Isotherm moisture sorption of composite desiccant made from rice husk biomass

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Abstract. The behavior of isothermal moisture sorption form rice husk-CaCl\textsubscript{2} composite desiccants was studied. The desiccant composite in various treatments was tested for its isothermal sorption using gravimetric method. Saturated solution of LiCl, CH\textsubscript{3}COOK, MgCl\textsubscript{2}, K\textsubscript{2}CO\textsubscript{3}, NaBr, NaNO\textsubscript{3}, NaCl, KCl, and K\textsubscript{2}SO\textsubscript{4} were used to obtain the moisture of 11 %, 22 %, 32 %, 44 %, 56 %, 64 %, 75 %, 84 % and 97 %. Water activity produced from these saturated salt solutions was measured using a\textsubscript{w} meter. The equilibrium moisture data was then fitted into several isothermal equation models that have been used and tested in several literature including the model of Courie, Oswin and Chen Clayton. This rice husk composite desiccant had exposed a J shape curve of equilibrium water content with a boundary zone A of a\textsubscript{w} 0.2 and zone B of a\textsubscript{w} 0.67. Based on the isothermic absorption curve, the Oswin equation model was able to predict the results of research with R\textsuperscript{2} of 0.96, 0.89 and 0.97, respectively for temperature of 30, 40 and 50 °C. This rice husk desiccant was able to absorb water vapor at low RH. It means that this desiccant is promising to be used for low water content or hygroscopic product such as flour based product, food flavor powder, chili powder, palm sugar and other products.

1. Introduction
Rice husk is already used for many commercial purposes such as traditional energy sources [1,2], carbon active for water treatment [3], soil amendment for fertilizer [4], nano silica for antimicrobial packaging [5], and filler for concrete producing [6]. Rice husk has a main chemical composition as polar components, namely lignin, cellulose, hemicellulose and high fiber content. The presence of OH groups and the polar side of cellulose makes the lignocellulose material naturally hydrophilic, so it has a high water-absorbing ability. This is due to the formation of hydrogen bonds of hydroxyl groups in the polymer chain with water molecules. The use of rice husk as moisture absorber for active food packaging would be very interesting to be developed, even more, the concern of food industries lately seem to look for natural moisture absorber sources as a substitute for synthetic of the silica gel one.

Nowadays, moisture absorber, also called desiccant, is widely attached into such food packaging to prolong the product self-life. This absorber would help the package dry thus it could maintain the crispiness of the product inside and also inhibit the growth of mold and other undesirable microbes. The development of desiccant so far is finding the more efficient moisture absorber by combining more than one active ingredient to improve the performance of the moisture absorbers in absorbing and controlling water vapor. The methods used include mixing two or more types of material [7,8] or using the method of impregnating active ingredients into a porous matrix [9] or co-materials polymer such as acrylamide [10]. The porous matrix of inorganic material is known as desiccant matrix, and is
commonly used to impregnate hygroscopic salts to form composite desiccant. The resulting composite desiccant is generally used for food and non-food products [11,12].

A salt of CaCl$_2$ could be inserted into rice husk to improve the performance of water vapor sorption of this desiccant [13,14]. The mechanism of sorption of moisture is closely related to the isothermic adsorption/desorption of a material. The stability of the solid state of the product, interactions in the early stages and influence of moisture on the physicochemical properties can be known from the absorption of isothermic. Sorption isotherms are also needed to determine the sorption capacity, thus the effectiveness of desiccation at the same temperature can be calculated. Based on the isothermic absorption curve, the critical points which affect the quality of the product would be obtained. Therefore, this study investigated isothermic moisture absorber of a composite desiccant made from rice husk powder and CaCl$_2$.

2. Materials and Methods

2.1. Materials

Rice husk was purchased from local market. A salt of CaCl$_2$ analytical grade and other chemicals of K$_2$SO$_4$, KCl, NaCl, NaBr, NaNO$_2$, LiCl, K$_2$CO$_3$, CH$_3$COOK, MgCl$_2$ were supplied by PT Merck Indonesia Tbk.

2.2. Methods

2.2.1. Production of desiccant composite of rice husk-CaCl$_2$

The production method is according to Wang et al. [15]. The rice husk was washed, dried and ground to make a powder rice husk in a size of 60 mesh and then it was dried at 105 °C for 8 h. The concentration of CaCl$_2$ solution was prepared in 5, 10, and 15 % w/v. A matrix of rice husk of 20 g was then put into CaCl$_2$ solution of 200 mL and stirred until mixed evenly and then soaked for 2 h. The composite of rice-husk-CaCl$_2$ then was dried at 105 °C for 4 h or until the weight was constant to get composite desiccant of rice husk-CaCl$_2$.

2.2.2. Characterization of isothermic water vapor sorption using static gravimetric method

Characterization of isothermic water vapour was carried out by storing samples in the isothermal desiccator [16]. The preparation of a saturated salt solution was prepared to regulate the humidity in the desiccator according to ASTM E104. Saturated salt solutions used was included LiCl, CH$_3$COOK, MgCl$_2$, K$_2$CO$_3$, NaBr, NaNO$_2$, NaCl, KCl, and K$_2$SO$_4$, respectively to produce moisture of 11 %, 22 %, 32 %, 44 %, 56 %, 64 %, 75 %, 84 % and 97 %. Water activity produced from these saturated salt solutions was measured using $a_w$ meters. $a_w$ meter is the equipment to measure the $a_w$ (water activity) of these salts.

The composite desiccant sample was dried at 105 °C until constant moisture content was reached. The desiccant was then put into a cup and arranged them in a desiccator. The desiccator then was stored in an incubator with temperature of 30, 40 and 50 °C and the desiccant scaled everyday to a constant weight for 2-4 weeks [17]. The sample was then measured for its water content using the gravimetric method to obtain equilibrium water content based on dry weight as in Equation 1. The relationship of water content equilibrium of composite desiccation at various $a_w$ will form an isothermic sorption curve.

$$M_t = \frac{W_{f} - W_{i}}{W_{i}}$$  \hspace{0.5cm} (1)

Where $M_t$ is desiccant water content (g H$_2$O/g desiccant) at time t, $W_{f}$ is final desiccation weight (g) at time t and $W_{i}$ = weight of initial desiccation at time t (g).
2.2.3. Isothermic Sorption Model and Model Accuracy Test
The equilibrium water content data was then fitted into several isothermal equation models that have been used and tested in several literature, so that an accurate curve and model of isothermic vapor absorption were obtained. Some of the equation use in this research was displayed in Table 1. These models will describe the relationship between $a_w$, equilibrium water content at certain temperature and constant value will be obtained from them.

| Model         | Equation                                      | Range of $a_w$ |
|---------------|-----------------------------------------------|----------------|
| Caurie        | $\ln M_e = \ln P_1 - P_2 \cdot a_w$          | 0.4-0.8; Tipe II |
| Oswin         | $M_e = P_1 [(a_w/(1-a_w))]^2$                 | 0.05-0.9; Tipe II dan III |
| Chen Clayton  | $a_w = \exp[-P/e^{P_2/\exp(P_2 M_e)}]$       | 0.1-0.9; Tipe II |

Note: $M_e$ is equilibrium water content; $K$ and $n$ are constant; $a_w$ is water activity; $P_1$ and $P_2$ are constant; Type II is the Sigmoid or S-shaped isotherm; Type III is known as the Flory-Huggin isotherm.

3. Result and Discussion

3.1. Isotherm sorption characteristic
The behavior of the desiccant composites in absorbing water vapor at various $a_w$ until equilibrium produced an isothermal sorption curve as presented in Figure 1. According to Monte et al. [18], sorption mechanism is occurred due to a specific interaction between moisture and oxygen groups on the surface such as (carbonyl and hydroxyl groups) of organic matter. The presence of additional pores causes the material to have the ability to absorb water molecules [19]. The water content of an equilibrium material at a certain temperature and humidity is called the equilibrium water content ($M_e$) [20].

When the $a_w$ environmental is greater than the composite desiccant water content (Figure 2), the equilibrium water content rises sharply at $a_w$ above 0.2. In this condition, the presence of CaCl$_2$ in the activated husk would expose two chemical absorption process, i.e., CaCl$_2$ as hygroscopic salts and CaCl$_2$ in form of hydrate, nH$_2$O, it is therefore the ability of activated husks to absorb water vapor increase [21] and resulted in a J Shape curve (Figure 3) as characteristic of amorphous material. At low $a_w$, it absorbs a little moisture and at high $a_w$, it will absorb very much water vapor. This illustrated that the adsorption process takes place quickly and the absorption process continues even though CaCl$_2$ has turned into a liquid. Calcium chloride (CaCl$_2$) has the highest vapor binding capacity, and melts within 22 hours of storage compared to sorbitol and KCl [22]. Based on isothermic curves (Figure 2), the boundaries of zones A, B and C which describe bounded water by composite desiccation [23]. According to Mathlouthi [24], zone A describes that water is bounded to the material very strong at low relative humidity. Furthermore, in zone B, water is bounded weakly to medium humidity and zone C is free water. However, the result of sorption curve showed that this composite desiccant was able to absorb moisture at very low RH.
Figure 1. Equilibrium water content (Mₑ) of composite desiccant (rice husk - CaCl₂) in 5, 10, 15 % b/v at temperature of 30 °C (a), 40 °C (b), and 50 °C (c).

Figure 2. Boundary zone of rice-husk composite desiccant at temperature of 30, 40, and 50 °C.

3.2 Isothermic sorption model and model accuracy test
Mathematical equation models that explain theoretical isothermic sorption phenomena have been developed, but in this study a mathematical equation only showed the relationship of two parameters of a_w and Mₑ [17]. The isothermal sorption curve obtained from this study was carried out to obtain high smoothness curves and can describe the state of composite desiccant sorption vapor phenomena in various a_w. Figure 3 showed the fitting of Courier, Oswin and Chen Clayton model with the experimental data.
Based on Figure 3, the relationship of $a_w$ and the moisture content of composite desiccant equilibrium can be described well by the Oswin Model. The Oswin model is an empirical equation that describe the state of water vapor absorption in the composite desiccant with a wide enough $a_w$ range at the three study temperatures, forming a curve like the letter S (sigmoid). In contrast to the other two models, the Oswin model was able to explain the hygroscopic characteristics of a material, which has a non-crystalline material which also describes the absorption of water vapor in a multilayer surface of a material [24].

The ability of water vapor absorption by composite desiccation is influenced by $a_w$ or environmental humidity. At low environmental humidity, the ability of desiccate in absorbing moisture is also low thus resulting in only small changes in equilibrium water content. The ability of water vapor absorption by desiccation increases at higher humidity following an exponential equation at $a_w$ more than 0.6. The increase in ambient temperature causes the level of sorption on the desiccation of the composite tend to decrease. This is shown from the achievement of lower equilibrium at higher temperatures. The zone B boundary on the isothermal sorption curve shifts at a higher $a_w$ as the temperature increases. Based on this behavior, it should consider how to keep the desiccant prior to use. This desiccant storage needs to be maintained at $a_w < 0.6$ (zone B boundary). Thus desiccant will have good moisture absorption performance when applied to maintain $a_w$ products in packages below 0.6. Therefore, moderate temperature is recommended to store this desiccant.

Predictions of increasing equilibrium water content caused by an increase in $a_w$ can be explained by the Oswin Model by following the equation as in Table 2. The characteristic of water vapor absorption in composite desiccation is not only influenced by humidity, but also influenced by ambient temperature. The results of the plot data in the Oswin Model at all three temperature studies produce a good coefficient of determination ($R^2$) which is around 0.89-0.97.

Table 2. Mathematical equation derived from Oswin model.

| Temperature (°C) | Equation | $R^2$ |
|-----------------|----------|-------|
| 30              | $\ln M_e = 3.291 + 0.583 \ln(a_w/(1-a_w))$ | 0.96  |
| 40              | $\ln M_e = 2.906 + 0.342 \ln(a_w/(1-a_w))$ | 0.89  |
| 50              | $\ln M_e = 3.145 + 0.5171 \ln(a_w/(1-a_w))$ | 0.97  |
4. Conclusion

Composite desiccation of rice husk – CaCl₂ comprises a J shape of equilibrium water content exposing in zone A, B and C similarly in temperature treatment of 30, 40, and 50 °C. This rice husk composite desiccant had exposed a J shape curve of equilibrium water content with a boundary zone A of αₑ 0.2 an, zone B of αₑ 0.67. This desiccant also demonstrated its ability to perform in vapour sorption at low RH. Based on the isothermic absorption curve, the Oswin equation model was able to predict the results of research with the smallest R² values, ranging between 0.89-0.97. It was recommended to store this desiccant in high moderate temperature prior to use for maintaining the good performance when it is applied for food products.

5. References

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