Multi absorber made from rice husk and CaCl$_2$-KMnO$_4$ in absorbing water vapor and ethylene

A Rahmah$^1$, E Warsiki$^2$ and A Iskandar$^2$

$^1$Post Graduate Program of Agroindustrial Technology, IPB University, Bogor Indonesia
$^2$Department of Agroindustrial Technology, Faculty of Agroindustrial Engineering and Technology, IPB University, Bogor, Indonesia

e-mail: endangwarsiki@apps.ipb.ac.id

Abstract. The excessive ethylene gas and water vapor are not desired particularly in the fruit post-harvest handling, since the substances can shorten the shelf life and accelerate the rootling of the fruits thus its presence in the fruit handling is needed to be control. In this research, a multi absorber has been manufactured from calcium chloride (CaCl$_2$) and potassium permanganate (KMnO$_4$) with active rice husk as a matrix. The purpose of this study is to observe the capability of multi absorber of CaCl$_2$ and KMnO$_4$ trapped into rice hush matrix in absorbing water vapor and ethylene. In this study, CaCl$_2$ and KMnO$_4$ solutions with mol ratio of 1:2 ; 2:1 ; 1:3 and control (with CaCl$_2$(1 mol) or KMnO$_4$(1 mol)) were impregnated into the matrix. The experiment resulted that the ratio of CaCl$_2$(1 mol): KMnO$_4$ (3mol) was able to absorb KMnO$_4$ as much as 0.89 mg ethylene per 3 g absorber for 1 h of exposure. It also worked for absorbing water vapor as much as 1.03 g/g absorber for 7 days of storage at RH97%. Based on this experiment, the multi absorber resulted from this research is potential to be applied as ethylene and water vapor absorber.

1. Introduction
Fruit, during transportation and distribution, often experience quality damage due to improper handling. After harvest fruits still carry out physiological processes of respiration by releasing ethylene gas, water vapor and energy. Ethylene gas is compound responsible in accelerating its ripeness thus controlling this compound could be done by slowing respiration and transpiration of the fruit. Water vapor can also cause damage by making physical changes in color, smell, texture and shape of fruits [1].

Today, packaging is not only to protect and provide information about products, but it is also actively developed to be able to interact with the space inside the packaging or known as active packaging. The modern application of active packaging is used to absorbing water, ethylene, oxygen and other gas. One example of active materials that can absorb water vapor is silica gel, CaCl$_2$ or other minerals [2].

Manufacture of ethylene absorber from active carbon with KMnO$_4$ was done by [3] in which this compound was inserted into active carbon porous and water absorber with high moisture sorption capacity , in this case [2] with CaCl$_2$ impregnated into rice husk matrix. The two studies have been
resulted on 0.0745 ppm ethylene/g absorber for 1 h exposure [3] and 0.251 g H$_2$O/g absorber for 14 days [2]. Based on this result, a multi-absorber water vapor and ethylene was manufactured in this research. KMnO$_4$ was used as an active ingredient to absorb ethylene. This compound will adsorb or bind ethylene produced from fruits and break ties existed in that ethylene into the form of ethylene glycol and mangan dioxide [3]. Furthermore, CaCl$_2$ was used as water vapor absorber. As mentioned by [4] CaCl$_2$ is able to absorb water vapor in condition of more than 10% - 75% relative humidity. Direct application of the two active compound for food is highly not recommended thus entrapment of KMnO$_4$ and CaCl$_2$ into suitable matrix was recommended [2][3]. It is therefore, a research on active packaging of multi absorber to absorb water vapor as well as simultaneously ethylene absorber needs to be developed in order to produce multi absorber with two functions of absorbing.

2. Research Methods

2.1 Material and equipment
The materials used in this research were rice husk, aquadest, NaOH 5%, CaCl$_2$ and KMnO$_4$. The equipment used were sieves mesh 60, grinding machines, thermometer, pH meters, beaker glass and oven.

2.2 Methods
This study was conducted by manufacturing multi absorber in variation of mol ratio of CaCl$_2$ and KMnO$_4$ and analyze the performance of absorber by measure its water content, amount of water vapor sorption and rate of absorption of ethylene

2.2.1 Manufacturing composite desiccant

2.2.1.1 Preparation matrix. Matrix was produced based in previous research [2]. Rice husk was sorted from impurities and then washed, and then dried at temperature 105 °C until the moisture content reaches 2%. The moisture content of the dried rice husk was observed using oven method. The dried husk and then mashed and sieved in 60 mesh.

2.2.1.2 Delignification process. Delignification was aimed to eliminate lignin and hemicellulose from husk using chemical modification process [3]. The delignification process was used for 200 g of dried powder rice husk and as much as 2 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 80-85 °C then filtered to obtain delignificated husk. The husk was 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 [5].

2.2.1.3 Preparation the solution of CaCl$_2$- KMnO$_4$. The mol ratio CaCl$_2$: KMnO$_4$ used in this research was 1 : 2, 2 : 1, 1 : 3, 1 mol CaCl$_2$ as a control and 1 mol of KMnO$_4$ as a control. One mol was calculated based on atomic number, 1 mole CaCl$_2$ = 110 g, 1 mole KMnO$_4$ = 158 g and multiple by the desired mole. Each solution was made and then mixed into a beaker glass with as much as 100 mL aquadest.

2.2.1.4 Impregnation process and water content calculation. The impregnation process was aimed to trap KMnO$_4$ and CaCl$_2$ into the rice-husk matrix. The husk was dried at 105 °C for 8 hours then weighed as much as 25 g and soaked in a mixture of CaCl$_2$-KMN0$_4$ mixture (with several combinations) as much as 200 mL and it was stirred evenly and allowed to stand for 2 hours. Then it was dried at 105 °C for 4 hours until the water content was constant. For the measurement of moisture content the oven method was used by comparing the initial and final weight of the material after being
heated in the oven until constant weight. The samples were weighed as much as 2 g and the sample was put in the oven at 105 °C for 4 hours. It was taken out and put into the desiccator for 15 minutes and then weighed. The weighing was repeated every 2 hours until the weight was constant then the moisture content was calculated by the equation (1) below:

\[
\text{Water content (\%) } = \frac{(a-b)}{a} \times 100\%
\]  

(1)

Where  
\(a\) = initial weight (g)  
\(b\) = final weight (g)

2.2.2 Performance analysis of multi absorber sample

2.2.2.1 Measure water vapor absorption with gravimetric method. Measurement refers to Song [6]. The materials used in this process was multi absorber. A storage space was prepared using jar bottles. Cleaned jar then added with as much as 50 mL of distilled water. The water will evaporate and reach a humidity of the space at about 97% [7]. Each multi absorber for each treatment 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 °C. The weight of the absorber was measured every day until it reached constant. Percentage of water vapor sorption was calculated with the equation (1)

2.2.2.2 Measure ethylene absorption with gas chromatography. Testing the performance multi absorber of CaCl\(_2\)-KMnO\(_4\) in the adsorption of ethylene was done by using the methods of the GC. Injecting gas ethylene much as 1 mL with a concentration of 100-500 ppm into 3,000 mL volume chamber. Chamber filled with sachets of multi absorber of CaCl\(_2\)-KMnO\(_4\) as much as 3 g, then incubated for 24 hours at room temperature. Measurement of concentrations of ethylene residuals was performed every 15 minutes ranging from 0 min to 60 min. 1 mL ethylene was taken using syringe from the chamber and then injected into the gas chromatography which was equipped with a flame ionization detector (FID). The conditions of equipment were: column temperature of 85 °C, injector temperature of 150 °C and detector temperature of 200 °C. Gas measurement results were calculated using the air press:

\[
\text{Ethylene concentration (ppm) } = \frac{\text{peak sample}}{\text{peak standard}}\times \text{ethylene concentration standard}
\]  

(2)

2.2.2.3 Kinetic model of multi absorber. The kinetic model was calculated using pseudo first order and pseudo second order. Pseudo first order models was used to calculate the amount of ethylene absorbed into a multi absorber as Equation [3] and Pseudo second was used to calculate the kinetics equation sorption of water vapor [4] as equation (4):

\[
\ln (Q_e - Q_t) = \ln Q_e - kt
\]  

(3)

\[
t/Q_t = 1/(kQ_e) + 1/Q_e t
\]  

(4)

Where \(Q_e\) and \(Q_t\) are the amount of KMnO\(_4\)/water vapor absorbed at \(t_{\text{equilibrium}}\) and \(t_{\text{time}}\). The k was constant rate of absorption obtaining from liner plotting of \(\ln (Q_e - Q_t)\) with time (t) for pseudo first order or linear plotting \(t/Q_t\) for versus t for pseudo second order.

3. Results and discussion

3.1. Water contents of multi absorber

The moisture contents were tested using the oven method with 5 samples. Rice husk matrix was very hygroscopic thus it can change the equilibrium of water content depending on temperature and RH [5]. The multi absorber will absorb moisture from the surrounding environment. Based on the Table 1, it
can be seen that the multi absorber containing high KMnO₄ exposed the extremely low water content amounting 0.008 g H₂O/g sample compared to that CaCl₂ with the value of 0.014 g H₂O/g sample. It can be understood that KMnO₄ is not included as humectant salt group [3]. In contrast, CaCl₂ is humectant and highly hygroscopic salt [2] thus this active material was responsible for water vapor uptake. The moisture content of all sample treatment in this experiment is displayed in Table 1.

### Table 1. Water content of multi absorber for each treatment.

| No | Treatment of sample (mol ratio of CaCl₂: KMnO₄) | Water content (g H₂O/g absorber) |
|----|-----------------------------------------------|---------------------------------|
| 1  | 0 : 1                                         | 0.013                           |
| 2  | 1 : 0                                         | 0.014                           |
| 3  | 1 : 2                                         | 0.010                           |
| 4  | 2 : 1                                         | 0.010                           |
| 5  | 1 : 3                                         | 0.008                           |

3.2. Performance of multi absorber for ethylene and water vapor
Husk rice is a waste from farm that has properties of highly hydrophilic because it contains a lot of hydroxyl group. However, the husk also contains non-cellulose material such as lignin in which the lignin can inhibit water absorption into the husk. Thus the process of activation of groups of hydroxyl need to be done to chase away the lignin either by chemical or physical process bases [3]. In this research, to increase the capability of the rice husk sorption water vapor and ethylene absorber was done by the addition of CaCl₂ and KMnO₄. The ability of the multi absorber in absorbing the ethylene gas was done by using methods Gas Chromatography and it was greatly influenced by KMnO₄ content that exist with in the matriks of absorber. The results of sorption ability of the absorber to water vapor for 7 days at temperature of 30 °C can be seen in the Table 2. Furthermore Figure 1 displayed a fitting model of pseudo second order to the experimental data.

### Table 2. The kinetic model of moisture sorption at temperature of 30 °C.

| Treatment of sample (mol ratio of CaCl₂: KMnO₄) | Equation         | R²  | K(absorbing rate g H₂O/g absorber/day) | Qₑ moisture capacity (g H₂O/ g absorber) |
|------------------------------------------------|------------------|-----|--------------------------------------|-----------------------------------------|
| 0 : 1                                         | Y = 2.0316x + 3.06 | 0.990 | 0.485                                | 0.492                                    |
| 1 : 0                                         | Y = 1.0698x + 0.7448 | 0.987 | 0.275                                | 0.934                                    |
| 1 : 2                                         | Y = 1.1847x + 3.0945 | 0.989 | 0.294                                | 0.844                                    |
| 2 : 1                                         | Y = 0.9625x + 2.3119 | 0.988 | 0.211                                | 1.038                                    |
| 1 : 3                                         | Y = 1.2792x + 3.0836 | 0.993 | 0.324                                | 0.781                                    |

Based on Tabel 2 and Figure 1, the largest absorption capacity of water vapor is obtained from the treatment of the formulation with the addition of CaCl₂ only. One mole of CaCl₂ inserted into rice husk pore exposes a highest capacity in holding moisture if compared to other hygroscopic salts. Moreover, the treatment of 2 mol CaCl₂ : 1 mol KMnO₄ has sorption capacity of 1.03 g H₂O/g absorber for 7 days. Absorption is a diffusion processes and the capillary effect is underlying of water vapor absorption [9]. Absorption is also influenced by the differences between the concentrations of water vapor found in the environment with water vapor in the multi absorber thus it causes a transfer of moisture from the environment into multi absorber [2]. In contrast, the performance of KMnO₄ absorber was not as high as CaCl₂, the case is due potassium permanganate has a value of density larger than CaCl₂ [9]. The higher density of the absorber, the lower sorption ability [10]. Multi absorber takes longer if it is stored in high temperatures but the ability to absorb water vapor is slower if it is applied at high temperatures [2].
Figure 1. Mass of water vapour vs time of exposure in temperature 30 °C.

Figure 2. Mass of ethylene versus time of exposure.

Table 3. The kinetic model of multi absorber for ethylene sorption.

| Treatment of sample (mol ratio of CaCl₂ : KMnO₄) | Equation       | R²  | k (mg C₂H₄/3g absorber/min) | Qₑ (mg C₂H₄/3g absorber) |
|------------------------------------------------|----------------|-----|----------------------------|--------------------------|
| 0 : 1                                          | Y = 0.0481x - 0.3084 | 0.9252 | 0.0481                      | 0.7346                   |
| 1 : 0                                          | Y = 0.0285x - 0.5706 | 0.9208 | 0.0285                      | 0.5512                   |
| 1 : 2                                          | Y = 0.0312x - 0.0156 | 0.9351 | 0.0312                      | 0.9845                   |
| 2 : 1                                          | Y = 0.0293x - 0.3521 | 0.9037 | 0.0293                      | 0.703                    |
| 1 : 3                                          | Y = 0.0342x - 0.062 | 0.9401 | 0.0342                      | 0.9632                   |

| Treatment of sample (mol ratio of CaCl₂ : KMnO₄) | Equation       | R²  | k (mg C₂H₄/3g absorber/min) | Qₑ (mg C₂H₄/3g absorber) |
|------------------------------------------------|----------------|-----|----------------------------|--------------------------|
| 0 : 1                                          | Y = 1.2015x + 82.278 | 0.805 | 5.436                      | 3.766                   |
| 1 : 0                                          | Y = 5.9338x + 519.12 | 0.949 | 109.885                    | 3.120                   |
| 1 : 2                                          | Y = 4.2676x + 347.39 | 0.886 | 23.448                     | 1.287                   |
| 2 : 1                                          | Y = 0.0166x + 134.3 | 0.002 | 0.108                      | 393.732                 |
| 1 : 3                                          | Y = 6.0696x + 455.23 | 0.828 | 16.185                     | 0.439                   |

Figure 2 and Table 3 show the increasing rate of ethylene absorption of multi absorber. The highest absorption of ethylene is obtained from a combination of the concentration of CaCl₂ (1 mol): KMnO₄ (3 mol) which amounted as much as 0.963 mg ethylene per 3 g absorber for 1 h of exposure. The kinetics model of ethylene absorption is calculated in Pseudo first order. Meanwhile, the R² value for the pseudo first order resulted more linear in the concentration of CaCl₂ (1 mol): KMnO₄ (3 mol). Thus, the smallest absorption is found in the 1 mol CaCl₂ without KMn₄ as much as 0.551 mg ethylene per 3 g for 1 h of exposure. The results of the observations proved that KMnO₄ can be absorbed in the pores husks then it was able to improve the performance of multi absorber. Moreover, the ability of KMnO₄ as oxidant will oxidize the ethylene roommates thus it makes the absorption process more concise and optimal. The use of KMnO₄ as an oxidizing agent is more effective if it is used in liquid
form and applied to a binding material [9]. Processing oxidation ethylene by KMnO₄ is more effective if the process takes place naturally and is accompanied by a diffusion process that facilitates the interaction between ethylene (C₂H₄) with material [8]. Based on the comparison of data of the concentration of the above, it can be concluded that the more KMnO₄ trapped in the rice husk matrix the more ethylene is absorbed from the environment.

Based on table 3, it shows that the ethylene absorption follows the model of pseudo first order reaction with R² ranging from 0.805 – 0.949 compared to pseudo second order model with R² = 0.828 starting from 0.925 to 0.940. This condition is similar to [3] which the behavior of ethylene sorption data can be approved as pseudo first order with value R² higher compared to other kinetics model.

4. Conclusion
Based on the experiment, it can be concluded that the water vapor absorption shows that the CaCl₂ absorber is the best absorber for reducing water vapor emitting from fruit while for the most optimal process of ethylene absorber, addition of KMnO₄ without any CaCl₂ possesses the highest performance compared to other treatment. Thus, the combination of CaCl₂ and KMnO₄ in the matrix of rice husk can be the best solution for delaying fruit maturity process.

5. Reference
[1] Widayanti S M, Syamsu K, Warsiki E and Yuliani S 2016 Int. J. Sci. Technol. 1710 030029
[2] Agriawati D P, Warsiki E, Iskandar A and Noor E 2019 Earth Environ. Sci. 347 012062
[3] Aprilliani F 2019 J. Hortic. Res. 27 2 doi:102478/johr-2019-0007
[4] Langergren S and Svenska B K 1898 Veterinskapskad Handlingar 24 4 1-39
[5] Nakabayashi M, Fujimoto T, Sawa T, Kabe K and Adachi T 2008 J. Pediatr. Surg. 43 358-361
[6] Asim N, Emdadi Z, Mohammad M, Yarmo MA and Sopian K 2015 J. Clean. Prod. 91 26-35
[7] Song Y, Lee D S and Yam K L 2001 J. Food Process Preserv. 25 49-70
[8] Napitupulu 2013 J. Hortic. 23 3 263-275
[9] Emdadi Z, Asim N, Ramali ZAC, Yarmo MA, Shamsudin R and Sopian K 2014 WSEAS Trans. Environ. Dev. 10 1 306-311
[10] Bhattacharjee D and Rabi S D 2017 J. Pure Appl. Biosci. 5 1 64-71
[11] Ho Y S and G McKay 1999 J. Process Biochem. 34 5 451-465
[12] Hartanto, Singgih and Ratnawati 2010 J. Sains Materi Indonesia 12 1 12-16
[13] Asim N, Asmadi Z, Mohammad M, Yarmo MA and Sopian K 2015 J. Clean. Prod. 91 26-35
[14] Yokotani N, Ryohei N, Shunsuke I, Masayasu N, Akitsugu I and Yasutaka K 2009 J. Exp. Bot. 60 12 3433-3442
[15] Atta-Ally M A, Jeffrey K B and Donald J H 2000 J. Postharvest Biol. Tech. 19 239-244

Acknowledgement
Author would like to sincerely thank to Directorate of Higher Education, The Ministry of Research Technology and Higher Education, Republic of Indonesia for finding this research through Master Thesis Research Scheme.