Study of isothermic absorption model of moisture content of fibrous instant corn rice

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Abstract. In general, storage of food products made from grains is carried out in an environment with uncontrolled air temperature and humidity. In this situation, changes in temperature and humidity will continue according to daily weather patterns. Food products stored in this environment will experience adsorption and desorption processes alternately and continuously throughout the day. Dried food that has not reached its equilibrium moisture content tends to absorb moisture during storage so that it will trigger a decrease in quality through a series of physical, chemical, and microbiological processes. The relationship between water activity and equilibrium moisture content during storage can be approached with an isothermic sorption model. The purpose of this research is to determine the equilibrium moisture content of fibrous instant corn rice in various relative humidity (RH) values and to find a mathematical model from isothermic sorption curve of fibrous instant corn rice. The research methodologies include the production of fibrous instant corn rice, the determination of equilibrium moisture content at various RH (40%-90%), and mathematical modeling of isothermic sorption curves with standard model approaches (Caurie, Hasley, and Oswin). The results showed that the water vapor adsorption process occurred in the isothermic sorption experiments of fibrous instant corn rice at a temperature of 30°C which was marked by an increase in the moisture content of the instant fibrous instant corn rice at 40-90% RH. Hasley equation model: (log [ln (1/aw)] = -3.2810 - 3.0945 log Me), Caurrie: (ln Me = -3.3084 + 1.8163 aw) and Oswin: (ln Me = -2.3301 + 0.2805 ln [aw/(1-aw)]) can accurately describe the isothermic adsorption of fibrous instant corn rice at 30°C because it has an Mean Relative Determination (MRD) value of less than 5.

1. Introduction
Corn is a strategic commodity that can be developed into an alternative staple food as seen from its nutritional value which contains important protein in the Indonesian menu. The main (72-73%) nutrient content of corn is starch, with 25-30% of amylase and 70-75% of amylpectin. Simple sugar levels of corn are glucose, fructose and globulin, prolamin, glutelin and nonprotein nitrogen [1].

To support the development of corn as staple food, processing technology is needed to produce corn products that can be accepted and easy to prepare. One example of a product that can be developed from corn is instant corn rice [2]. Instant corn rice (ICR) is a type of food product that is easy to serve in a relatively short time.

ICR is stored in containers with a moisture content below 10%. The moisture content of ICR will change according to the environmental air conditions. Moisture content and water activity of foodstuff during storage can be studied using the isothermic water absorption model approach. The parameters of
the relationship between equilibrium moisture content and water activity can describe sorption constants and material characteristics. The material absorption constant can inform the heat energy of the adsorption material and the amount of gas adsorbed. In addition, with the sorption isotherm model, it is possible to predict changes in temperature and partial pressure of air vapor against the amount of water absorbed by the material so that it can be used as data in the drying, pickling and packaging processes [3].

Indonesia’s tropical climate with an average relative humidity of air above 60% increases the chance of moisture absorption and therefore the moisture content of dry food during storage also increases. High moisture content in food from agricultural products will degrade the quality through a series of physical, chemical and microbiological processes [4]. The greater the moisture content of food, the higher the water activity. Food with a relatively high moisture content tends to experience damage more quickly than food with lower moisture content.

Storage of dry food products in a humid environment lead to absorption of water vapor from the air until products reach the equilibrium moisture content with that of the surrounding air. The new moisture content that occurs in the stored products is called the equilibrium moisture content (EMC). This study aims to study or examine the equilibrium moisture content model of fibrous ICR. The resultant model will be useful for storing ICR in various circumstances (storage space humidity), so that steps can be taken to prepare the condition of storage space as well as for the drying operation of ICR.

2. Materials and methods

The main materials used in this study were fibrous ICR produced by the Research Center for Appropriate Technology – Indonesian Institute of Sciences, distilled water and chemical salts including Potassium Carbonate (K₂CO₃), Sodium Nitrite (NaNO₂), Sodium Chloride (NaCl), Ammonium Sulfate ((NH₄)₂SO₄), and Potassium Sulfate (K₂SO₄).

The tools needed in this research were mercury thermometer, Trisense meter, analytical scale, slicer, oven, dryer, pyrex excavator, temperature incubator, cup clamp, stopwatch and a set of computers. Adsorption experiments were performed using static methods at a temperature of 30°C and five levels of relative humidity (40% - 90%) with two replications. Data fitting was done according to the Caurie, Hasley and Oswin equation models. Stages of the experiment consisted of sample preparation, determination of equilibrium moisture content, determination of absorption parameters for instant corn rice, comparison between experimental results and the data fitting to the equation model.

2.1. Determination of Equilibrium Moisture Content

Determination of equilibrium water content was carried out by making saturated salt solutions in glass jar by mixing chemical salt with distilled water using the Pyro Mag Stir tool (procedure for making saturated chemical salt solutions to produce relative humidity values based on ASTM 1991 vol. 14.02), then the sample container is weighed on a scale and then add 10 g of ICR. Weighing is done periodically every 24 hours. In addition to measuring weight, temperature and humidity are also observed using a thermometer and RH-meter and the observation is stopped after the equilibrium state indicated by a constant sample weight, e.g. Change in sample weight not more than 0.005 g.

After the sample weight was constant, the water content was calculated by the method of oven (gravimetry) based on SNI 01-2891-1992 and carried out with two replications. The water content obtained is the equilibrium water content (EMC). Determination of the isothermic adsorption curve is based on water activity and equilibrium water content data from the experimental results.

2.2. Isotherm Sorption Model for Fibrous Instant Corn Rice

Caurie Equation Model. This equation model is suitable for most foodstuffs in the aₒ interval from 0.00 to 0.85 [5]. The form of the Caurie model in mathematical equations is:

\[ \ln Me = \ln P1 - (P2 Aw) \]  

(Eq. 1)
Equation 1 was transformed to linear equation with general form: \( y = a + b \cdot x \)
In which:
\[
\begin{align*}
P &= \text{Constant} \\
y &= \ln \text{Me} \\
a &= \ln P1 \\
x &= \text{Aw} \\
b &= -P2
\end{align*}
\]

**Oswin equation model.** This equation model is for food with \( a_w \) from 0.0-0.85 aw

\[
\text{Me} = P1 \left( \frac{aw}{1-aw} \right)^{P2} 
\]  
(Eq. 2)

Equation 2 was changed to straight line equation form with general form: \( y = a + b \cdot x \)
In which:
\[
\begin{align*}
P &= \text{Constant} \\
y &= \ln \text{Me} \\
a &= \ln P1 \\
x &= \ln[aw/(1-aw)] \\
b &= P2
\end{align*}
\]

**Hasley equation model.** This equation model for foodstuffs at the interval aw 0.1 - 0.81.

\[
aw = \exp \left[ -\frac{P1}{\text{Me}^{P2}} \right] 
\]  
(Eq. 3)

Equation 3 was changed to straight line equation form with general form: \( y = a + b \cdot x \)

\[
\log[\ln \left( \frac{1}{aw} \right)] = \log P1 - P2 \log \text{Me} 
\]  
(Eq. 4)

In which:
\[
\begin{align*}
P &= \text{Constant} \\
y &= \log \left[ \ln \left( \frac{1}{aw} \right) \right] \\
a &= \log P1 \\
x &= \log \text{Me} \\
b &= -P2
\end{align*}
\]

3. Results and Discussion

To obtain various constant values in the equilibrium moisture content equation, an experiment was carried out by storing samples of fibrous ICR in storage containers. The air in the storage package was adjusted for its RH by adding chemical salts. The results of setting the air RH in the storage are presented in Table 1.

**Table 1.** The comparison between the observed RH in the storage containers at 30°C saturated chemical salt and the theoretical RH.

| Salt types   | Theoretical RH (%) | Observed RH (%) | Deviations |
|--------------|--------------------|-----------------|------------|
| K₂CO₃        | 45.0               | 46.9            | 1.9        |
| NaNO₂        | 65.0               | 66.6            | 1.6        |
| NaCl         | 75.0               | 75.4            | 0.4        |
| (NH₂)₂SO₄    | 81.0               | 84.8            | 3.8        |
| K₂SO₄        | 96.0               | 95.1            | 0.9        |

*Source: Bukle et al. 1987 [6]*

Deviation values range from 0.4 to 3.8%. This deviation could occur due to several reasons, including the purity of the salt solution used or the fluctuations in temperature and humidity that occurred around the time of measurement. Based on ASTM 1967 part 15 standard, the RH measurement deviation can reach 4.0 to 5.0%. According to Labuza (1968), in order to get good and accurate results, the purity of the saline solution used needs to be considered in determining the equilibrium moisture content [7].
The sample, in the form of ICR with a dry-based 7.90% moisture content, were stored in packages with a RH corresponding to a saturated chemical salt solution, at room temperature of 30°C. The sample was weighed every 24 hours until the sample weight reached constant value, meaning that an equilibrium of water vapor pressure between the stored material (sample) and the surrounding air (in the package) was reached. The moisture content measured in the material (sample) is expressed as the equilibrium moisture content. The results of the measurement of the equilibrium moisture content of ICR experiment results are presented in Table 2.

**Table 2.** Equilibrium Moisture Content (EMC) for Fibrous ICR and the Time needed to reach the EMC in several storage RH.

| Salt type   | RH (%) | Equilibrium Moisture Content (%) | Time needed (days) |
|-------------|--------|---------------------------------|--------------------|
| K$_2$CO$_3$ | 47.4   | 8.90                            | 4                  |
| NaNO$_2$    | 68.0   | 12.65                           | 7                  |
| NaCl        | 75.9   | 14.00                           | 9                  |
| (NH$_2$)$_2$SO$_4$ | 86.1 | 16.09                           | 11                 |
| K$_2$SO$_4$ | 95.7   | 22.65                           | 16                 |

Table 2 demonstrates that the higher the relative humidity of the surrounding air (in the packaging), the higher the equilibrium moisture content of the instant corn rice. The initial moisture content of instant corn rice was 7.90% dry basis and increased to 8.90% dry basis at 47.4% RH and reached 22.65% at 95.7% RH. The increase in moisture content will continue until equilibrium with the surrounding air was reached. The increase in the level of instant corn rice occurs because the partial pressure of environmental water vapor (in the experimental container) is higher than the partial pressure of water vapor in instant corn rice, so that the flow of water vapor into the instant corn rice or adsorption of water vapor occurs by instant corn rice. According to Hall (1957), migration or flow of water from places with high steam pressure to places with low pressure is proportional to the difference in partial pressure of water vapor [8].

The movement of water during the isothermal adsorption process can be caused by several factors including relative humidity (RH) of air, water activity ($\alpha_w$), air flow velocity, diffusivity, capillarity, gravity, evaporation and condensation [9].

From Table 2, it can be explained that if instant corn rice is stored in an environment that has a temperature of 30°C with %RH as high as the %RH of air (second column), then the water content of ICR will go to the value as stated in column 3. From the results of the experiment, equilibrium moisture content of ICR was achieved in the range of 4 to 16 days. The higher RH storage value, the longer the time needed for fibrous ICR to reach its equilibrium point. In addition, the smaller the difference between the $\alpha_w$ of the product and its RH environment, the faster the time required for fibrous ICR to reach its equilibrium point. In addition, information on equilibrium moisture content at various air humidity values can be used as a factor in selecting packaging material. Each packaging material has a permeability value to water vapor or other gas present in the storage air.

### 3.1. Isothermic Adsorption Curves of Instant Corn Rice

#### 3.1.1. Isothermic Sorption Model

Labuza (2002) states that the water activity in food can be calculated by comparing the water vapor pressure of the material (P) with the pure water vapor pressure (Po) under the same conditions, or by dividing the ERH of the environment by 100 [10].

$$Aw = \frac{P}{Po} = \frac{ERH}{100}$$  \hspace{1cm} (Eq. 5)
In which:

- $A_w$ = water activity
- $P$ = partial pressure of water vapor material
- $P_0$ = partial pressure of pure water vapor at the same temperature
- $ERH$ = relative humidity

The use of isothermic absorption curve equation models of equilibrium moisture content is intended to get a more reliable picture of the tendency of the relationship between water activity and equilibrium moisture content.

### 3.1.2. Hasley

The general form of Hasley equation is

$$a_w = e^{\left(\frac{P_1}{M^P_2}\right)}$$

(Eq. 6)

The equation is transformed into a linear regression equation of:

$$y = a + bx$$

(Eq. 7)

with

- $x = \log Me$
- $y = \log \left[\ln \left(\frac{1}{a_w}\right)\right]$
- $a = \log P_1 = -3.2810$
- $b = -P_2 = -3.0945$

After the equation is obtained, the values of $a$ and $b$ can be calculated which will be used for the linear regression equation for the Hasley equation model. From the experimental data, it was found that the values of $a = -3.2810$ and $b = -3.0945$ so that the Hasley equation model becomes:

$$\log[\ln(1/aw)] = -3.2810 - 3.0945 \log Me$$

Next, the linear Hasley equation can be drawn into the isothermic absorption curve for the Hasley model. The curve illustrates the relationship between the equilibrium moisture content of the equation model in each salt RH.

### 3.1.3. Caurrie

The general form of the Caurrie equation is:

$$\ln Me = \ln P_1 - (P_2 a_w)$$

(Eq. 8)

The equation already linear with the form: $y = a + bx$. From the calculation results, it was found that the values of $a = -3.3084$ and $b = 1.8163$ so that the form of the Caurrie equation model becomes:

$$\ln Me = -3.3084 + 1.8163 aw$$

Next, the linear Caurrie equation can be drawn into isothermic absorption curve for the Caurrie model. The curve illustrates the relationship between the equilibrium moisture content of the equation model in each salt RH.

### 3.1.4. Oswin

The general form of the Oswin equation is:
The equation is transformed into a linear regression equation

\[ y = a + bx \]

with

\[ x = \ln \left( \frac{aw}{1-aw} \right) \]
\[ y = \ln Me \]
\[ a = \ln P1 = -2.3301 \]
\[ b = P2 = 0.2805 \]

After the equation is obtained, the values of \( a \) and \( b \) can be calculated and the results will be used for the linear regression equation for the Oswin equation model. From the calculation results, it was found that the values of \( a = -2.3301 \) and \( b = 0.2805 \) so that the form of the Oswin equation model becomes:

\[ \ln Me = -2.3301 + 0.2805 \ln[aw/(1-aw)] \]  

(Eq. 10)

Then, the linear Oswin equation can be drawn into the isothermic absorption curve for the Oswin model. The curve illustrates the relationship between the equilibrium moisture content of the equation model in each salt RH.

![Figure 1. Model of isothermic sorption curve of fibrous instant corn rice.](image)

### 3.1.5. Mean Relative Determination (MRD) Test

Comparison between the observed isothermic sorption curve with the predictive isothermic sorption models shows that some isothermic sorption models can describe the overall isothermic sorption curve at different levels of precision. This is reinforced by the MRD value which is a measure of accuracy between the predicted EMC and the observed EMC. MRD calculation uses the following formula:

\[ \text{MRD} = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{Mi - Mpi}{Mi} \right| \]  

(Eq. 11)

in which,
\[ a_w = \text{water activity} \]
Me  = Equilibrium moisture content
Mi  = Experimental moisture content
Mpi = Calculation result of moisture content
N   = number of data

MRD values for each model can be seen in Table 3

| Model    | Equation                                           | MRD value |
|----------|----------------------------------------------------|------------|
| Hasley   | \(\log(1/aw) = -3.2810 - 3.0945 \log Me\)         | 5.0340     |
| Caurrie  | \(\ln Me = -3.3084 + 1.8163 aw\)                  | 4.7640     |
| Oswin    | \(\ln Me = -2.3301 + 0.2805 \ln[aw/(1-aw)]\)     | 3.7460     |

The three models could be used to predicted the isothermic absorption of ICR as indicated by MRD value <5. The model chosen was the Oswin model with the smallest MRD value of 3.7460. The Oswin model was chosen to describe the actual state of the phenomenon of isothermic sorption of fibrous ICR by the following formula:

\[ \ln Me = -2.3301 + 0.2805 \ln[aw/(1-aw)] \] (Eq. 12)

Best model (Oswin) for adsorption isotherm at different temperatures of lyophilized grugru palm powder with 8% maltodextrin [11]. Chen and Morey [12–13] evaluated four models: the modified Henderson model, modified Chung-Pfost model, the modified Halsey model and the modified Oswin model for fitting the sorption isotherms data from 18 grains and seed crops.

Aviara et al and Oyelade in Ndubisi [14] reported that the modified Oswin model gave the best fit to the EMC of soya bean and lafun, respectively. If the storage of fibrous ICR follows the chosen equation model, Oswin model, it must be stored in environmental conditions with relative humidity of 75.90% (RH) to reach a value of the equilibrium moisture content which is less than 14 percent.

4. Conclusion
Water vapor adsorption process occurred in isothermic sorption experiments of fibrous ICR at 30°C, which was marked by an increase in moisture content of fibrous ICR under the treatment of air relative humidity (RH) of 40-90%. Based on observations, the equilibrium water content of fibrous instant corn rice was achieved at intervals of between 4 and 16 days. The Caurrie and Oswin equation models could be used to predict the isothermic adsorption of fibrous ICR at 30°C because it had an MRD value below 5. Oswin equation was the best equation model with the highest accuracy because it had the smallest MRD value (3.7460). In contrast, the Hasley equation model was not suitable because it has an MRD than 5.

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