Effect of temperature on water vapor sorption on commercial desiccant and rice husk -CaCl₂ composite desiccant

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Abstract. Many efforts have been made to control the moisture in the package by the addition of the active ingredients which absorb this moisture. In the modern retail, moisture or water vapor absorber, known as desiccant has been widely used to extend the shelf life of the food product. Composite desiccants comprising the high active ingredient has been developed to improve the performance of single absorber material in absorbing and controlling moisture in the food package. The purpose of this research was to observe the effect of temperature storage in moisture sorption of commercial desiccants (silica gel and active clay) comparing to the composite desiccant of rice husk-CaCl₂. This research proved that the sorption ability of these desiccants were different, and it was influenced by the temperature of the storage. The results showed that rice husk-CaCl₂ composite desiccant possessed the highest absorption capacity especially at temperature of 40 °C with value of 1.2342 g H₂O/g desiccant for 7 days of storage. The increase of temperature has been resulted on increasing absorption rate (k), for example, rice husk-CaCl₂ composite desiccant, the k value was 0.2587 g H₂O/g desiccant/day at 30 °C, 0.7828 g H₂O/g desiccant/day at 40 °C and 0.9562 g H₂O/g desiccant/day at 50 °C. It looks that the moisture absorption followed pseudo second order for all treatment with R² at 99% for almost all treatments.

1. Introduction
Permeability of packaging is a condition where moisture has the ability to penetrate the packaging at certain conditions of temperature and Relative Humidity (RH). If the packaging permeability is low, then moisture penetrate the packaging is also low [1]. Many attempts have been made to control the amount of moisture in packaging such as vacuum packaging techniques, packaging with the addition of nitrogen, modified atmosphere packaging and packaging with the addition of the active ingredient absorbing. Other packaging techniques such as moisture absorber, commercially has been widely used to inhibit the growth of pathogen microorganisms. These absorbers are found in the form of sachets, pads or films. The application form will determine the method of manufacture and selection of the appropriate active ingredient. Active material can be any absorbent humectant salts, silica gel and mineral [2].

In the modern retail, moisture absorber has been widely used to extend the shelf life of products. Moisture absorber is widely used in water vapor resistant products such as chips, biscuits, and crackers. Moisture absorbers that used are silica gel, potassium oxide, and active clays, which will work as an absorbt of the moisture as well as absorbing oxygen [3]. One of the moisture absorber
materials that have been used commercially is silica gel. Silica gel (SiO$_2$) is granular that is synthesized from sodium silicate. Silica gel can absorb water easily because it has a high absorption rate of 35-50% of the weight of silica itself. Also, composite absorbers consisting of active materials have been developed to improve the performance of single material moisture absorbers in absorbing and controlling moisture. Combining techniques can be done by mixing two or more materials [4] [5] or impregnation of active materials into a porous matrix [6] or into a polymer [7] [8]. Moisture absorbers include CaCl$_2$, KCl and sorbitol could absorb the moisture quickly, thus these materials commercially mix with slow absorption desiccants such as bentonite [4].

Safe desiccation for food products is still being developed to replace chemical desiccants, a researcher [9] have been developed the use of calcium chloride (CaCl$_2$) impregnated on rice husk and coconut fiber to make composite desiccant. The results of this study stated that the best composite desiccant was activation rice husks with CaCl$_2$ in 15% w/v and it had an absorption capacity of 49% in the first 24 hours of storage in 90% relative humidity. In further, this research should be improve on the effect of storage temperature on the moisture of this rice husk-CaCl$_2$ desiccant comparing to commercial desiccants such as silica gel and active clay. It also necessary to demonstrate the application of this composite desiccant of rice husk CaCl$_2$-based to prolong the sensitive moisture product such bread. It is therefore the aimed of this research were to observe the absorption rate of the desiccants in various storage temperatures and to develop the mathematical model of the desiccants sorption to describe the behaviour of the absorber.

2. Research Method

2.1 Materials and equipment
The material used in this research was active rice husks, NaOH, CaCl$_2$, commercial desiccants (active clay and silica gel) and distilled water (aquades).

2.2 Method
The steps in this research were (i) manufacturing composite desiccant, (ii) commercial desiccant sample preparation, and (iii) measurement of composite and commercial desiccant water vapor sorption at many temperatures. Manufacturing composite desiccant started with the reducing the size of dried rice husk, delignificating the husk and impregnating into CaCl$_2$. The next step was the preparation of commercial desiccant samples. The samples of silica gel was bought from online shop with brand Imco and for activated clay with commercial name of desipack. Firstly, the sampled was heat in the oven for 15 minutes at temperature of 105 °C for being chase away of the vapor containing in the desiccant.

2.2.1 Manufacturing of rice husk CaCl$_2$ composite desiccant

2.2.1.1. Reduction the size of rice husk. The dried husk with at about 2.8% of water content was grinded using husk grinding machine. After that, it was sifted to produce 60 mesh of powdered rice husk.

2.2.1.2. Delignification process. The delignification process was used for 100 grams of dried powder rice husk and added with as much as 1 L of NaOH solution (5% w/v) to remove lignin contained in rice husk. The mixture was heated for 2 hours at a temperature of 80 °C then filtered to obtained delignificated husk. The husk and then washed with running water until it showed a neutral pH (pH 7). The rice husk then was dried for 24 hours at temperature of 105 °C or until the water content reached ±2%. The water content of the husk was measured by the oven method. The sample was dried using an oven, with a temperature of 105 °C. Then the sample was weighed until it reached a constant weight [10].
2.2.1.3. Impregnation process. The impregnation process was done using 20 grams of delignificated husk into the 15% CaCl₂ solution (w/v) for 2 hours at room temperature and then it was filtered to take impregnated rice husk-CaCl₂. This material and then was dried in the oven for 4 hours until the water content was constant at about 2%. This process would obtained rice husk-CaCl₂ composite desiccant.

2.2.2. Measurment of moisture sorption with gravimetric method. The materials used in this experiment were silica gel, active clay and rice husk-CaCl₂ composite desiccant. A storage space were prepared using jar bottles. Cleaned jar then was added as much as 50 mL of distilled water. The water will evaporate and reach a humidity of the space at about 97% [10]. Each desiccant was used as much as 1 g and was placed into a plastic cup and then was hung into the jar using a 7 cm thread of wool yarn to hold the desiccant cup. The jar was closed with lid and ready to store in an incubator with a temperature treatment of 30, 40 and 50 °C. The weight of the desiccants was measured every day until it reached constant. Percentage of water vapor sorption was calculated with the equation (1) (gravimetric method).

\[
\% \text{ Moisture sorption} = \left[ (W_i-W_f) / W_i \right] * 100
\]  \hspace{1cm} (1)

Description: \( W_i \) = initial weight of sample (g) at time of 0  
\( W_f \) = final weight (g) at time of t (day)

2.2.3. Kinetic model of desiccant. The kinetic model was calculated using pseudo second order model as equation 2 below [11]:

\[
\frac{t}{Q_t} = \frac{1}{kQ_e} + \frac{1}{Q_e}t
\]  \hspace{1cm} (2)

Where \( Q_e \) and \( Q_t \) are absorber moisture amount at t=equilibrium and t=t (day), \( k \) is the absorption rate (g H₂O/g desiccant/day) and t is t (day). Plotting a linear relationship between \( t/Q_e \) (g H₂O/g desiccantat t) with t (time) will produce \( Q_e \) and \( k \). If the value of \( R^2 \) is almost 1 thus it is expected that the experiment of moisture sorption is follow this model of pseudo second order.

3. Results

3.1. Moisture sorption at temperature of 30 °C
The result of moisture sorption at temperature of 30 °C is presented in Table 1. The experiment data and then plotted into the model of pseudo second order as displayed in Figure 1. It look that all absorber follow this model prefectly with \( R^2 \) ranging from 0.997 – 1, it means that model could describe the behaviour of the sorption process in that active materials.

| Absorber                | Equation         | \( R^2 \)  | \( k \) (absorbing rate g H₂O/g sample/day) | \( Q_e \) moisture capacity (g H₂O/g sample) |
|-------------------------|------------------|------------|------------------------------------------|--------------------------------------------|
| Rice husk-CaCl₂         | \( y = 1.0675x + 1.7412 \) | \( R^2 = 0.997 \) | 0.2587                                   | 0.227                                      |
| Silica gel              | \( y = 3.9247x + 4.0568 \) | \( R^2 = 1 \) | 0.979                                    | 0.0636                                     |
| Active clay             | \( y = 6.4091x + 9.1678 \) | \( R^2 = 0.998 \) | 1.6415                                   | 0.0399                                     |

Table 1 showed that the highest absorption rate in clay was 1.6415 g H₂O/g sample/day. While the lowest absorption rate was rice husk-CaCl₂ with a value of 0.2587 g H₂O/g sample/day. However, rice husk-CaCl₂ has the highest value of moisture capacity, which was 0.227 g H₂O/g of the sample.
Moisture sorption capacity of the silica was 0.0636 g H$_2$O/g sample and the active clay has the lowest moisture capacity value that was 0.0399 g H$_2$O/ g sample. So it could be concluded that the absorption of active clay and silica gel was saturated after the second day. In contras, the rice husk-CaCl$_2$ continued doing absorbing the moister until 7 days.

From figure 1, it can be seen that the absorption of moisture increaser sharply for the comprise husk-CaCl$_2$ composite desiccant has increased compare to silica and clay which seem constant on the second day to the seventh day. The smaller the pore, the greater the affinity [12]. Besides, the higher the temperature used, the water vapor from the storage environment evaporates faster and relative humidity decreases. The effect of capillarity and diffusion underlies the absorption of water vapor on composite desiccation. The moisture capacity absorbing in each active material was different due to a diffusion process and movement of water vapor from the environment into the composite desiccant was also different [9].

### 3.2. Moisture sorption at temperature of 40 °C

The result of moisture sorption at temperature of 40 °C is presented in Table 2. The experiment data and then plotted into the model of pseudo second order as displayed in Figure 2. It look that all absorber follow this model prefectly with $R^2$ ranging from 0.993 - 0.999, it means that model could describe the behaviour of the sorption process in that active materials.

| Absorber              | Equation          | $R^2$  | k (absorbing rate g H$_2$O/g sample/day) | q$_e$ moisture capacity (g H$_2$O/g sample) |
|-----------------------|-------------------|--------|----------------------------------------|-------------------------------------------|
| Rice Husk-CaCl$_2$    | $y = 0.7964x + 1.0918$ | $R^2 = 0.993$ | 0.7828 | 1.2342 |
| Silica gel            | $y = 2.9341x + 0.1208$ | $R^2 = 0.999$ | 0.7258 | 0.0843 |
| Active clay           | $y = 6.1429x + 3.0052$ | $R^2 = 0.994$ | 1.2396 | 0.0329 |

Table 2 showed that the highest absorption rate in clay was 1.2396 g H$_2$O/g sample/day. While the lowest absorption rate was gel silica with a value of 0.7258 g H$_2$O/g sample /day. However, rice husk-CaCl$_2$ has the highest value of moisture capacity, which was 1.2342 g H$_2$O/g of the sample. Moisture sorption capacity of the silica was 0.0843 g H$_2$O/g sample and the active clay has the lowest moisture capacity value that was 0.0329 g H$_2$O/ g sample. So it could be concluded that the absorption of active clay and silica gel was saturated after the first day. In contras, the rice husk-CaCl$_2$ continued doing absorbing the moisture until 7 days.
From figure 2, it can be seen that the absorption of moisture increases sharply for the husk-CaCl₂ composite desiccant has increased compared to silica and clay which seem constant on the first day to the seventh day. At temperature of 40 °C silica has the lowest absorption rate, because silica gel can absorb moisture from the air due to steam pressure. When the air is humid, the pressure in the air becomes high. The process of removing moisture from the air causes faster pressure equilibrium to be achieved [13].

3.3. Moisture sorption at temperature of 50 °C

The result of moisture sorption at temperature of 50 °C is presented in Table 3. The experiment data and then plotted into the model of pseudo second order as displayed in Figure 3. It look that all absorber follow this model perfectly with R² ranging from 0.996 - 0.999, it means that model could describe the behaviour of the sorption process in that active materials.

| Absorber          | Equation          | R²     | K (absorbing rate g H₂O/g sample/day) | qₑ moisture capacity (g H₂O/g sample) |
|-------------------|-------------------|--------|--------------------------------------|--------------------------------------|
| Rice Husk-CaCl₂   | y = 1.0067x + 0.8039 | R² = 0.999 | 0.9562                                  | 0.9435                                |
| Silica gel        | y = 3.3526x − 0.1239 | R² = 0.996 | 3.3083                                  | 0.2943                                |
| Active clay       | y = 8.0446x − 1.0316 | R² = 0.999 | 7.8476                                  | 0.1213                                |

Table 3 showed that the highest absorption rate in clay was 7.8476 g H₂O/g sample/day. While the lowest absorption rate was rice husk – CaCl₂ with a value of 0.9562 g H₂O/g sample/day. However, rice husk-CaCl₂ has the highest value of moisture capacity, which was 0.9435 g H₂O/g of the sample. Moisture sorption capacity of the silica was 0.2943 g H₂O/g sample and the active clay has the lowest moisture capacity value that was 0.1213 g H₂O/g sample. So it could be concluded that the absorption of active clay and silica gel was saturated after the first day. In contrast, the rice husk-CaCl₂ continued doing absorbing the moisture until seventh days.
From figure 3, it can be seen that the absorption of moisture increase sharply for the comprise husk-CaCl₂ composite desiccant has increased compare to silica and clay which seem constant on the second day to the seventh day. That bentonite or activated clay has a slow absorption so it must be mixed with a moisture absorber that can absorb quickly including CaCl₂, KCl, and sorbitol [4].

Based on the overall results of measurements made on each of the moisture absorbent material known to affect the temperature of the moisture sorption respective moisture absorbent material. Of the three known moisture absorbent material that has a highest absorption capacity was rice husk-CaCl₂ composite desiccant that is 1.2342 g H₂O/ g sample. This is because the composite desiccant containing CaCl₂, which according to [4] that the moisture absorber which can absorb quickly include CaCl₂, KCl and sorbitol are mixed with a desiccant that absorption is slow as bentonite, in addition to the power holding capacity of water vapor on CaCl₂ higher than the salt humectant or hygroscopic salt other, and will melt with long storage time to 22 hours.

Effects of capillarity and diffusion processes on materials may underlie the absorption of water vapor. In a small pore affinity for water also increased significantly [12]. The higher temperature causes the moisture in the more environment, so that the moisture moved from the environment. Besides, the higher the temperature used, the water from the storage evaporates faster and relative humidity decreases.

4. Conclusions
The conclusion from this research were increasing temperature has been resulted on increasing absorption rate (k), for example, rice husk-CaCl₂ composite desiccant, the k value was 0.2587 g H₂O/ g sample/day at 30 °C, 0.7828 g H₂O/g sample/day at 40 °C and 0.9562 g H₂O/g sample/day at 50 °C. It looks that the absorption kinetic followed pseudo second order for all treatment with R² at 99%. The highest moisture capacity of sorption was the composite desiccant of rice husk-CaCl₂ in temperature of 40 °C with a value of 1.2342 g H₂O/g sample.

5. References
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