, 1969–1970; McCurdy, Leung, & Swanson, 1980) were collected and analyzed (Table 4). It must be mentioned that the data in the literature were always given as averages. Adjusting the Oswin and the White and Eiring equations to these data it was found that the last one provided generally the

<table>
<thead>
<tr>
<th>Equation</th>
<th>Variety</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oswin</td>
<td>1.54</td>
<td>1.88</td>
<td>1.22</td>
<td>2.03</td>
<td>1.55</td>
<td></td>
</tr>
<tr>
<td>White and Eiring</td>
<td>1.74</td>
<td>2.33</td>
<td>1.50</td>
<td>2.70</td>
<td>2.05</td>
<td></td>
</tr>
</tbody>
</table>

---

**Table 2**

<table>
<thead>
<tr>
<th>Source</th>
<th>Degrees of freedom</th>
<th>Sum of squares</th>
<th>Mean square</th>
<th>F-statistic</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_w = 0.577)</td>
<td>Variety 4</td>
<td>2.206E-03</td>
<td>5.514E-06</td>
<td>2.98</td>
<td>0.0801</td>
</tr>
<tr>
<td></td>
<td>Residual 9</td>
<td>1.666E-03</td>
<td>1.851E-06</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total 13</td>
<td>3.871E-03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a_w = 0.752)</td>
<td>Variety 4</td>
<td>6.695E-03</td>
<td>1.664E-06</td>
<td>1.90</td>
<td>0.1866</td>
</tr>
<tr>
<td></td>
<td>Residual 10</td>
<td>8.743E-03</td>
<td>8.743E-06</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total 14</td>
<td>1.540E-04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a_w = 0.842)</td>
<td>Variety 4</td>
<td>7.675E-05</td>
<td>1.919E-06</td>
<td>3.36</td>
<td>0.0606</td>
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<tr>
<td></td>
<td>Residual 9</td>
<td>5.142E-05</td>
<td>5.713E-06</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Total 13</td>
<td>1.282E-04</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>(a_w = 0.903)</td>
<td>Variety 4</td>
<td>1.695E-04</td>
<td>4.238E-06</td>
<td>0.47</td>
<td>0.7591</td>
</tr>
<tr>
<td></td>
<td>Residual 9</td>
<td>8.170E-04</td>
<td>9.078E-06</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Total 13</td>
<td>9.866E-04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a_w = 0.927)</td>
<td>Variety 4</td>
<td>9.197E-04</td>
<td>2.299E-04</td>
<td>2.92</td>
<td>0.0768</td>
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<tr>
<td></td>
<td>Residual 10</td>
<td>7.862E-04</td>
<td>7.862E-06</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total 14</td>
<td>0.00171</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

**Fig. 1.** Absolute standardized residual values (SR) versus dry basis moisture content (m.c.) for the Oswin equation and for Variety 2.
best adjustment. The values of \( P \), included in Table 4, were always less than 5%.

4. Conclusions

The five commercial black bean varieties studied could be considered as belonging to the same group for storage purposes.

Between the equations considered, the Oswin and the White and Eiring equations provided the best adjustments. As the five varieties may be considered as belonging to a same group, general equations relating moisture content and \( a_w \) were obtained for black beans.

The analysis of data found in the literature showed that generally the best adjustment was provided by the White and Eiring equation. For this reason we recommend the use of this equation to model the behavior of the moisture content as a function of water activity for any type of beans.

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References


