Preparation of porous carbon as ethylene adsorbent by pyrolysis of extraction waste *Mangosteen* rinds

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Abstract. *Mangosteen* rind is an important source of natural antioxidants. Due to the growing interest in extracting this anti cancer substances from the *mangosteen* rind, the amount of this lignocellulosic residu has been generated significantly as byproduct. In this research, extraction-waste *mangosteen* rind (EMP) was used as alternative precursor for production of carbon-based adsorbent for ethylene removal. Steam was used as activating agent and the effect of carbonization time and temperature on the development of pore structure were examined. Pyrolysis process was carried out by heating the *mangosteen* rinds powder (180 μm - 355 μm) from ambient temperature up to carbonization temperature of 848 K and kept for 3 hours then followed by heating up to 1123 K and kept for 15 minutes under flowing N_2 and steam. This process was repeated for several pyrolysis temperature (1053 K, 1073 K, 1083 K and 1103 K) and carbonization time (0 hours, 1 hour, 2 hours, and 3,5 hours). The carbon obtained was characterized in terms of its pore structure and ethylene uptake capacity. The results show that porous carbon obtained from pyrolysis of extraction-waste *mangosteen* rind can be characterized as mesoporous carbon. The highest surface area of 1080 m^2/g was obtained from pyrolysis of extraction-waste *mangosteen* rinds with carbonization time of 3.5 hours and pyrolysis temperature of 1123 K. Furthermore, the mesopore portion and the specific surface area increased with the increasing carbonization time. From the ethylene uptake experiment, it was noted that the ethylene adsorption capacity of EMPC is 40.12 cm^3/g .

1 Introduction

Porous carbon with high surface area has been produced from a variety of carbonaceous materials. In practice, coal and lignocellulosic materials are often used as raw materials. The production of porous carbon from lignocellulosic material has been widely studied. There are the production of porous carbon from coconut shell, *mangosteen* rind, corn cob, bagasse, durian rind [2,3,8]. From the several previous studies, the *mangosteen* rinds has the potential as a raw material for the preparation of porous carbon with high surface area so that it can be used as an adsorbent with the large capacity [6,8].

Mangosteen fruit (*Garcinia mangostana* L.) is a fruit immensely produced in Indonesia. Every part of the fruits contains an antioxidants, especially on the rind. Antioxidant compounds in the form of xanthones in *mangosteen* rind can be obtained through extraction process. Extraction process will extract a compound to obtain xanthones and will leave a residue in the form of *mangosteen* rind which the antioxidant compounds has been extracted. Because of the increasing demand of *mangosteen* rind extraction recently, it will also increase the *mangosteen* rind residue leftover from the extraction process. Because of the potential of the *mangosteen* rind residual waste, the research will conduct the utilization of waste as a new potential that can be used as raw material

for producing porous carbon to obtain economic value. Porous carbon produced will be used as an ethylene adsorbent.

The pore structure of the porous carbon was highly depended on a raw materials and production methods. Activation process was a very important step in the preparation of porous carbon which aims to increase the porosity of the carbon produced. The increasing porosity of the carbon, the specific surface area of the carbon will increase. The activation methods were used among others by using physical activation through a partial gasification with CO_2 and steam and chemical activation using chemicals such as K_2CO_3 , KOH , ZnCl_2 . Increased porosity with partial gasification consists of only one stage in which the pyrolysis beginning with carbonization process and proceed with partial gasification carried out in a single step [7]. While pyrolysis with the addition of chemicals was carried out in two steps. The first steps was the addition of chemicals and the next step was pyrolyzed the materials from ambient temperature to the desired temperature [1].

One of the methods in prolonging postharvest life of fruits is carried out by controlling ethylene concentration in the stored environments. It is necessary therefore to develop lower cost and more effective ethylene adsorption materials. This study was aimed to explore the feasibility of preparing ethylene adsorbent by pyrolysis of

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extraction waste *mangosteen* rinds under different carbonization conditions. The carbon obtained was characterized in terms of its pore structure and ethylene uptake capacity.

2 Materials and methods

2.1 Material

Mangosteen rinds powder (180 μm – 355 μm) was obtained from Bina Agro Mandiri, Bantul, D.I. Yogyakarta. Nitrogen with a purity of 99.95% was used as an inert gas in the carbonization process, and to determine the N_2 adsorption-desorption at 77 K was used N_2 with ultra high purity (99.9995) as adsorbate. Ethylene with a purity of 99.9% was obtained from PT. Aneka Gas Industri as adsorbate.

2.2 Experimental

2.2.1 Raw materials characterization

Mangosteen rinds were characterized by lignocellulose content analysis using Chesson Method (Datta, 1981). Proximate analysis carried out by GB/T12496. Thermal Gravimetric Analysis (TGA) using Diamond TG/DTA Analyzer, PerkinElmer Instruments was carried out by heating a sample of ± 7 mg from 303 K up to 1123 K with a heating rate of 5 K/min under flowing nitrogen of 20 mL/min.

2.2.2 Preparation of porous carbon

Porous carbon for ethylene adsorbent in this study was prepared by pyrolysis of extraction waste *mangosteen* rinds (EMP). The carbon obtained from the former precursor is noted as EMP. Furthermore EMPCT1 (1053 K), EMPCT2 (1073 K), EMPCT3 (1083 K), EMPCT4 (1103 K) and EMPCT5 (1123 K) were adjusted for variations in the temperature of pyrolysis and EMPCH1 (0 hour), EMPCH2 (1 hour), EMPCH3 (2 hours), EMPCH4 (3 hours) and EMPCH5 (3.5 hours) were adjusted for carbonization time. Precursors were pyrolyzed in furnace under flowing N_2 from ambient temperature up to carbonization temperature of 848 K and kept for 3 hours, then followed by heating up to 1123 K and kept for 15 minutes under flowing N_2 and steam. This process was repeated for several pyrolysis temperature (1053 K, 1073 K, 1083 K and 1103 K) and carbonization time (0 hours, 1 hour, 2 hours, and 3.5 hours).

2.2.3 Porous carbon characterization

N_2 adsorption-desorption obtained using NOVA 2000 adsorption analyzer (Quantachrome) at 77 K. Specific surface area (S) calculated from isotherms data on the range of relative pressure (P/P_0) between 0.05 to 0.30. Total pore volume (V) estimated from the amount of adsorbate adsorbed at P/P_0 of 0.99 and a mesopore area (S_{mes}), mesopore volume (V_{mes}) determined using α

plot method. Pore size distribution studied using Horvath-Kawazoe method (HK) and Barret-Joyner-Haleda method (BJH).

2.2.4 Ethylene Adsorption

Ethylene Adsorption capacity test were carried out using the volumetric method at temperature of 303 K. The ultra high vacuum adsorption measurement apparatus rig was constructed by using Swagelok® VCR valve and fitting. The schematic diagram of adsorption system can be seen in Fig. 1. All carbon samples were first degassed at 423 K for 6 hours until the static pressure in the system was at least 1×10^{-2} Torr. The data obtained is presented as an adsorption isotherm curve. Ethylene adsorption analysis was began with ensuring all the valve in the closed state (V1, V2 and V3). To fill the loading cell, valve V1 was opened slowly to achieve the desired pressure and recorded as P1, then closed again. Furthermore, to make the process of adsorption, valve no. V2 was opened and observed a pressure decrease in the pressure gauge until the pressure in equilibrium obtained and recorded as P2. Adsorption equilibrium was indicated by stable pressure in the adsorption system. To proceed to the next equilibrium point, valve V2 was closed again and the steps were repeated until the maximum pressure that was able to operate (± 1.2 atm).

Fig. 1. Schematic Diagram of The Adsorption System by Static Volumetric

3 Results and Discussion

3.1 Raw materials characterization

3.1.1 Proximate Analysis and Lignocellulose properties

The results of lignocellulose analysis and proximate analysis are shown in Table 1. From the results show the composition of lignocellulosic of extraction waste *mangosteen* rind is mostly lignin of 48.52% and the proximate analysis shows that the maximum amount of carbon that can be obtained from *mangosteen* rind is 32.29%.

Table 1. Proximate Analysis and Lignocellulose Analysis

Proximate Analysis	
Component	Composition, %
Water	3.58
Ash	1.85
Volatile matter	62.28
Fixed carbon	32.29
Lignocellulose Analysis	
Component	Composition, %
Cellulose	26.22
Hemicellulose	15.39
Lignin	48.52

3.1.2 Thermal Gravimetric Analysis (TGA)

TGA was carried out by heating a sample from 303 K up to 1123 K with a heating rate of 5 K/min under flowing nitrogen. The results of TGA are shown in Fig. 2. TGA analysis result shows the carbonization process of *mangosteen* rind was divided into several steps. The first step at temperatures <150°C, the weight loss due to evaporation of free and bound water. The second step at temperature of 200–375°C, the weight loss due to the decomposition of cellulose and hemicellulose into condensable gases (methanol, tar and acetic acid) and uncondensable gases (CO₂, CH₄, etc). Furthermore, at a temperature of 375–575°C, the weight loss due to the decomposition of lignin. At temperatures > 575°C, the weight loss was not significantly. The temperature of 575°C (848 K) is taken as temperature carbonization.

Fig. 2. TGA Curves of *Mangosteen* Rinds

3.2 Porous carbon characterization

3.2.1 Effect of pyrolysis temperature

Fig. 3(a) shows burn off number from porous carbon at various pyrolysis temperatures. Burn off can be used for quality criteria of carbon. If thermal degradation generates porous on material, when the burn off is high, it will increase the number of porous and internal surface area. Fig. 3(a) shows burn off number increasing by increase pyrolysis temperature.

(a)

(b)

Fig 3. Burn off (a) EMPC at various T and t = 3 hours; (b) EMPC at various t and T= 1123 K

Fig. 3(b) shows number of burn off increasing when time of carbonization increased. Table 2 shows the pore structure of the carbon EMPC at various pyrolysis temperature. The Table 2 shows that the highest surface area is 1066.77 m²/g obtained from carbon obtained by pyrolysis of extraction waste *mangosteen* rinds up to 1123 K and carbonization time for 3 hours. Table 2 also shows that the specific surface area increased with the increasing pyrolysis temperature. Because of the formation of pore structure by N₂ gas or superheated H₂O will be growing at high temperature. Table 2 also provides information that the resulting pore volume also increased with higher pyrolysis temperature. The similar thing is seen for mesoporous volume. Wherein the resulting mesoporous volume increases with the increasing pyrolysis temperature.

Pore size distribution for carbon EMPC at various temperatures are shown in Fig. 4 (a). In Fig. 4(a) can be seen that for all carbon EMPCT1 until EMPCT5 have tendency of similar pore size distribution with the peak between 2-100 nm and have not any significant change. However, it can be seen that the pore size distribution is widened with increasing pyrolysis temperature. This is caused by the higher the pyrolysis temperature made micropore size widening thus increasing the amount of mesopore size. Therefore, it can be concluded that the portion of mesopore size also increase with the increasing temperature.

Table 2. Characterization of EMPC at Various T and t = 3 h

Sample	S, m ² /g	S _{mes} , m ² /g	% S _{mes}	V, cm ³ /g	V _{mes} , cm ³ /g	% V _{mes}	D _{avg} , nm
EMPCT1	657.61	565.96	86.06	1.115	0.835	74.89	6.78
EMPCT2	839.31	527.32	62.83	1.051	0.749	71.27	6.62
EMPCT3	979.55	543.35	55.47	1.172	0.969	82.68	4.78
EMPCT4	1032.71	562.97	54.51	1.197	0.978	81.70	4.64
EMPCT5	1066.77	603.61	56.58	1.276	1.069	83.78	4.79

Table 3. Characterization of EMPC at Various t and T=1123K

Sample	S, m ² /g	S _{mes} , m ² /g	% S _{mes}	V, cm ³ /g	V _{mes} , cm ³ /g	% V _{mes}	D _{avg} , nm
EMPCH1	697.89	527.32	75.56	1.051	0.749	71.27	6.03
EMPCH2	951.12	556.70	58.53	1.201	1.030	85.76	5.05
EMPCH3	1018.57	662.88	65.08	1.230	1.069	86.91	5.32
EMPCH4	1066.77	603.61	56.58	1.276	1.069	83.78	4.79
EMPCH5	1079.94	762.06	70.57	1.528	1.389	90.90	5.66

3.2.2 Effect of carbonization time

Carbonization process of natural materials is affected by the decomposition process of the constituent material composition such as cellulose, hemicellulose and lignin. Therefore, if the cellulose, hemicellulose and lignin of the material decomposed perfectly, the quality of the carbon produced will be better characterized by the increasing on specific area of the carbon. To enhance the decomposition process of cellulose, hemicellulose and lignin from EMPC, the process on hold at the final temperature decomposition of lignin (848 K). Carbonization time variation was performed to determine the effect of the produced carbon character.

Fig 4. Pore Size Distribution BJH Method (a) EMPC at Various T and t = 3 Hours; (b) EMPC at Various t and T=1123 K

Table 3 shows the pore structure of the carbon EMPC at various carbonization time. The Table 3 provide information that the largest surface area is 1079.94 m²/gram produced from carbon derived from extraction waste *mangosteen* rinds with carbonization time for 3.5 hours and a final pyrolysis temperature of 1123 K. From these data, it is known that the specific surface area of the carbon produced will increase with the longer time of carbonization. It is due to the cellulose, hemicellulose and lignin from extraction waste *mangosteen* rinds will decompose perfectly so that the porosity of the carbon produced will also increase. Table 3 also informs that the longer carbonization time, the pore volume generated will also increase. Similarly, for mesoporous volume, the mesoporous volume will increase with the longer carbonization time. From these results, it can be stated that the structure of mesoporous carbon increase with the longer carbonization time.

Fig 5. SEM Analysis for EMPC

Pore size distribution of carbon EMPC at various time can be seen in Fig. 4 (b). Fig. 4 (b) shows that all carbon EMPCH1 until EMPCH5 have the same pore size distribution with peaks between 2-100 nm. Pore size distribution was also widened with increasing carbonization time. This is caused by the higher the pyrolysis temperature made the micropore size widening thus it is increasing the amount of mesopore size. It can be concluded that the portion of mesopore size increase with the longer of carbonization time.

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The morphology of carbon analyzed by Scanning Electron Microscope Analysis (SEM). Fig. 5 shows the result of SEM analysis for EMPC.

3.3 Ethylene Adsorption

Calculation of the ethylene adsorption capacity carried out by volumetric methods. The results of adsorption experiments evaluated using adsorption isotherm models. Some adsorption isotherm models used are (Do, 1998):

$$\text{Langmuir equation: } C_{\mu} = C_{\mu s} \left(\frac{bP}{1+bP} \right) \quad (1)$$

$$\text{Freundlich equation: } C_{\mu} = KP^{1/n} \quad (2)$$

$$\text{Unilan equation: } C_{\mu} = \frac{C_{\mu s}}{2s} \ln \left(\frac{1+be^s P}{1+be^{-s} P} \right) \quad (3)$$

$$\text{Sips equation: } C_{\mu} = C_{\mu s} \frac{(bP)^{1/n}}{1+(bP)^{1/n}} \quad (4)$$

$$\text{Toth equation: } C_{\mu} = C_{\mu s} \frac{bP}{[1+(bP)^t]^{1/t}} \quad (5)$$

Table 4. Parameter Value of Ethylene Adsorption Isotherm on EMPC at T = 303 K

Adsorption isotherm parameter	Carbon Type EMPC
Langmuir	
$C_{\mu s}$	3.1808
b	1.1998
Freundlich	
K	1.6196
n	1.8361
Toth	
$C_{\mu s}$	14.4335
b	0.5834
t	0.3805
Sips	
$C_{\mu s}$	8.7359
b	0.1479
n	1.3929
Unilan	
$C_{\mu s}$	3.1809
b	1.1998
s	0.0143

The calculation result of the parameter values on various equilibrium equation can be seen in Table 4. The result of adsorption ethylene capacity for KSME carbon can be find on Fig 6. Fig 6 shows the ethylene adsorption capacity of EMPC is 1,792 mmol/g or 40.12 cm³/g.

4 Conclusions

The feasibility of preparing carbon-based adsorbent for ethylene removal from extraction waste *mangosteen* rind were examined. In this study, porous carbon obtained from pyrolysis of extraction-waste *mangosteen* rind (EMPC) can be characterized as mesoporous carbon.

Carbon-based ethylene adsorbent with highest surface area of 1080 m²/g was obtained from pyrolysis of extraction waste *mangosteen* rinds with carbonization time of 3.5 hours and pyrolysis temperature of 1123 K. Mesopore portion and the specific surface area increased with the increasing pyrolysis temperature. In addition, the mesopore portion and the specific surface area increased with the increasing carbonization time. The ethylene adsorption capacity of EMPC is 40.12 cm³/g.

Fig 6. Ethylene Adsorption Isotherm on EMPC at T=303 K

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