Carbon monoxide and methane adsorption of crude oil refinery using activated carbon from palm shells as biosorbent

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Abstract. Carbon monoxide and methane gas are widely present in oil refineries**.** Off-potential gas is used as raw material for the petrochemical industry. In order for this off-gas to be utilized, carbon monoxide and methane must be removed from off-gas. This study aims to adsorb carbon monoxide and methane using activated carbon of palm shells and commercial activated carbon simultaneously. This research was conducted in 2 stages: 1) Preparation and characterization of activated carbon, 2) Carbon monoxide and methane adsorption test. The activation experiments using carbon dioxide at a flow rate of 150 ml/min yielded a surface area of 978.29 m^2/g, Nitrogen at flow rate 150 ml/min yielded surface area 1241.48 m^2/g, and carbon dioxide and nitrogen at a flow rate 200 ml/min yielded a surface area 300.37 m^2/g. Adsorption of carbon monoxide and methane on activated carbon of palm shell systems yielded results in the amount of 0.5485 mg/g and 0.0649 mg/g and using commercial activated carbon yielded results in the amount of 0.5480 mg/g and 0.0650 mg/g

Keywords: Activated carbon, Adsorption, Carbon monoxide, Off gas, Methane, Palm shells

1. Introduction

Off-gas in refinery oil, specifically in the cracking unit which produces the products which include LPG, light naphtha, heavy naphtha, light and heavy kerosene, Automotive Diesel Oil (ADO), unconverted oil, and off-gas. Off-gas has not been widely used on the world. This is not economical because off-gas still contains many hydrocarbons such as ethane (C_2), propane (C_3) and butane (C_4), in which these hydrocarbons still has economic value because it can still be used as raw material in petrochemical industry. So far, carbon monoxide in refinery oil is generally reacted with steam to covert it into carbon dioxide and hydrogen. This process requires a higher cost, in terms of unit operating costs and steam production than adsorbing carbon monoxide, while methane is discharged directly through the flare. The adsorption process is an alternative to removing carbon monoxide and methane. Currently there have been several studies on adsorption by using activated carbon as biosorbent, such as adsorption of SO_2, NO and chlorobenzene [1], adsorption of CO_2 and CH_4 [2] and CO adsorption [3].

Activated carbon is a potent biosorbent used to adsorb carbon monoxide and methane gas present in off-gas [4]. Based on the structure pattern of the activated carbon, it is a material in the form of amorphous carbon consisting mostly of free carbon and has an inner surface that has a higher adsorption capacity than other adsorbents [5]. Organic and inorganic materials containing lignin, hemicellulose and cellulose can be utilized as feedstocks for activated carbon, as they are highly effective for adsorption [1].
One of the most potential materials and is being developed as a feedstock for the manufacture of activated carbon is the shell of palm [6]. When compared to the coconut shell, the palm shell has more mesoporous pore and the micropore is much larger [7]. The amount of palm shell that is being produced as one of the palm oil processing industry waste are quite large, reaching 12% of the weight of oil palm fruit. Indonesia is the largest palm oil producing country in the world. The average annual production of palm fruit is 5.6 million tons, so there are about 672 thousand tons of shells produced. This amount will continue to increase along with the increase of palm oil production. With the

availability of such waste, a further process is needed to convert the waste of oil palm shells into a product of high economic value.

The quality of activated carbon of palm shells used as biosorbent in adsorption of carbon monoxide and methane is strongly influenced by the conditions of manufacture. Among other parameters that affect the process of making activated carbon such as activation solution, activation gas flow rate, activation temperature, and duration of the activation process. While the effectiveness of the adsorption process is strongly influenced by several parameters, including the mass of activated carbon, contact time, and surface area.

This research will be conducted by making activated carbon from palm shells and comparative performance test of commercial activated carbon activated carbon and activated carbon from palm kernel shells that have been activated with KOH as an activating agent or that have been activated through physical activation at 850ºC temperature, where this temperature is the optimum temperature of activation [8]. This activation temperature is expected to produce activated carbon with a high surface area[9]. Commercial activated carbon and activated carbon from activated palm shells are then used to adsorb carbon monoxide and methane gas with batch and continuous systems. Tests of the adsorption parameters were carried out in the adsorption process so that the optimal conditions in adsorbing carbon monoxide and methane can be known.

2. Methodology/Experimental
2.1 Chemical and Physical Activation
The 177-micron palm shell is activated by mixing it with KOH solution. Impregnation is done on the palm shell with KOH (b/b). The mixture is stirred until it becomes a homogeneous structure. The stirring process is done in order to impregnate the activating agent on the raw material of palm shell. This mixing result will form a mixture of a slurry. After that, the mixture is heated in the oven for 1 hour at 110ºC to remove the water content. Then the mixture of raw materials and activating agent in the form of a slurry is then put into the reactor. Nitrogen gas must be injected into the reactor before the reactor is used to ensure that there is no oxygen in it. The reactor operates at 850°C for 1 hour. Nitrogen, carbon dioxide, and carbon dioxide followed by nitrogen are emitted with flow rates of 100, 150 and 200 ml/min. After all the procedures are performed, the activated carbon is activated through chemical and physical means. This active carbon must go through the next treatment stage to get a truly pure result. Activated carbons are then washed with HCl 5 N to attain a neutral pH. Activated carbon is then washed with distilled water to remove the chloride. Characterization includes reactivated carbon-iodine and SEM-EDS test results. To change the amount of iodine in the surface area, a linear regression equation is used which refers to ASTM [6] D-4607-94. The equation is as follows:

$$\text{Iodine Number} = 0{,}6366 \times \text{surface area} + 174{,}34$$

2.2 Adsorption Test on Activated Carbon
The isothermal adsorption test on the batch system is performed by preparing 1 to 2.5 g of active carbon which is inserted rapidly into 10 mL glass bottles. The glass bottle is equipped with a silk-sealed septum and there is residual air that must be quickly removed as much as the amount of off-gas injected. This is done by using a syringe (1 mL), with variations in the concentration of CO: CH_4, the gases are imbued with BOC gas. The bottle is shaken at the equilibrium concentration at the batch reactor during the 15th, 30th, 45th, and 60th min. Subsequently, the samples (the unadsorbed concentration of CO and CH4) were taken and analyzed using Shimadzu-8A GC-TCD. Isothermal adsorption for CO and CH4 with activated carbon was determined using the equilibrium adsorption model of Langmuir model [10].

3. Result and discussion
3.1 Chemical Activation with KOH Activating Agent and Physical Activation

Chemical activation is the process of disconnecting carbon chains on active carbon feedstock by using KOH. The use of KOH as an activator because KOH is able to oxidize volatile compounds so as to increase the number of pores and surface area. Physical activation is the process of disconnecting the carbon chain on the raw material of activated carbon at high temperature by flowing steam, N_2 and CO_2. In this research, the physical activation process is done using N_2 and CO_2 with a variation of the flow rate of these gases and a combination between N_2 and CO_2 at flow rate 100, 150 and 200 ml/minute. Activators have a high temperature where the activator can react with carbon so as to develop pores and surface area[11]. Then we can determine the effect of activator gas and activator flow rate to the surface area of activated carbon as shown below:
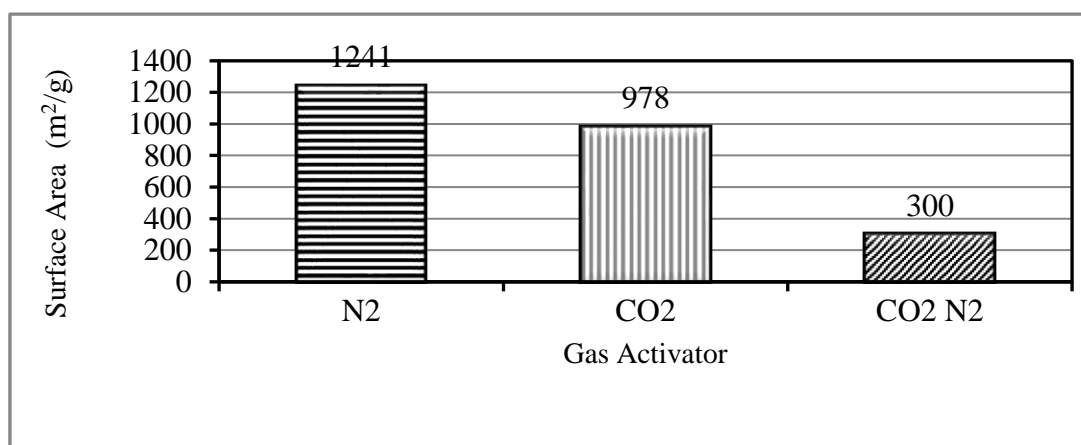

Figure 1 Effect of Gas And Flow Rate Activator Against The Area of Activated Carbon Surface

A high surface area is generated because the activation process removes volatile things and isolates the material from the air.

3.2 Test of iodine
Activated carbon with high iodine adsorption capability also has a larger surface area and has a larger micro and mesoporous structure.Figure 2 shows the differential ratio of the activation treatment to the iodine adsorption on the activated carbon.
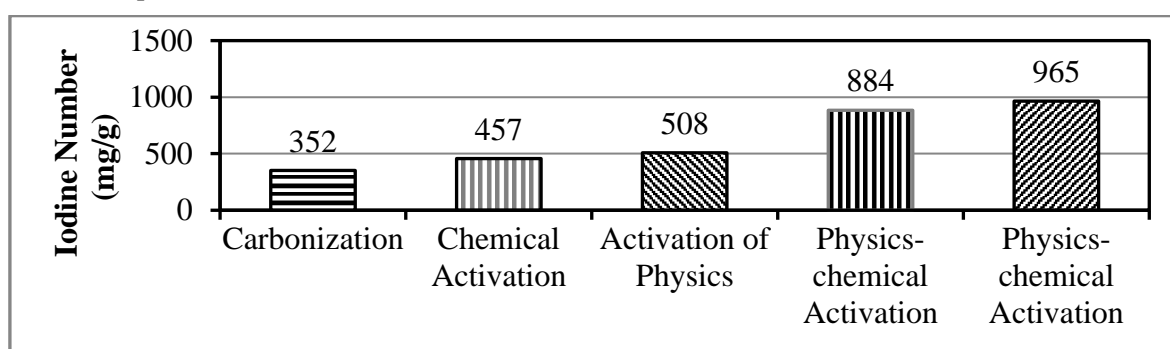

Figure 2 Effect of Activation Treatment on Iod Adsorption

From Figure 2, it can be seen that the activation treatment determines the adsorption capacity of iodine, in which activated carbon without activation has the smallest specific surface area. The principle of carbonization and activation is to form pores. A small number of pores causes the activated carbon to be unable to absorb iodine solution effectively; the amount of iodine absorbed in the carbonization process is 352 mg/g and in the physical-chemical activation process it was 884 mg/g [12]. The process of physical activation adsorbs 508 mg/g and the chemical activation process adsorbs

457 mg/g [13]. Whereas in this experiment iodine adsorption capacity with physical and chemical activation process is 964.67 mg/g.

Then as the optimum treatment, variations of the flow rate of the physical activator is done on the chemical-physical activation. Figure 3 shows the effect of physic activator on iodine adsorption.
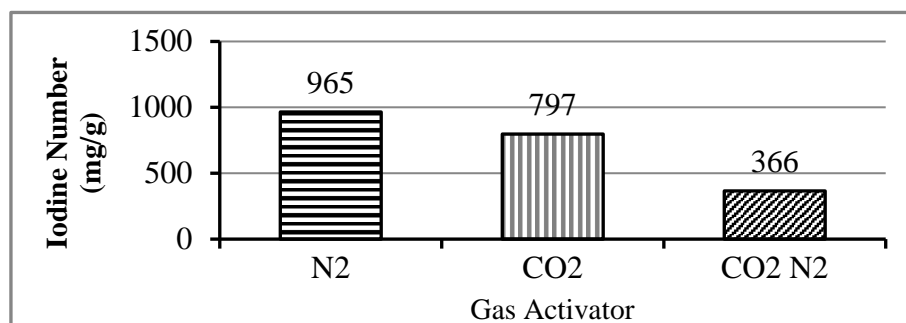

Figure 3 Effect of Gas Activator On Iodine Numbers

Figure 3 shows the effect of CO_2, N_2, and $CO_2 + N_2$ activators, where N_2 activator is able to increase iodine absorption capacity to 965 mg/g. Another study also mentioned that activation using KOH for chemical activation and $CO_2 + N_2$ for physical activation resulted in a surface area of 596 m^2/g, which also has a low iodine absorption due to the long period of physical activation process [8]. The difference of the activator gas and the activator flow rate on the activated carbon sample significantly affected the adsorption capacity of the activated carbons. The high adsorption of activated iods of carbon indicates the surface that has been formed by the activation process is also increasing - higher iodine adsorption indicates higher surface area. Additionally, it was also determined that increased activation time causes decreased iodine adsorption [14]. Increased activation time causes a decrease in microporous volume, thereby decreasing the iodine absorption capacity. In another study, the increase in iodine adsorption capacity also reflects an increase in the porosity of activated carbon by increasing the impregnation ratio. This may be due to the minimization of tars and other liquids, which can clog pores and inhibit the development of pore structures [8].

3.3. SEM (Scanning Electron Microscopy) Characterization
SEM characterization in the study was conducted to determine the pore conditions formed on commercial activated carbon and activated carbon from palm shells. Figure 4 shows the SEM characterization results.

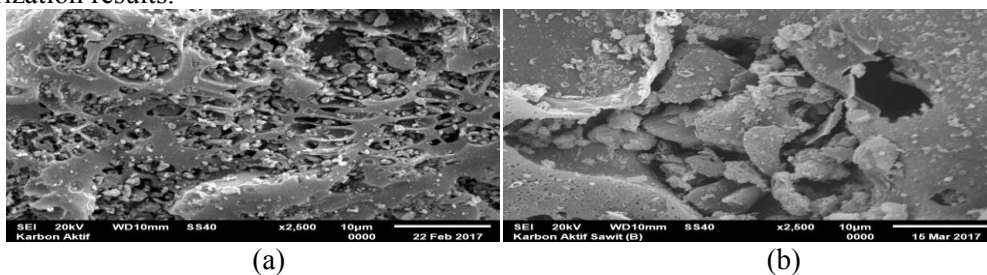(a)   (b)

Figure 4 SEM characterization results

Based on Figure 4 it can be seen that the pores have formed. This is due to the influence of KOH activators in activating activated carbon and also influenced the physical activation using nitrogen.During the activation process, KOH activates carbon based on dehydration function and eliminates hydrogen and oxygen atoms from carbon material in the form of water rather than as an oxygen organic component, thereby inducing porosity generation and increasing carbon content.

3.4. EDS (Energy-Dispersive X-Ray Spectroscophy)Characterization

EDS characterization aims to determine the composition of the commercial activated carbon and activated carbon created in the study.The composition under consideration is the composition of the weight of the commercial activated carbon content and the activated carbon of the oil palm shell. Table 1 shows the results of EDS characterization.

Table 1 EDS Characterization of Commercial and Palm Shells Activated Carbon

Activated Carbon	Mass Percent			
	C	O	Cu	Zn
Commercial	80.06	6.75	8.04	8.63
Palm Shells	60.44	13.73	8.040	8.63

According to the EDS characterization, the dominant element contained in activated carbon is a carbon element. Increasing the carbon element indicates that the activation of activated carbon is running well. Meanwhile, the difference in carbon content of both activated carbon is due to the production process of each activated carbon is different; on the activated carbon of the palm shell the influence of high temperature on the physical activation causes the release of other elements such as oxygen and impurities attached to the surface of activated carbon. Figure 5 shows the EDS characterization results.

Fig. 5 shows the EDS characterization results of the diffraction patterns of the content of O, Cu, and Zn on the surface of the activated carbon by 4.84%, 8.54%, and 4.57%, respectively. Figure 4.11 shows the EDS characterization of the diffraction patterns of the content of O, Cu and Zn on the surface of activated carbon, each with a mass percentage 13.73%, 8.040%, and 8.63% with KOH chemical activation and heating or physical activation at $850^{O}C$. This ensures the presence of ion-in on the surface of the activated carbon adsorbent. This can be attributed to the effect of the activation and screening washing step of the adsorbent used which may cause losses that may affect the adsorbent composition [15].
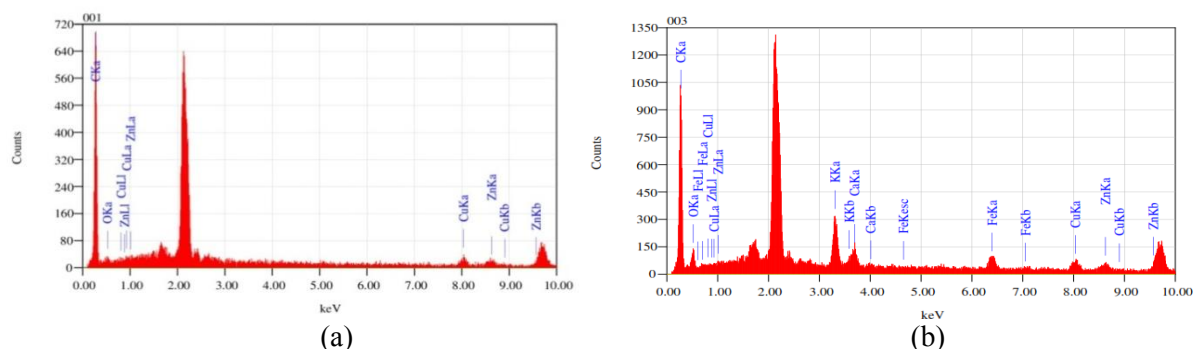

(a)   (b)

Figure 5 EDS Characterization of commercial (a) and palm shell (b) activated carbon

3.5. Adsorption of CO and CH₄ On Commercial Active Carbon

Adsorption is carried out to determine the adsorption capacity of activated carbon in carbon monoxide and methane.Various amounts of carbon monoxide and methane are injected into glass bottles.The concentrations used in CO and CH_4 in this experiment were 75% and 25%, respectively.The effect of mass of activated carbon on CO adsorption simultaneously on commercial activated carbon is shown in Figure 6.
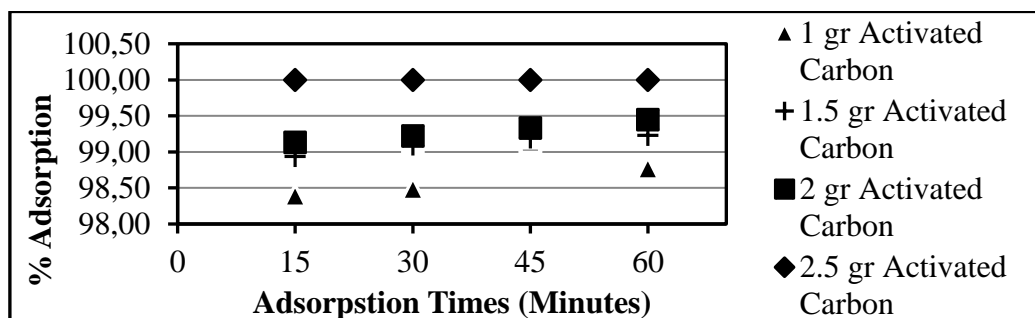
Figure 6 Adsorption Result of Carbon Monoxide

Based on the graph shown in Fig. 8 it is seen that the increase of carbon monoxide adsorbed on each of the activated carbon always increases as the adsorption time increases where 1 gram of activated carbon is able to adsorb at 98.39% in the 15-minute mark then increase until 98.77% in the 60-minute mark. Then, 1.5 gram of active carbon is able to adsorb 98.94% in the 15-minute mark then increase until 99.23% in the 60-minute mark. Lastly, 2 grams of activated carbon has the adsorption ability of 99.13% in the 15-minute mark then increase until 99.45% in the 60-minute mark and 2.5 grams of activated carbon is capable of adsorbing CO completely at 15 minutes to 60 minutes.

In other studies, the greater the contact area or the surface between the adsorbent, the gas the absorption rate will increase [4], so it can be said that 2.5 grams of active carbon has a better adsorption capacity. And, the effect of mass of activated carbon on CH_4 adsorption simultaneously on commercial activated carbon is shown in Figure 7.
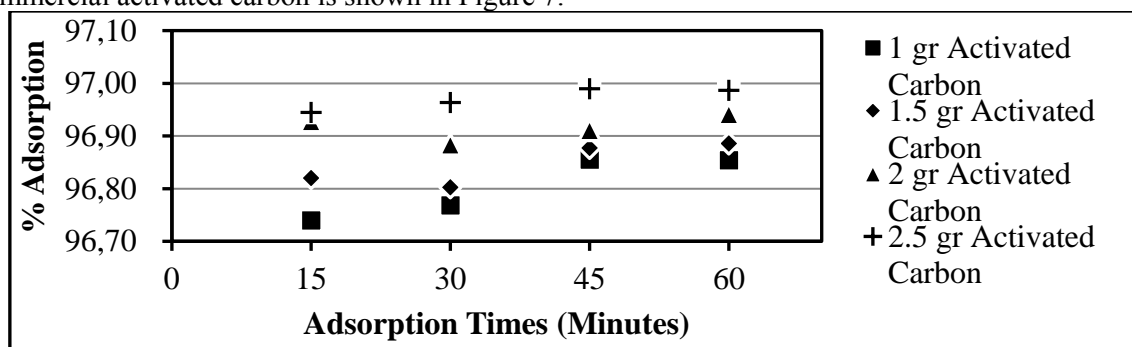

Figure 7 Adsorption Results of Methane

In Fig. 7 it is seen that the increase in the amount of CH_4 absorbed in each of the activated carbon always increases with the increase of adsorption time where on 1 gram activated carbon is able to adsorb 96.74% of methane in the 15-minute mark then increase until 96.85% in the 60-minute mark. Then, 1.5-gram active carbon able to adsorb 96.82% in the 15-minute mark then increases until 96.89% in the 60-minute mark. 2 grams of activated carbon is able to adsorb 96.93% in the 15-minute mark then increase until 96.94% in the 60-minute mark. Lastly, activated carbon in the amount of 2.5 grams has the ability to adsorb 96.94% in the 15-minute mark then increase until 96.99% in the 60-minute mark.

The surface of activated carbon has an important function in the adsorption process because it is an organic electrolyte, so it is important to consider the content of the surface of the activated carbon because it determines the adsorption capacity of the activated carbon by ion exchange. In a polar molecule having a strong dipole moment, adsorption can occur in the presence of an oxygen group on the surface. CO and CH_4 are adsorbed in the activated carbon as follows:
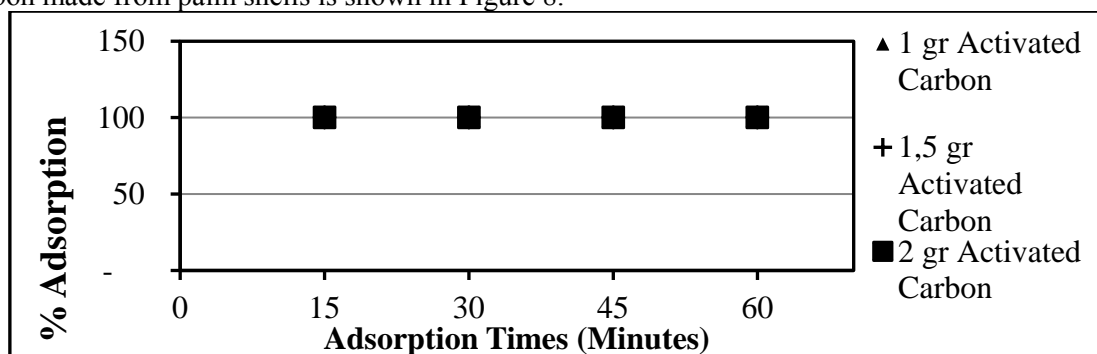
Table 2 Isothermal Equilibrium in CO and CH$_4$

Carbon Monoxide			Methane		
Co	Ce	Qe (mg/g)	Co	Ce	Qe (mg/g)
731	12	0.5476	260	0.91	0.0623
731	11	0.5477	260	0.83	0.0623
731	6	0.5480	260	0.60	0.0624
731	9	0.5478	260	0.60	0.0624

Table 2 shows the amount of how much CO and CH$_4$is absorbed in the activated carbon in which the adsorption process of the amount of CO and CH$_4$ keeps escalating over time [18], and indicates that the CO gas at the 15-minute mark is absorb as much as 0.5476 mg/g and increased to 0.5478 mg/g. Likewise, in CH$_4$ gas where increasing amount of CH$_4$ gas absorbed in activated carbon also occurs, that is 0.0623 mg/g to 0.0624 mg/g.

3.6. Isothermal Adsorption of CO and CH$_4$ On Activated Carbon from Palm Shells
Isothermal adsorption is carried out to determine the adsorption capacity of activated carbon in the gas CO and CH$_4$.The concentrations used in CO and CH$_4$ in this experiment were 75% and 25%, respectively. The effect of mass of activated carbon on CO adsorption simultaneously on activated carbon made from palm shells is shown in Figure 8.

Figure 8. Adsorption Result of Carbon Monoxide

Based on the graph shown in Fig. 8 it is seen that carbon monoxide adsorbed by activated carbon occurs maximally in the active carbon mass of 1, 1.5, 2, and 2.5 gram with 100% adsorbed gas.From this phenomenon, it shows that the activated carbon produced by itself is able to adsorb the CO that is injected into the tube.This is due to the increasing number of adsorbent molecules capable of adsorbing adsorbates in units of time and the same volume of space.In other studies, the greater the contact area or the surface between the adsorbent and CO, the absorption rate will increase [4]. And then, the effect of mass of activated carbon on CH$_4$ adsorption simultaneously on conventional activated carbon is shown in Figure 9.
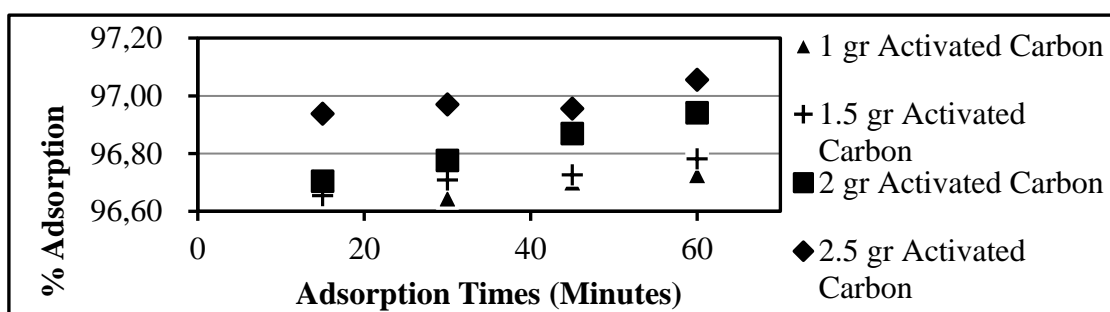

Figure 9. Methane Adsorption Results

Figure 9 shows that the increase of CH$_4$ adsorbed in each of the activated carbon always increases as the adsorption time increases where 1 gram of activated carbon is able to adsorb 96.67% in the 15-minute mark then increase 96.73%in the 60-minute mark.Then 1.5 gram of active carbon is able to adsorb 96.65% in the 15-minute mark then increase until 96.78%in the 60-minute mark. 2 grams of activated carbon is able to adsorb 96.70% in the 15-minute mark then increase until 96.94%in the 60-minute mark. Lastly, activated carbon of 2.5 grams has the ability to adsorb 96.94% in the 15-minute mark then increased until 97.05%in the 60-minute mark.

The surface of activated carbon has an important function in the adsorption process because it is an organic electrolyte, and determines the adsorption capacity of the activated carbon by ion exchange. The adsorption study on the activated carbon from the oil palm shell is done to obtain isothermal equilibrium.

Table 3 The isothermal equilibrium of the gas on the activated carbon of the palm shell

Carbon Monoxide			Methane		
Co	**Ce**	**Qe (mg/g)**	**Co**	**Ce**	**Qe (mg/g)**
731	-	0.5485	260	1	0.0648
731	-	0.5485	260	1	0.0648
731	-	0.5485	260	1	0.0648
731	-	0.5485	260	0.94	0.0649

Table 3 shows the amount of how much CO and CH$_4$ is absorbed in the activated carbon in which the adsorption process of the amount of CO and CH$_4$ keeps escalating over time [16], and shows that at 15 to 60 minutes, the amount of CO absorbed is 0.5485 mg/g.In CH$_4$ gas where increasing amount of CH$_4$ gas absorbed in activated carbon has increased, which is 0.0648 mg/g to 0.0649 mg/g.

3.7. Comparison of Adsorption Capability of Carbon Monoxide and Methane on Activated Carbon from Palm Shells with Commercial Active Carbon
Adsorption is carried out to determine the adsorption capacity of activated carbon in carbon monoxide compared to its adsorption capacity as shown in Figure 10 below.
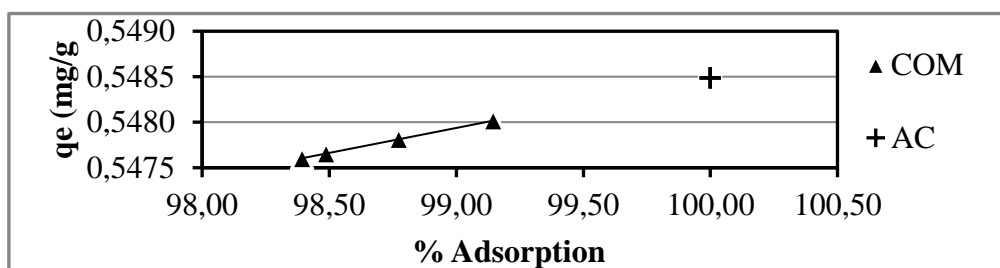

Figure 10 Representation of Langmuir Isotherm Carbon Monoxide Adsorption Model

Figure 10 shows the commercial activated carbon's maximum ability to absorb carbon monoxide. At minute 15 the amount of carbon monoxide absorbed is 0.5480 mg/g while the activated carbon from the palm oil shell which in its own production is able to absorb more carbon monoxide gas that is 0.5485 mg/g.This is due to the physical and chemical activation process carried out on the activated carbon of the palm shell that can increase the surface area and the pore area of the activated carbon obtained. Figure 11 shows the methane adsorption capacity ratio.
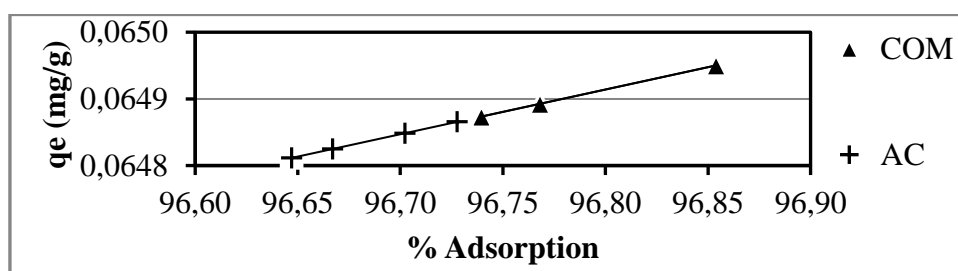
Figure 11 Representation of Langmuir Isotherm Methane Adsorption Model

Figure 11 shows the commercial activated carbon's maximum ability to absorb methane is 0.0649 mg/g while the activated carbon from the palm oil shell in production alone is able to absorb 0.0650 mg/g of methane.This is due to the difference in adsorption rates on carbon monoxide so that the activated carbon of palm shell carbon monoxide is faster adsorbed to cover the surface and pore of activated carbon so that the available surface area to accommodate less methane.While the commercial activated carbon absorbs less carbon monoxide then the methane is absorbed in the activated carbon will be more.

4. Conclusions
The activated carbons of the best palm shells produced with Nitrogen activators with a flow rate of 150 ml/min resulted in a surface area of 1241.48 m^2/g. While on carbon dioxide activators with a flow rate of 150 ml/min produced a surface area of 978.29 m^2/g and carbon dioxide activator mixed with nitrogen with a flow rate of 200 ml/min yielded a surface area of 300.37 m^2/g. From these results, it can be concluded that nitrogen with a flow rate of 150 ml/min produces a better surface area. Adsorption of activated carbon monoxide activated carbon from palm shell adsorbing carbon monoxide as much as 0.5485 mg/g and commercial activated carbon is 0.5480 mg/g. In methane gas commercial activated carbon is able to adsorb methane as much as 0.0625 mg/g, while activated carbon from palm shell adsorb 0.0649 mg/g.

5. Acknowledgement

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