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# Preserving Climacteric Fruits by Ripening Hormone Oxidation using nano-$KMnO_4$ Confined within Nanoporous Carbon

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Climacteric fruits naturally can be over-ripened because of ripening hormone composed of ethylene gas. Removal of ethylene gas by potassium permanganate ($KMnO_4$) has successfully preserved the fruit, but there is still a room for improvement through nano-confinement process. This study was conducted to compare the ethylene oxidation rate and fruit preservation ability of $KMnO_4$ and nano-$KMnO_4$. Ethylene oxidation experiment was conducted in a gas-tight vial filled with ethylene gas (~20%v) and either $KMnO_4$ or nano-$KMnO_4$. Ethylene gas concentration inside the vial was periodically measured using gas chromatography (GC). The result revealed that ethylene oxidation rate by nano-$KMnO_4$ is higher than $KMnO_4$. The ethylene oxidation rate kinetic was modeled with a gas-solid reaction model, which is fundamentally more accurate than first-order reaction model. Fruit preservation experiment was conducted in sealed containers filled with banana (*Musa acuminata*) samples and either $KMnO_4$ or nano-$KMnO_4$, and stored at room temperature. The result revealed that banana preservation duration by nano-$KMnO_4$ is remarkably longer than $KMnO_4$, where unpreserved fruit was ripened after 7 days and fruit preserved by $KMnO_4$ and nano-$KMnO_4$ were ripened after 13 and 16 days respectively.

**Keywords:** Ethylene, Fruit preservation, Gas-solid reactions, Potassium permanganate

## INTRODUCTION

Climacteric fruit is one of many economic potentials of tropical countries e.g. The Association of Southeast Asian Nations (ASEAN) countries. As a commodity, climacteric fruits possess a challenging aspect, which is its ripening time. From post-harvested, distributed, until received by consumers, climacteric fruits naturally undergo a ripening process because of ripening hormone composed of ethylene gas ($C_2H_4$). This process often causes a climacteric fruit becomes over-ripened, losing its market value. Climacteric fruit is capable to produce ethylene gas by itself (Silve et al., 2009). Even worse, ethylene gas with concentration as low as 12 ppm is enough to significantly speed up the ripening process (Beaudry et al., 1987). Removal of ethylene gas will prolong the ripening process and prevent the fruits to become over-ripened. Methods developed include ethylene control atmosphere (Romero et al., 2007), adsorption using cobalt oxide (Prasetyo et al., 2018, 2019), and oxidation using potassium permanganate (Hernandez et al., 2007). The removal of ethylene gas by oxidation process using potassium permanganate ($KMnO_4$, a strong oxidizer) has advantages such as converting ethylene to carbon dioxide, hence no possibility of ethylene presence anymore and utilizing a relatively cheap material.

Potassium permanganate oxidizes ethylene gas through a gas-solid reaction. The absence of ethylene gas will prevent climacteric fruits to become ripened. Potassium permanganate oxidize ethylene in a series of reactions, through acetaldehyde and acetic-acid pathway. Further oxidation will completely convert ethylene gas into $CO_2$ and $H_2O$ (Platt, 2017). The overall reaction stoichiometry of those series of reactions is described as follows.

$$3C_2H_4+12KMnO_4 \longrightarrow 12MnO_2+12KOH+6CO_2 \quad (1)$$

Pure $KMnO_4$ solid is already capable of oxidizing ethylene gas, but its oxidizing ability can be improved through nano-confinement process. Nano-confinement process will increase the area of contact between reactant, shorten the diffusion distance, and increase the number of atom in grain boundary, as reported in various studies (Prasetyo et al., 2018, 2019). These changes may enhance $KMnO_4$ oxidizing ability. Moreover, confining $KMnO_4$ within porous material hinders a direct contact between relatively hazardous $KMnO_4/MnO_2$ and fruit. Hence, it is safer. In this study, porous carbon was employed as support material since it has a high surface area and high pore volume (Prasetyo et al., 2017).

Several studies have been done on climacteric fruits preservation with $KMnO_4$ (Wabali et al., 2017, Azad et al., 2016, Akbari et al., 2014). Peel or fruit's skin color is often used as the parameter of ripeness in fruits preservation experiment. This parameter is good enough to determine the ripeness of fruits, as peel color is also the most common ripeness parameter used by consumers. A novel method is developed in this study to diversify ripeness parameter and diminish the observer's subjectivity. Banana (*Musa acuminata*) was used as a sample in the experiment. As a banana becomes more ripened, more brown spots appear in its yellow peel. Image processing tool is used to measure the area of these brown spots. The measured area will be a convincing parameter of the banana's ripeness, providing a more objective comparison between the samples.

Ethylene oxidation rate models have also been investigated in those corresponding studies. Unfortunately, most of the ethylene oxidation rate models used is a first-order kinetics. Even though most of the results are quite precise, a first-order kinetics model is not fundamentally accurate to represent a gas-solid reaction. A gas-solid reaction kinetic is affected not only by rate constant but also by diffusion constant. This study aimed to compare the oxidation of ethylene by $KMnO_4$ and nano-$KMnO_4$ and model the kinetic using gas-solid reaction kinetic models.

## MATERIALS AND METHODS

### Nano-$KMnO_4$ Preparations through Nano Confinement

The activated carbon (denoted as AC) provided by PT Home System Indonesia has an average particle size of 0.355 μm and a surface area of 1000 $m^2/g$. AC was first oxidized using commercial $H_2O_2$ solution (33%w/v, Merck Germany). The contact between AC and $H_2O_2$ solution occurred inside a flask with a reflux system using water as coolant. The contact occurred at 70°C and at atmospheric pressure. The ratio between AC and $H_2O_2$ solution was 0.1 g/mL. The contact time between AC and $H_2O_2$ solution was 2 h. Then, the solution was filtered and the remaining AC was dried in oven at 60°C for 8 h (Serano et al. 1997).

Nano-$KMnO_4$ was produced through nano confinement process which was carried out by carefully dripping 0.1 g/mL $KMnO_4$ solution onto the AC. The $KMnO_4$ solution was prepared by dissolving $KMnO_4$ solids in distilled water. The ratio between AC and $KMnO_4$ solution was 1 g AC/mL solution. Then, the AC was dried at 50°C for 8 h, so that the resulting AC confines nano-$KMnO_4$ with a ratio of 0.1 g nano-$KMnO_4$/g AC.

### Ethylene Oxidation by $KMnO_4$ and Nano-$KMnO_4$

The experiment of ethylene oxidation was conducted in a 10 mL gas-tight vial at room temperature (28°C). Ethylene gas (20% ethylene, 80% nitrogen) was obtained by blending pure ethylene gas with pure nitrogen gas. $KMnO_4$ solids as much as 0.01 g was put inside a gas-tight vial and nano-$KMnO_4$ as much as 0.01 g (confined in 0.1 g AC) was put inside another gas-tight vial. Both of those vials were then vacuumed again to remove the air that went inside when $KMnO_4$ was put into the vial. To ensure that no air leaked into the gas-tight vials, silicone glue was applied near the vials' opening. Ethylene gas was injected in those vials by using a 10 mL injection syringe. The timer started after ethylene gas was injected into a vial respectively. The ethylene oxidation experiment was held for 1 h. Several gas samples were taken during the run by using a 0.2 mL syringe to analyze the degraded ethylene concentration.

### Ethylene Oxidation Rate Models and Rate Constants

Gas-solid reaction has two distinct models, which are the shrinking spherical particle model and a more common model, shrinking core model (Levenspiel, 1999a). The equation describing shrinking core model has been developed by Levenspiel (1999a), but the model is divided into three kinds, depending on the controlling step. The controlling step can be gas film diffusion, ash diffusion, or surface reaction. This model become inaccurate if more than one controlling step occurred in a single reaction. Knoor et al. (2012) has developed another model that accommodate ash diffusion and surface reaction, by neglecting gas film diffusion as it is usually small compared the other two. By using mass balance, general equation in terms of $KMnO_4$ conversion ($X_B$) is developed (Eqs. (2)).

$$\frac{dX_B}{dt} = \frac{3r_c^2 akC_{A,core}}{r_0^3 \rho_B} \tag{1}$$

*$r_c$* and *$C_{A,core}$* are described by Knoor et al. (2012) as shown in Eqs. (3) and (4). *$r_c$* is the remaining core radius and *$C_{A,core}$* is ethylene concentration at reacting core surface.

$$r_c = r_0 \left(1 - X_B\right)^{1/3} \tag{2}$$

$$C_{A,core} = -\frac{D_{A,eff} C_{Ag} r_0}{-r_0 D_{A,eff} - r_c^2 a + r_c k r_0 a} \tag{3}$$

Ethylene oxidation by nano-$KMnO_4$ is described by different equations, although it is also a gas-solid reaction. A shrinking core model usually controlled by those three-step mentioned above, but nano-$KMnO_4$ is confined inside porous AC so that pore diffusion may become another controlling step. Simplifying the model, a general first order reaction in terms of ethylene concentration is employed. Effectiveness factor (denoted as ε) as described by Levenspiel (1999b) is applied as the correction factor because reaction occurred inside a porous material tend to be slowed down by pore diffusion. By using mass balance, general equation in terms of ethylene conversion (*$X_A$*) is developed as shown in Eqs. (5)-(7).

$$\frac{dX_A}{dt} = k'''\left(1 - X_A\right)\varepsilon \tag{4}$$

$$\varepsilon = \frac{1}{M_T}\left(\frac{1}{\tanh 3M_T} - \frac{1}{3M_T}\right) \tag{5}$$

$$M_T = \frac{R}{3}\sqrt{\frac{k'''}{D_a}} \tag{6}$$

## Fruit Preservation

Fruit preservation experiment was done on *Musa acuminata* or as the locals named it 'dwarf' banana. The banana was harvested when they were not ripened yet, in which all of the peel surface presenting a green color. The banana was harvested from a farm in Sleman Regency Region, Special Region of Yogyakarta, Indonesia. Banana selection and standardization were done by using only banana with around 50 g mass and has a similar shape and appearance.

Set of three bananas were packed in sealed translucent polypropylene containers, with a size of $18 \times 30 \times 24$ cm. Silica-based desiccant as much as 10% of banana mass was placed in each storage to control the air humidity. The first storage contained no preservative at all, hence being used as the control variable. The second storage contained $KMnO_4$ preservative as much as 0.5% of banana mass. The third storage contained nano-$KMnO_4$ preservative as much as 0.5% of banana mass. All of the preservatives were packed in a circular non-woven paper and were placed beside the preserved banana.

After being packed, banana packages were stored in a closed room with minimum sunlight. The storage temperature depended on atmospheric temperature during the experiment and closely ranged 26-29°C. The experiment took 19 days, which at the end of the experiment all of the bananas were considered already ripened. The analysis conducted were peel color changes assessment and a more quantitative analysis, which is brown spots area measurement. The peel color changes assessment is a semi-quantitative assessment where a set of numbers is given to describe banana's peel colors, based on a scale by Prabawati et al. (2008). The scale representing banana's peel colors is presented in Table 1.

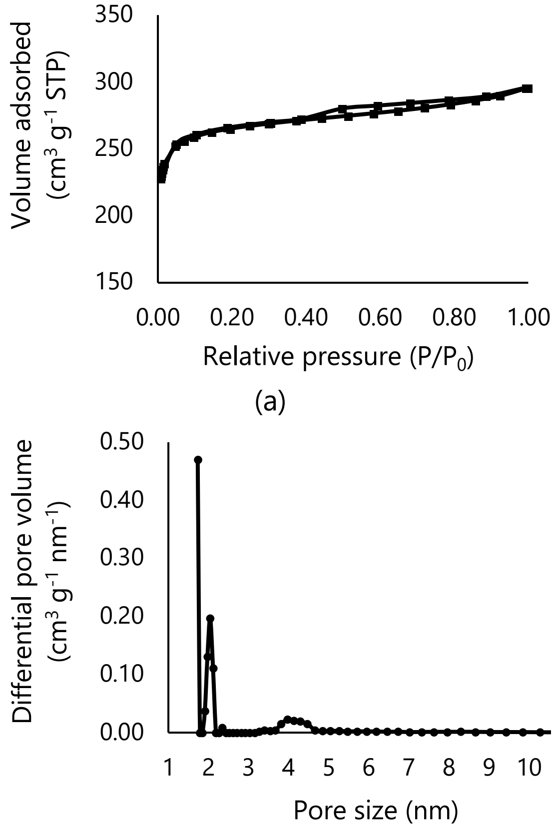
**Table 1.** Description of value assigned for peel color scale for quantifying banana observation

| Value | Peel Color Description |
|---|---|
| 1 | Green (post-harvested) |
| 2 | Green with yellow tinge |
| 3 | Green with yellow overlap |
| 4 | Yellow with green tinge |
| 5 | Yellow with green at the tip |
| 6 | Yellow (ripened) |
| 7 | Yellow with a few brown spots |
| 8 | Yellow with a large number of brown spots (over-ripened) |

## RESULTS AND DISCUSSION

### Material Characterization

Activated carbon was characterized by isotherm $N_2$-sorption analysis, in the pressure range of 0-760 mmHg. The result of $N_2$-sorption is presented in Fig. 1a. The activated carbon has a BET specific surface area of ca. 1000 $m^2/g$. Pore size distribution was evaluated and is presented in Fig. 1b. The activated carbon possesses pore size distribution which is highly peaked in the micropore (<2 nm) regimes and has a tiny portion in mesopore (2-50 nm) regimes. These pores will be the host of $KMnO_4$ which is impregnated into the activated carbon.



(a)

(b)

**Fig. 1.** $N_2$-sorption isotherm (a) and pore size distribution of activated carbon (b)

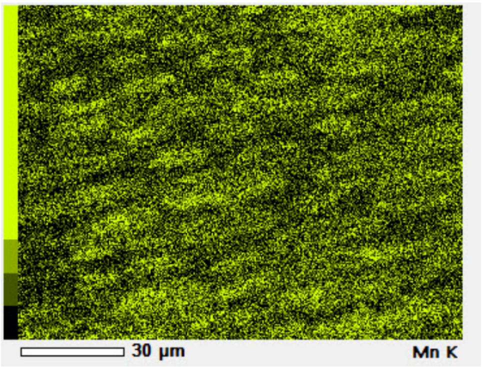


**Fig. 2.** SEM-EDX mapping of nano-$KMnO_4$ inside activated carbon's pore, showing even distribution of elemental Mn

SEM-EDX mapping was conducted on nano-$KMnO_4$ to ensure that $KMnO_4$ is dispersed thoroughly in the activated carbon's pore, thus forming 'nano-$KMnO_4$'. The result of SEM-EDX mapping presented in Fig. 2 shows that $KMnO_4$ (represented by elemental Mn) is evenly dispersed in the activated carbon's pore.

### Rate of Ethylene Oxidation

The ethylene oxidation rates by $KMnO_4$ and nano-$KMnO_4$ were investigated. The experiment were conducted in 10 mL gas-tight vials at room temperature (28°C). A graph showing the oxidation of ethylene by either material of $KMnO_4$ or nano-$KMnO_4$ is presented in Fig. 3. It can be seen that over the reaction time, the amount of ethylene decreases. However, the trends between $KMnO_4$ and nano-$KMnO_4$ are different. The ethylene oxidation by nano-$KMnO_4$ has the steepest $C/C_0$ curve, compared to the ethylene oxidation by $KMnO_4$. This slope could give a hint that ethylene oxidation by nano-$KMnO_4$ has higher rate compared to the ethylene oxidation by $KMnO_4$.

This higher rate of oxidation might also be caused by partial adsorption of ethylene into activated carbon's pore. However, adsorption of ethylene in activated carbon's pore is low, as previously proven by Prasetyo (2018). Activated carbon has adsorption capacity of pure ethylene of 1.79 mol $kg^{-1}$. The amount of ethylene that is partially adsorbed will be even lower in this experiment because of the use of ethylene mixture (20% ethylene, 80% nitrogen), in contrast with pure ethylene.

The data of ethylene oxidation were fit with reaction model to evaluate the kinetic rates. The data and fitted lines (small dashed: $KMnO_4$ fit and dash-dot line: Nano-$KMnO_4$ fit) shown in Fig. 3 have a good relationship. The values of rate constants obtained from ethylene oxidation experiments of both materials are presented in Table 2. Since kinetic constants is evaluated using different reaction models, it is difficult to be compared. For apparent diffusion constant, noticeably the diffusivity of ethylene in nano-$KMnO_4$ material ($6.68 \times 10^{-5}$ $m^2$ $s^{-1}$) is remarkably higher than that of in bulk $KMnO_4$. Nano-confinement process will reduce ash layer resistance in $KMnO_4$, hence showing a higher diffusivity constant.

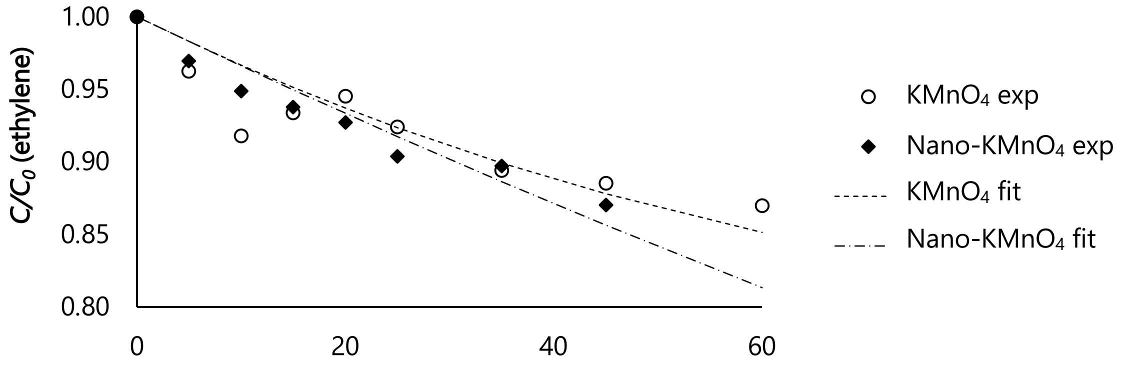


**Fig. 3**. Ethylene oxidation rate by $KMnO_4$ and nano-$KMnO_4$. Initial concentration of ethylene ($C_0$) of 20%v/v; 10 mL volume of gas, 0.01 g $KMnO_4$; 28°C temperature

**Table 2**. Rate constant of ethylene oxidation by $KMnO_4$ and nano-$KMnO_4$ at 28°C

| | **$KMnO_4$** | | **nano-$KMnO_4$** | |
|---|---|---|---|---|
| **Rate Constants** | **Value** | **Unit**[a] | **Value** | **Unit**[a] |
| k | $1.5012\times10^{-6}$ | $m\ s^{-1}$ | $3.4425\times10^{-3}$ | $s^{-1}$ |
| D | $1.0660\times10^{-8}$ | $m^2\ s^{-1}$ | $6.6800\times10^{-5}$ | $m^2\ s^{-1}$ |

[a] Units denoting rate constants *k* differ because differences in equation models (see Eqs. (4) and (7))

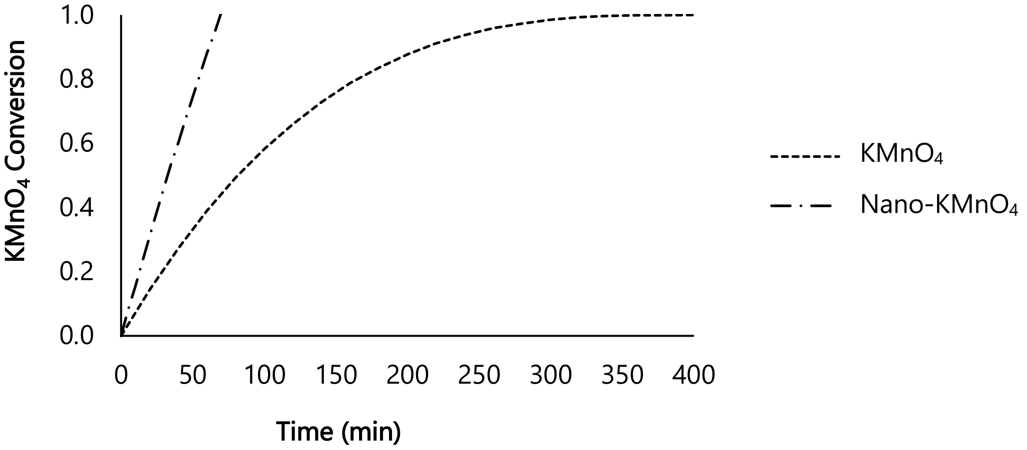
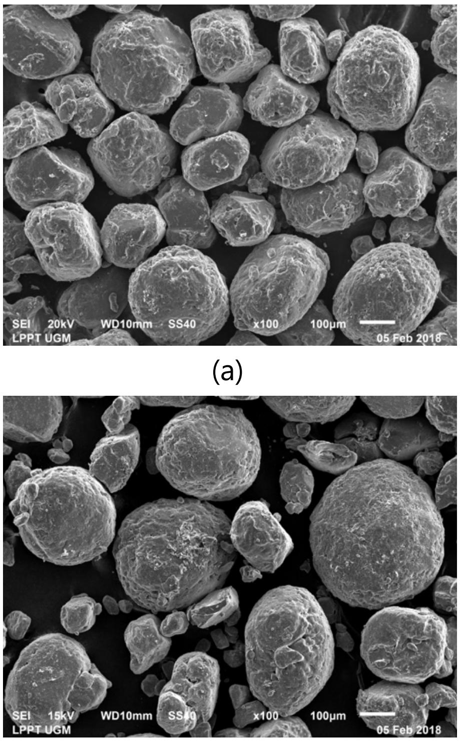


**Fig. 4**. Simulation of complete reaction represented by $KMnO_4$ conversion ($KMnO_4$ as limiting reactant and ethylene gas in excess). Initial concentration of ethylene ($C_0$) of 20%v/v; 10 mL volume of gas, 0.01 g $KMnO_4$; 28°C temperature

The rate constant data in Table 2 are used for further ethylene oxidation simulation. The same conditions are applied: initial concentration of ethylene ($C_0$) of 20%v/v; 10 mL volume of gas, 0.01 g $KMnO_4$; 28°C temperature. Simulation of time needed for a complete reaction of ethylene and $KMnO_4$ or nano-$KMnO_4$ was done and presented in Fig. 4. In Fig. 4, $KMnO_4$ conversion is presented instead of ethylene conversion because the limiting reactant is $KMnO_4$ while ethylene gas is in excess.

The time needed for a complete reaction between ethylene gas and nano-$KMnO_4$ is 70 minutes, meanwhile $KMnO_4$ needs 380 minutes. This huge time difference proves that nano-confinement process enhances the reaction rate of ethylene and $KMnO_4$, thus increasing the oxidation ability of $KMnO_4$. Slow reaction rate in pure $KMnO_4$ is occurred because as oxidation progressed, pure $KMnO_4$ solid will be enveloped in ash layer which will gradually thicken. The ash layer inhibits ethylene diffusion into the solid core and slows down the oxidation rate.

Further experiment was done to confirm that the unchanging size shrinking core model actually occurred in the ethylene oxidation by $KMnO_4$. The $KMnO_4$ solid mean diameter, before and after oxidation experiment, were analyzed using SEM. The SEM analysis results of $KMnO_4$ solid are presented in Fig. 5. The mean diameter of $KMnO_4$ solid before and after ethylene oxidation experiment are 264.63 μm and 271.75 μm, respectively.



(a)

(b)

**Fig. 5.** Results of SEM analysis on $KMnO_4$ solid before (a) and after (b) ethylene oxidation experiment.

This measurement result confirms that the unchanging size shrinking core model actually occurred in the ethylene oxidation by $KMnO_4$. Potassium permanganate solid is converted to $MnO_2$ solid after its reaction with ethylene gas. The $MnO_2$ solid causes the 'ash' formation outside unreacted $KMnO_4$ core. This 'ash' formation is getting thicker by time, as the $KMnO_4$ core is getting smaller because it is reacting with ethylene gas. A similar phenomenon was found in the reaction between $KMnO_4$ solid and $H_2S$ gas (Goldnik et al. 2016). The size of $KMnO_4$ solid before and after reaction is retained by the $MnO_2$ 'ash' formation, so that the reaction is fit with an unchanging size shrinking core model.

### Test of Banana Preservation

The preservative characteristic of $KMnO_4$ and nano-$KMnO_4$ toward *Musa acuminata* were investigated. The experiment was done in a small container at room temperature (28°C) with minimum sunlight exposure. The object of observation of this experiment are peel color changes and brown spots area measurement. This experiment lasted for 19 days, when all the bananas already developed brown spots.

Peel color changes are observed every 24 h. The observed color are then quantified based on peel color scale as described in preceding chapter. A graph showing observed peel color change is presented in Fig. 6.

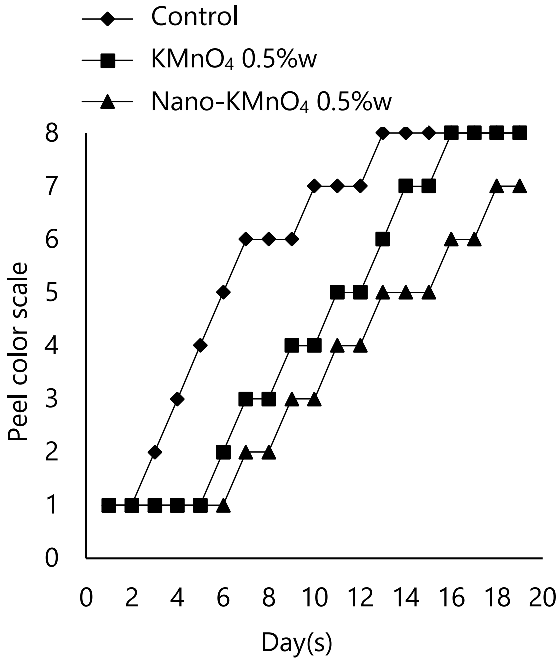


**Fig. 6.** Peel color changes value of different banana sample at various time

The banana without any preservative (Control) ripened (yellow peel color, scale

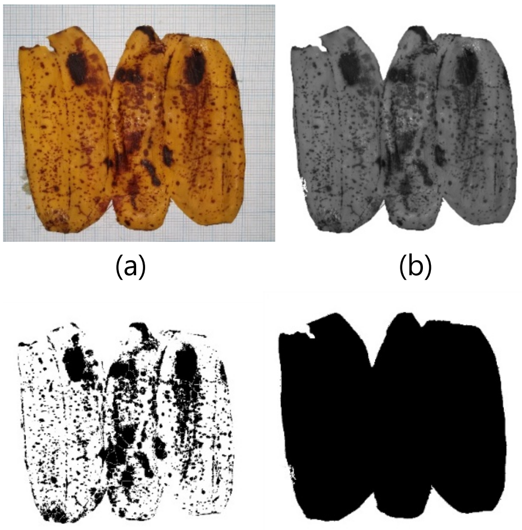
= 6) after 7 days. Meanwhile, the bananas with $KMnO_4$ 0.5%w and nano-$KMnO_4$ 0.5%w preservatives ripened after 13 and 16 days respectively. All of the banana sample showed brown spots after 18 days (scale = 7), indicating that the banana is almost over-ripened. These results indicate that ethylene oxidation rate by $KMnO_4$ solid is contributing to its performance as banana preservative, especially banana.

These results is still a bit lower than banana preservation experiment by using $KMnO_4$ confined in clay. The sample banana was 'Barangan' banana which originated from North Sumatera, Indonesia. 'Barangan' banana normally ripened after 10 days, but $KMnO_4$ confined in clay can preserve the sample up to 20 days (Napitupulu, 2016). The preservative was made by soaking 15 g of clay in 6% w/v $KMnO_4$ solution. This difference in preservation duration might be caused by either different banana species or different mass ratio of banana and preservative.

Peel color quantification by observation is considered to be subjective, because every person has their own color perception. A phenomenon which observer can agree whether banana is ripened or not is when brown spots appeared. As the banana become more ripened, more spots appeared, until all banana peel turns dark brown. This brown spot area can be measured by using image processing tools. This measurement was done after peel color quantification, by using the same banana as the sample. The banana peel was carefully peeled with a knife so it did not broke into smaller pieces. All of the banana peel was photographed on top of a scaled graph paper. This step is needed to scale up pixel unit into centimeter unit. The image processing tools used in this measurement is ImageJ, a public domain image processing program developed by National Institutes of Health and the Laboratory for Optical and Computational Instrumentation.

The first step in this measurement is setting up a scale on the photograph, to convert pixel unit into centimeter unit. The photograph is then changed into an 8-bit image, so that ImageJ measurement can be more accurate because of more distinct color between brown spots area and yellow peel area. To measure brown spots area, the threshold is adjusted. This adjustment is done automatically by ImageJ. After threshold adjustment, brown spots area measurement can be done to the image. To measure the total banana peel area, the threshold is adjusted manually to near its max value (Threshold = 253, maximum value is 255). After maximum threshold adjustment, total peel area measurement can be done to the image. The image result from each step is presented in Fig. 7 by using banana sample preserved by nano-$KMnO_4$ 0.5%w.

Brown spots area quantification is represented by the percentage of brown spots area by total peel area. After 19 days of storage, banana with no preservative shows the highest brown spots percentage of 53.75%. Bananas preserved with $KMnO_4$ 0.5%w and nano-$KMnO_4$ 0.5%w show lower brown spots percentage of 36.17% and 28.02% respectively. The results are presented in Fig. 8. These results are in accordance with peel color changes, where banana with no preservative started to over-rip (scale = 8) after 13 days, meanwhile banana preserved with $KMnO_4$ 0.5%w started to over-rip after 16 days.


(a) (b)

(c) (d)

**Fig. 7**. (a) Unprocessed image, (b) 8-bit image, (c) automatic threshold adjustment, (d) near-maximum threshold adjustment

## CONCLUSIONS

The oxidation of ethylene by $KMnO_4$ and nano-$KMnO_4$ was observed. Nano-$KMnO_4$ has slightly higher ethylene oxidation rate than $KMnO_4$. Nano confinement of $KMnO_4$ inside nanoporous carbon results in higher oxidation rate of ethylene. Result of SEM analysis on $KMnO_4$ particle before and after the reaction shows that the diameter of $KMnO_4$ particle is not so much changed, indicating an unchanging size shrinking core model. Nano-$KMnO_4$ also shows a better climacteric fruit preservation ability with banana (*Musa acuminata*) as the sample. The banana without any preservative ripened after 7 days, meanwhile the bananas with $KMnO_4$ and nano-$KMnO_4$ preservatives ripened after 13 and 16 days respectively. Brown spots measurement in banana's peel also proves this, in which after 19 days of storage banana with no preservative shows the highest brown spots percentage of 53.75%. Bananas preserved with $KMnO_4$ and nano-$KMnO_4$ show lower brown spots percentage of 36.17% and 28.02% respectively. It is also observed that nano-$KMnO_4$, having a higher ethylene oxidation rate, also have better fruit preservation ability. This observation might indicates that a preservative for climacteric fruit can be improved by using materials with higher ethylene degradation rate.

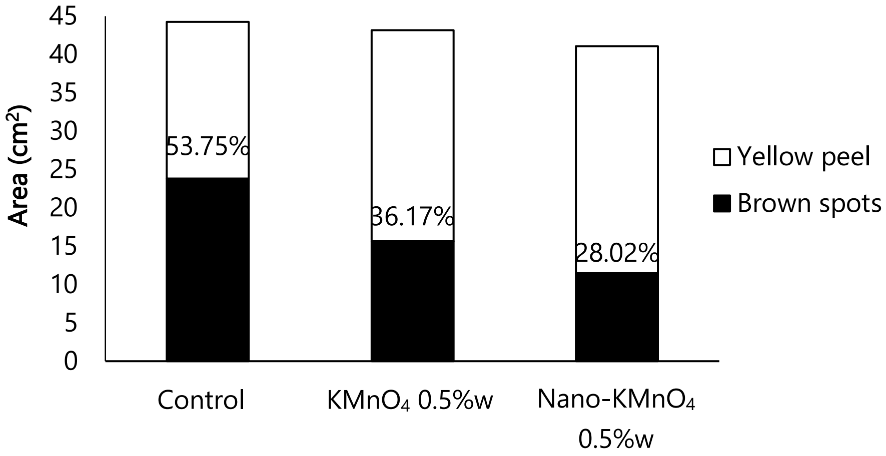


**Fig. 8**. Area of yellow peel and brown spots in each banana sample after 19 days. Value in percentage shows percentage of brown spots area by total area.

## ACKNOWLEDGEMENT

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## NOMENCLATURE

$k$ : overall rate constant [m $s^{-1}$]
$a$ : stoichiometry coefficient for ethylene
$r_0$ : initial $KMnO_4$ particle radius [m]
$r_c$ : $KMnO_4$ core radius [m]
$\rho_B$ : $KMnO_4$ bulk density [kg $m^{-3}$]
$D_{A\,eff}$ : effective diffusion constant [$m^2$ $s^{-1}$]
$C_{Ag}$ : ethylene bulk concentration [kg $m^{-3}$]
$R$ : carbon particle radius [m]
$M_T$ : Thiele modulus
$D_a$ : apparent diffusion constant [$m^2$ $s^{-1}$]
$t$ : time [s]
$X_A$ : ethylene conversion
$X_B$ : $KMnO_4$ conversion

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