INCREASING ADSORPTION OF ACTIVATED CARBON FROM PALM OIL SHELL FOR ADSORB H$_2$S FROM BIOGAS PRODUCTION BY IMPREGNATION

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ABSTRACT

Biogas is the combustible gas produced through a biological process, known as anaerobic digestion which is the process operated at low-temperature and without air. Biogas consists of 55-80% CH$_4$, 20-45% CO$_2$ with trace amount of H$_2$S and other impurities. Common H$_2$S removal technologies from biogas fall into one of adsorption on a solid such as iron oxide based materials, activated carbon or impregnated activated carbon. Conventionally, activated carbon is produced from biomass residues and agricultural residues such as palm oil shell which promising approach for the production of cheap. It is so due to the palm oil shell carries a large amount of carbon content which it is the main composition of activated carbon. Therefore, it is usable as raw material for producing impregnated activated carbon and used as adsorbents. The aim of this study is a produce the activated carbon from palm oil shells by chemical activation using ZnCl$_2$ and optimal conditions after impregnated them with NaOH, KI and K$_2$CO$_3$ for H$_2$S absorption from biogas product. In this research, production of activated carbon involved three stages; (i) carbonization of raw material in an inert atmosphere which was carbonized in a muffle furnace at 600°C for 1 h; (ii) secondly activation of char product from the first stages at fixed bed reactor (stainless steel with 54.1 mm internal diameter and 320 mm length) which was studied to observe the effect of char product: Chemical agent ratio (ZnCl$_2$, 1:1 to 1:3), which there are activated at 700°C activation temperature for 2 h; and (iii) finally alkali impregnated activated carbon which were immersed 1:3 ratio in 500 mL of 1 N NaOH, KI and K$_2$CO$_3$ solutions and stirred for 30 min. The result showed that the surface area and the pore volume increased progressively with increasing the char product: Chemical agent ratio. The maximum surface area total pore volume of activated carbon product was 532.31 m^2/g and 0.2973 cc g^{-1} was obtained on ACZn13. While, the maximum surface area and the pore volume of modified impregnated activated carbon was 741.71 m^2/g and 0.4210 cc g^{-1} was obtained on K$_2$CO$_3$-AC. The results of the experiment demonstrated that with regard to adsorption of H$_2$S on K$_2$CO$_3$-AC which it had more than on KI-AC and NaOH was 3.26 and 8.8%, respectively. The conclusion showed that surface area, total pore volume and micropore volume were increasing with increased the char product: Chemical agent ratio (1:1 to 1:3). ACZn13 has good chemical and physical

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properties such as chemical content and surface area, which showed that the highest surface area (532.21 m^2/g) and total pore volume (0.2973 cc g^{-1}). Therefore, K_2CO_3-AC impregnated activated carbon has a high surface area and showed be an efficient adsorbent for removal of H_2S from biogas product. Moreover, evaluating the content of H_2S adsorption was suggested.

Keywords: Activated Carbon, Palm Oil Shell, Chemical Activation, Pottasium Carbonate, Pottasium Iodide, Sodium Hydroxide, Impregnated Agentsand Hydrogen Sulfide Adsorption

1. INTRODUCTION

Thailand has been well recognized as one of the top exporters of agricultural biotechnology with traditional energy sources. The amount of waste from agriculture has increased due to rapid industrial development in recent years. Agricultural industries and livestock farms generally produce several organic wastes and wastewaters, which greatly affect air and water pollution (Sitthikhankaew *et al.*, 2014). Focus on environmental problems from industrial waste, palm oil shells from factory wastes agriculture in Thailand. Palm oil shells from oil palm occurs carbon primarily in large quantities. Utilization of agricultural wastes to produce activated carbon is an important approach in air pollution control strategy. Converting these wastes into value added product such as activated carbon could solve environmental problems such as accumulation of agricultural waste, air pollution and water pollution (Nor *et al.*, 2013). The products of palm oil mill are to plant oil palm in Thailand can be produced 1.7×10^6 tons/year. Palm oil extraction process had palm oil shell as by product. Considering the amount of substances from the image processing palm oil palm shell were left over from production of about 9% by weight, or to enter a scope with a bunch of tons into the production process. Palm oil shell occurs from extraction process about 153,000 tons/year of general machinery, appliances, palm fiber and shell as fuel to power the boiler. The heat loss from the burning of fibers was less than 5 MJ kg^{-1}. The heat loss from palm oil shell (dry) were about 17 MJ kg^{-1}. Heat from the burning palm shell was higher than the needs of the plant. Most people prefer to use the fibers in burning more fuel. Cause the accumulation of shells in the palm oil mill up. Choice of using palm shell to use is the production of activated carbon. Presently, low cost palm oil residues are considered promising adsorbents for adsorption applications. Besides, it is cheaper and readily available materials.

Activated carbon is one of the most widely used adsorbents because of its high adsorptive capacity; therefore, it has been widely used as adsorbent and in catalysis or separation processes. As results, the demand for activated carbon is increasing (Saka, 2012).

An Activated Carbon (AC) adsorbent is usually dominated by micropores (width<2 nm) whereas its specific volume of mesopores (width 2-50 nm) is less than 0.2 $Cm^{3-1}g$. Highly mesoporous AC powders have industrial relevance, such as for desulfurization, adsorption of large molecules, catalyst supports and high capacitance-carbon electrodes (Sun and Hong, 2011). Production of activated carbon involved two stages; (i) carbonization of raw material in an inert atmosphere and (ii) secondly activation if the carbonized char. The product is categorized in laboratory scale into two: Which is, on includes the synchronous process of carbonization and activation (one-stage process), the other is asynchronous process in which a separate carbonization process is included prior to the activation process (two-stage process). The carbonization involves thermal decomposition of the carbonaceous material in an inert environment to eliminate volatile components to produce fixed carbon with limited or undeveloped pores. Activation enlarges the pores created during carbonization together with formation of new pore structures. Activation is achieved via physical or chemical means: Physical activation involves oxidation of char using steam, air, oxygen or carbon dioxide at high temperature (800-1100°C), chemical activation involves impregnation of chemicals (such as $ZnCl_2$, NaOH, HNO_3, KI, Na_2CO_3, K_2CO_3) and then pyrolysis at 500-800°C (Nasri *et al.*, 2014).

Hydrogen sulfide is one of the major environmental pollutants having its source in natural and anthropogenic activities. One of the methods of its removal is adsorption. Various material have been extensively investigated either as H_2S adsorbents or adsorbent' supports. High distribution of catalytic enters promoting oxidation and ability to retain water is considered as important factors promoting an enhancement in the adsorption capacity of various media. While water is the pore system contributes to dissolution of H_2S, the basic surface promotes it dissociation to HS-ions, which then are oxidized either to elemental sulfur or sulfur oxides/oxysulfur acids. Even though zinc oxide exhibits good capacity at elevated temperatures at room temperatures

activated carbons are widely used in desulfurization processes (Seredych and Bandosz, 2011). Biogas is the combustible gas produced through a biological process, known as anaerobic digestion, which is the process, operated at low-temperature and without air. Biogas consists of 55-80% CH_4, 20-45% CO_2 with trace amount of H_2S and other impurities (Pipatmanomai *et al.*, 2009). Biogas can be utilized for generation of electrical power and heat production, generally; biogas (as well as natural gas and synthesis gas from coal gasification) contained hydrogen sulfide (H_2S) that was highly toxic for human body and corrosive for machine. The content of H_2S in biogas was about 0-1% and H_2S must be removed from fuel gases prior utilization (Sitthikhankaew *et al.*, 2011). Common H_2S removal technologies for H_2S removal from biogas fall into one of the following (Pipatmanomai *et al.*, 2009): (i) Absorption into a liquid either water or caustic solution; (ii) adsorption on a solid such as iron oxide based materials, activated carbon or impregnated activated carbon and (iii) biological conversion by which sulfur compounds are converted into elemental sulfur by sulfide oxidizing microorganisms with addition of air/oxygen. Each technology has its own advantages and disadvantages.

In this study, H_2S removal by NaOH, KI and K_2CO_3 impregnated activated carbon adsorption was selected and compared to commercial activated carbon. The aim of the study is to produce activated carbon from palm oil shell by chemical activation $ZnCl_2$. The aim of this study to achieving the following: (i) Production of activated carbon by chemical activation with $ZnCl_2$ using palm oil shell as a raw material, (ii) impregnation activated carbon with NaOH, KI and K_2CO_3 asimpregnation agent, (iii) analysis of chemical and physical properties for activated carbon product is performed by ultimate analysis, proximate analysis, FTIR, XRD, SEM and surface area and (iv) Hydrogen Sulfide (H_2S) adsorption.

2. MATERIALS AND METHODS

2.1. Materials

Palm Oil Shell (POS) was used as staring material in the preparation of activated. POS, AS Received from Suratthani provice, southen Thailand, in successive steps were first air-dried, crused and sized, the fraction of particle sizes between 2-2.8 mm being chosen. The proximate, ultimate and component analyses of Pam Oil Shell (POS) are shown in **Table 1**. The commercial activated carbon (Commercial grade; code No.CGC-11A) was supplied from C. Gigantic Carbon Co. Ltd. Zinc Chloride ($ZnCl_2$),

potassium carbonate (K_2CO_3), sodium hydroxide (NaOH), potassium iodine (KI) were dissolved in distilled water to prepare a saturated solution.

2.2. Experimental Method

The experiments methods used in this study include the following steps: (i) Adsorbent preparation, (ii) impregnated activated carbons and (iii) adsorption of Hydrogen Sulfide (H_2S) by modified activated carbon. **Figure 1** shows flow chart of experiments.

2.2.1. Adsorbent Preparations

The preparations of adsorbents were divided into two steps: Carbonization and activation process;

2.2.2. Carbonization Process

Carbonization process was the first step of the experiment. Palm Oil Shell (POS) was dried in a hot air oven at 110°C for 24 h to remove any surface moisture. They were then ground and sieved to a size range of 2-2.8 mm. In the carbonization step, a stainless steel tube reactor of length 320 mm and internal diameter of 54.1 mm. filled with 40 g of palm oil shell was carbonized in a muffle furnace at 600°C for 1 h under the flow of N_2 gas at 150 Cm min$^{3-1}$. The heating rate was controlled at 10°C min^{-1}, which the char products were allowed to cool to room temperature. **Figure 2** shows the schematic diagram of the experimental set-up.

2.2.3. Activation Process

Activated carbon produced by chemical activation with zinc chloride ($ZnCl_2$) under conditions of activation 1:1-1:3 of char ratio: $ZnCl_2$ (w/w %), activation temperature 500°C for 2 h (as shown in **Table 2**), which the chemical activation was poured to a beaker containing 0.1 M (mol/dm^3) HCl and stirred for 10 min. Finally, the activated carbon sample was washed with hot water and water until pH of the washing solution reached 6-7 and dried in an oven at 105°C for 3 h.

2.2.4. Modified Activated Carbon

Preparation of impregnated activated carbon; three types of alkali-impregnated activated carbons were prepared by the same procedure but with various impregnation solutions. The activated carbons were immersed 1:3 ratio in 500 mL of 1 N NaOH, KI and K_2CO_3 solutions and stirred for 30 min. The immerged activated carbons were then filtered at from the impregnation solutions and dried in an oven at 120°C for 60 h. The activated carbons immersed in NaOH, KI and K_2CO_3 solution were noted as NaOH-AC, KI-AC, K_2CO_3-AC, respectively.

2.2.5. H₂S Adsorption by Modified Activated Carbon

The H_2S adsorption using small column test equipment was conducted on the adsorbents of the activated carbon product. Adsorbent (10g) of the impregnated activated carbon was placed in a PVC column 5 Cm diameter, using biogas product (Saitawee *et al.*, 2014) as test gas with the total flow rate 15 Cm^3 min^{-1}. Biogas detector was used to

analyze the concentration of H_2S in the inlet and outlet gases, as shown **Fig. 3**.

2.3. Characterization of Sample

2.3.1. Characterization of Palm Oil Shells

The chemical composition of palm oil shell was determined by CHNS analysis.
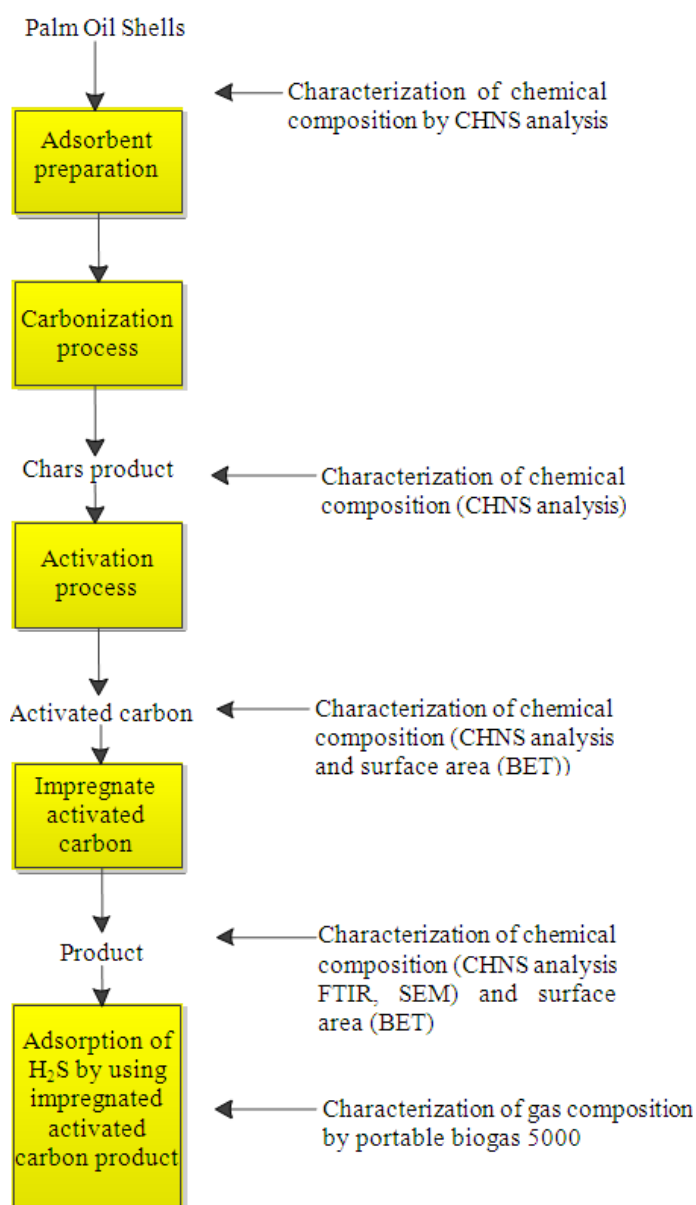

Fig. 1. Flow chart of experiments (Nasri *et al.*, 2014)

Fig. 2. Experimental set up for activated carbon production

Fig. 3. Shows the fixed bed reactor system used for H2S adsorption studies

2.3.2. Characterization of the Carbonized Carbon and Activated Carbon

Moisture and dry matter content, an amount of 1.0 g each have carbonized sample was placed in a clean silica crucible that was previously dried in desiccators and weighed. They were then dried in an air-circulated oven at 105°C for 3 h after which they were cooled in desiccators and weighed. Results were expressed as percentage of the initial weight carbonized samples.

Ash content, crucibles were heated in a furnace at 500°C, then cooled in desiccators and weighed. The oven-dried samples from the previous section were placed in the crucible and transferred into the muffle furnace at 900°C for 3 h. The crucibles/content were allowed to cool in desiccators and then weighed to obtain the weight of the ash. The ash content was expresses as percentage of the oven dry weight.

The chemical composition of product was determined by CHNS/O analyzer (PE2400 Series II) and Fourier Transform Infrared (FTIR) using a diffuse reflectance infrared fourier transform spectrometer. A total of 256 scans were recorded per spectrum over the range 4000-650 cm^{-1} at a resolution of 4 cm^{-1}. To improve the reflectivity of the samples, the samples were diluted with KBr is ratio of KBr: Sample, 20:1. The FTIR spectra of the adsorbents were obtained under 50 mL helium flows at 25°C. A spectrum of KBr recorded in He served as background.

The surface area of samples was analyzed using nitrogen adsorption at 77 K in a Quanta chrome Autos orb automated gas sorption system.

Scanning Electron Microscope (SEM) images of activated carbon produced from palm oil shell by $ZnCl_2$ activation and K_2CO_3, KI, NaOH impregnation was recode by using JSM-6400.

2.3.3. Characterization of Inlet and Outlet Gas from H_2S Adsorption Test

The inlet and outlet gas from H_2S adsorption test were analyzed the chemical composition by using Portable gas analyzer (BIOGAS 5000).

3. RESULTS

3.1. Effect of Activated Ratio on Activated Carbon Product

The results of the proximate analysis of palm oil shell indicated in **Table 1**. The results are compared with previous research on palm oil shell. The fixed carbon, volatiles, moisture and ash content for POS are 10.39, 87.78, 3.86 and 1.83 respectively. The high volatile matter (87.78%) and moderate amount of fixed carbon (10.39%) is a typical property of agricultural residues. The results from the proximate analysis are within the range of literature review (Nasri *et al*., 2014). The high volatile contents make it more reactive and therefore aid during the carbonization process in creating more pores on the carbonaceous material. The ultimate analysis of POS indicated a carbon, hydrogen and nitrogen content

of 47.26, 6.18 and 0.94%, respectively (**Table 1**). These values are similar to those previously determined (Nasri *et al*., 2014). The low nitrogen content from the analysis indicates that POS is environmental friendly. The preparation of the activated carbons from palm oil shell was carried out at carbonized in a muffle furnace at 600°C for 1 h and activation temperature 500°C for 2 h for $ZnCl_2$ are given **Table 2**.

The chemical content of activated carbon is shown in **Table 3**. The carbon content was found to be between 72.42 and 74.81 wt %. The result showed that the ratio of char product: Activating agent used for zinc chloride has effect on the chemical content of activated carbon, which the carbon content in the activated carbon increased with increasing the char product: $ZnCl_2$ ratio. Furthermore, the carbon content to obtain the maximum was increased with the increasing of $ZnCl_2$, which it is ACZn13. The ultimate analysis of AC, ACZn13, ACZn12 and ACZn11 indicated a carbon, hydrogen and nitrogen content of 72.70, 1.12 and 0.60% (AC), 74.81, 0.76 and 0.28% (ACZn13), 72.44, 0.87 and 0.42% (ACZn12), 72.42, 0.88 and 0.65% (ACZn11), respectively.

3.2. Comparison of Three Impregnated Agent for Activated Carbon Production on Chemical Content

These studies were performed to compare the impregnated activated carbon from three agents (K_2CO_3, KI and NaOH) and the results are given in **Table 4**, which activated carbon was produced from char product: $ZnCl_2$ at 1:3 on 500°C and 2 h. Due to this conditions had the highest carbon content. It is to note that the average carbon, hydrogen and nitrogen content for impregnated activated carbon of the three impregnate agents was not the same, varied in the range 73.31-78.60, 0.79-0.49 and 0.71-0.87%, respectively. According to **Table 4**, the K_2CO_3-AC gave the highest average carbon content, followed with NaOH-AC and KI-AC.

3.3. Characterization of Impregnate Activated Carbon

Alkali carbonate, alkali hydroxides and alkali iodine (specifically K_2CO_3, NaOH and KI) are generally used as impregnated agents for the activated carbon production because of the valuable properties of materials produced by this activator. In particular, porosity development by alkali activation is associated with a well-established gasification mechanism. Sitthikhankaew *et al*. (2014), studies the alkali

impregnated activated carbon and found that impregnated activated carbon had higher surface area than commercial grade impregnated activated carbon. **Table 5** is presented BET surface area and total pore volume of commercial grade activated carbon, activated carbon and impregnated activated carbon product. It can be seen that the ACZn13 BET surface area and total pore volume had higher than ACZn12 and ACZn11, which it is 532.31, 515.12 and 515.12 m^2/g and 0.3112, 0.2973 and 0.2899 cc/g, respectively.

Comparison of N_2 adsorption experiment, the surface properties of impregnated activated carbon can be calculated as presented in **Table 5**. It was found that K_2CO_3-AC has BET surface area of 743.71 m^2/g, total pore volume of and 0.4210 cc/g, which there was more than commercial standard, KI-AC has BET surface area of 627.02 m^2/g, total pore volume of and 0.3536 cc/g, while NaOH-AC has BET surface area of 551.04 m^2/g, total pore volume of and 0.3112 cc/g. This improvement is due to the chemical agent (especially alkali carbonate) of activated carbon during impregnated, which eventually increases the porosity of the samples. Okman *et al*., (2014) produced activated carbon from agricultural by chemical activated carbon with K_2CO_3 and KOH, it was found reported that K_2CO_3 as activated had higher surface area. Our results are in good agreement with these reports.

The FTIR spectra, which were obtained from the impregnated activated carbon, kept under 50 mL/min He flow, for all the impregnated activated carbon are given in **Fig. 4** and **Table 6**. It is convenient to investigate the FTIR spectra in seven regions: 3872.54-3564.52 cm^{-1} (O-H stretching vibration), 2970.42-2918.80 cm^{-1} (C = C stretching vibration), 1739.85-1729.82 cm^{-1} (C = O stretching vibration), 1652.14 cm^{-1} (C = C stretching vibration in aromatic rings), 1365.57-1351.32 cm^{-1} (c-H deformation vibration in CH_2 or $C(CH_3)_3$ groups), 1216.47-1202.92 cm^{-1} (c-O-C stretching vibrations in ether) and 1058.55-1044.20 cm^{-1} (C-OH stretching vibrations).
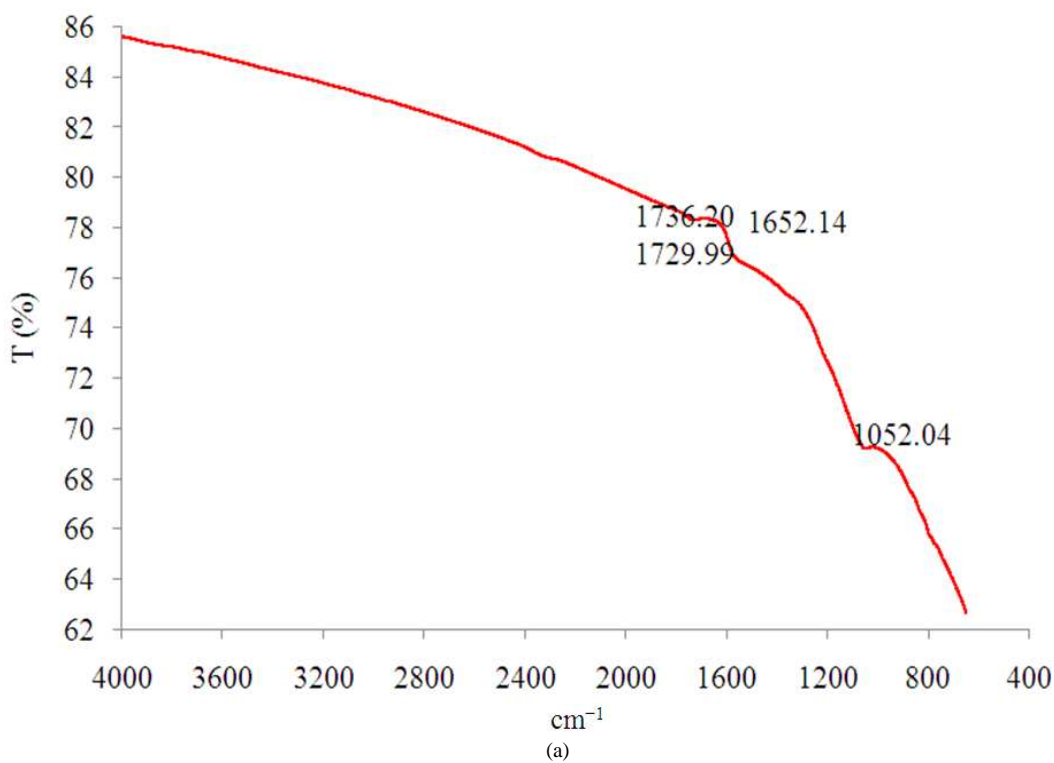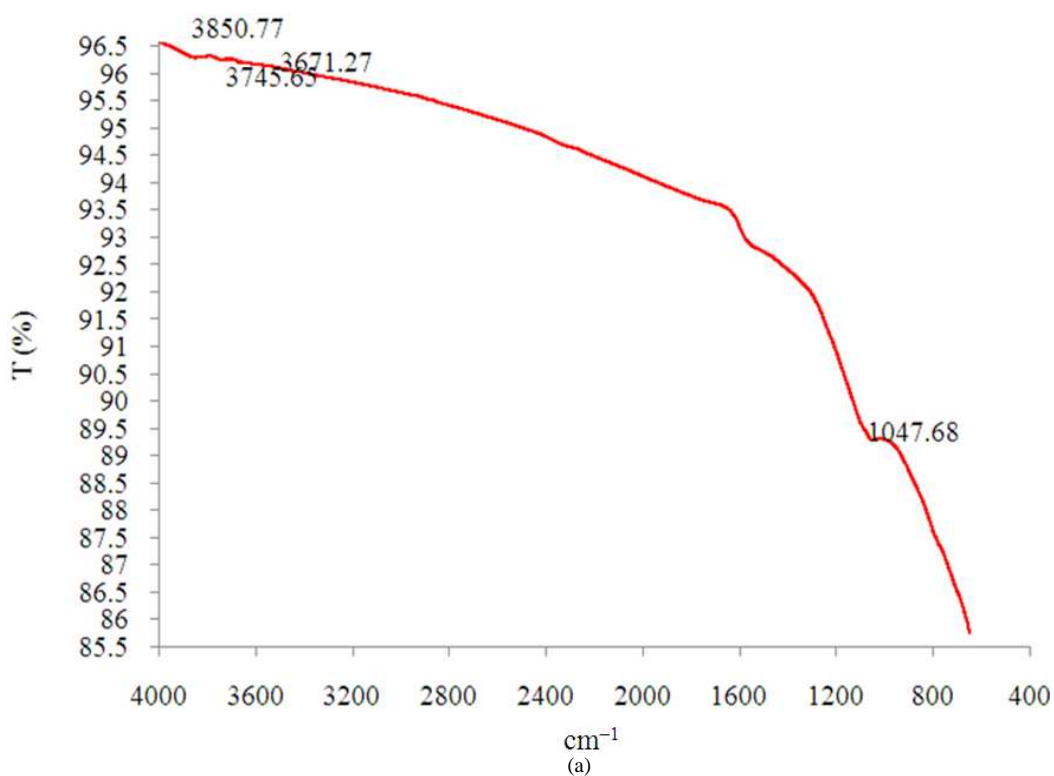
The spectral zone 3872.54-3564.52 cm^{-1} Range Displays Bands Mostly Attributable To hydroxyl species. The position of the band is characteristic of stretching vibration of hydroxyl compounds from carboxyl's, phenols or alcohols. This band diminishes with the K2CO3 and NaOH impregnated activated carbon (**Fig 4b and d**). There are five main bands in the spectral regional 1800-800 cm^{-1} confirming the presence of surface oxygen groups: (i) A band of 1739.85-1729.82 cm^{-1} characteristic of C = O stretching vibration in carboxylic groups, lactones and anhydrides which occurred in impregnated activated

carbon (K_2CO_3-AC, KI-AC and NaOH-AC), (ii) a band of 1652.14 cm^{-1} attributed to C = C stretching vibration in aromatic rings of quinone and keto-enol groups which occurred only in K_2CO_3-AC show that the extent of aromatization is very high, (iii) a band of 1365.57-1351.32 Cm^{-1} which occurred KI-AC and NaOH-AC may be attributed to C-H deformation vibration in CH_2 or $C(CH_3)_3$ groups, (iv) a band of 1216.47-1202.92 cm^{-1} is the C-O-C stretching vibration in lactones and ethers which occurred in only KI-AC and (v) a band of 1058.55-1044.20 cm^{-1} attributed to C-OH stretching vibration. These results were comparable with the work done by (Tan *et al*., 2008) (9) which reported that more acidic groups such as carboxylic and ether were produced by acid treatment on a modified oil palm shell activated carbon.

Surface morphology of impregnated activated carbon was then performed using a Scanning Electron Microscope (SEM), as shown in **Fig. 5**. It can be observed that the activated carbons contain pores of different sizes which are a common characteristic of activated carbon as can seen in the other hand (Sitthikhankaew *et al*., 2014). The micrographs that the external surface of impregnated activated carbon have cracks, crevices and some grains in various sizes in large hole. It can conclude from SEM images taken during operated as a carbonization temperature of 600ºC that porous structure was formed because of most of the organic volatiles were evolved, leaving behind the ruptured surface of activated carbon with a small number of pores. These results are agreement with in the other hand (Saka, 2012). In addition, SEM images of K_2CO_3-AC showed spongy-like structures with many of small and large holes more than KI-AC and NaOH.

3.4. H_2S adsorption

The H_2S adsorption of commercial activated carbon and impregnated activated carbon were investigated at ambient temperature. **Table 7** gives the summary of H_2S content from biogas before adsorption and H_2S content after adsorption with impregnated activated carbon for AC, K_2CO_3-AC, KI-AC and NaOH-AC. There is increase in adsorption and there is lower H_2S content after adsorption at 26.75 ppm, 21.71 ppm and 20.5 ppm with impregnated in NaOH, KI and K_2CO_3, respectively. One can see that K_2CO_3-AC exhibited a higher H_2S adsorption than KI-AC, AC and NaOH-AC due to development of more porosity in the impregnated activated carbon which it had both far larger surface area and total pore volume than comercial activated carbon and other impregnated activated carbon.
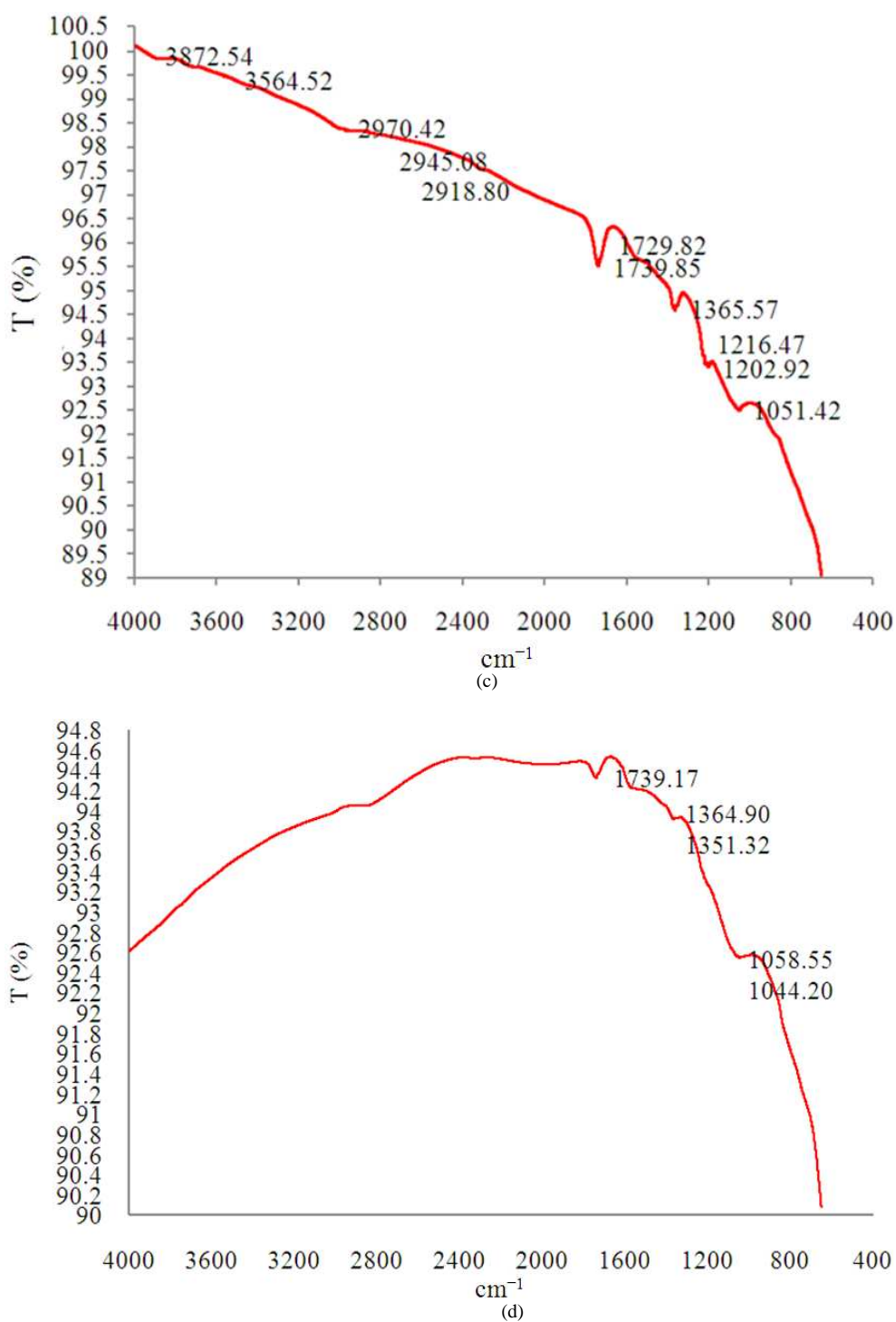
(a)

(a)

(c)

(d)

Fig. 4. FTIR spectra of commercial activated carbon and impregnated activated carbon: Of (a) commercial activated carbon (AC); (b) K_2CO_3 impregnated activated carbon (K_2CO_3-AC), (c) KI impregnated activated carbon (KI-AC) and (d) NaOH impregnated activated carbon (NaOH-AC)
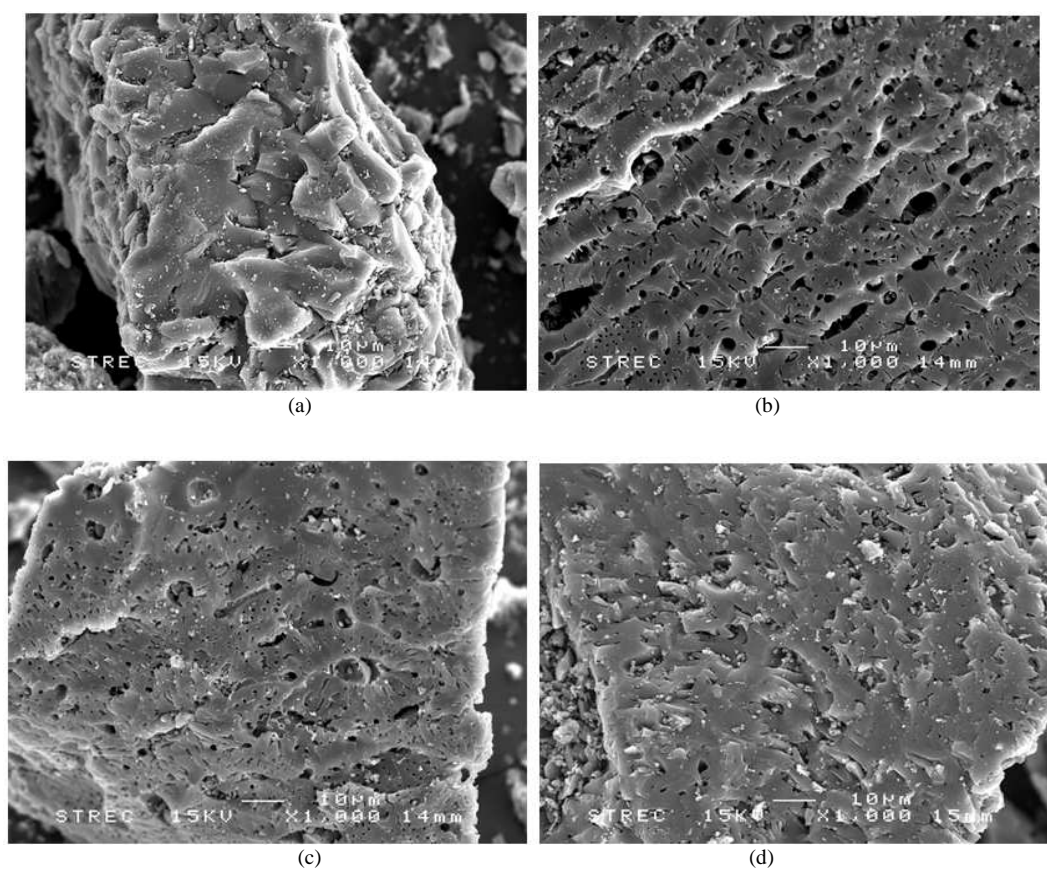
Fig. 5. SEM images of commercial activated carbon and impregnated activated carbon: (a) AC, (b) K_2CO_3-AC, (c) KI-AC and (d) NaOH-AC

Table 1. Ultimate and proximate analyses of palm oil shell

Proxiamte analysis (wt, %)	Palm oil shell	Char product
Moisture	3.86	4.03
Ash	1.83	4.41
Volatiles	87.78	23.18
Fixed carbon	10.39	72.41
Ultimate analysis (wt, %)		
C	47.26	
H	6.18	
N	0.94	
HHV (cal/g)	4735.00	

Table 2. Activated carbon process conditions

Samples	Activated agent	Char: Agent ratio	Activation temperature (°C)	Retention time
ACZn11	$ZnCl_2$	1:1	500	2
ACZn12	$ZnCl_2$	1:2	500	2
ACZn13	$ZnCl_2$	1:3	500	2

Table 3. Characteristics of palm oil shell, standard activated carbon and activated carbon product (AC, ACZn11, ACZn12 and ACZn13)

Proximate analysis dry basis, wt (%)

Samples	Description			Results (%)
Palm oil shells	Moisture			3.86
	Ash			1.83
	Volatile matter			87.78
	Fixed carbon			10.39

CHNS/O ANALYZER (PE2400 series II)

Samples	No	C (%)	H (%)	N (%)
Palm oil shells	Average	47.26	6.18	0.94
AC (standard)	Average	72.70	1.12	0.60
ACZn13	1	75.08	0.49	0.10
	2	74.87	0.99	0.15
	3	74.47	0.80	0.59
	Average	74.81	0.76	0.28
ACZn12	1	72.52	0.83	0.31
	2	72.59	0.83	0.29
	3	72.20	0.95	0.65
	Average	72.44	0.87	0.42
ACZn11	1	72.56	0.83	0.99
	2	72.46	0.62	0.31
	3	72.25	1.20	0.64
	Average	72.42	0.88	0.65

Table 4. Ultimate analysis of impregnated activated carbon

CHNS/O ANALYZER (PE2400 series II)

Samples	No	C (%)	H (%)	N (%)
K_2CO_3-AC	1	78.30	0.51	0.67
	2	78.76	0.38	0.77
	3	78.74	0.58	0.69
	Average	78.60	0.49	0.71
NaOH-AC	1	75.96	0.77	0.70
	2	76.14	0.93	0.72
	3	76.11	0.66	0.81
	Average	76.07	0.79	0.74
KI-AC	1	72.49	0.95	0.80
	2	73.52	0.43	0.95
	3	73.47	0.83	0.85
	Average	73.31	0.74	0.87

Table 5. Surface area of commercial grade activated carbon, activated carbon and impregnated activated carbon product

Samples	Multipoint BET (m^2/g)	Total pore volume (cc/g)
AC (Standard)	707.11	0.3906
K_2CO_3-AC	743.71	0.4210
KI-AC	627.02	0.3536
NaOH-AC	551.04	0.3112
ACZn13	532.31	0.2973
ACZn12	515.12	0.2934
ACZn11	515.07	0.2899

Table 6. The peak values of the main bands in FTIR spectra to all impregnated activated carbon and commercial activated carbon

Samples	Peak values (cm^{-1})					
	O-H stretching Vibration vibrations in ether	C≡C stretching vibration	C = O stretching vibration	C = C stretching aromatic rings	C-H deformation vibration in	C-O-C stretching vibration in CH_2 or C $(CH_3)_3$ groups
AC	3850.77, 3745.65, 3671.27	-	-	-	-	-
K2CO3-AC	-	-	1736.20, 1729.99	1652.14	-	-
KI-AC	3872.54, 3564.52	2970.42, 2945.08, 2918.80	1729.82, 1739.85	-	1365.57	1216.47, 1202.92
NaOH-AC	-	-	1739.17	-	1364.90, 1351.32	-

Table 7. H_2S adsorption of commercial activated carbon and impregnated activated carbon

Samples	H_2S content from biogas before adsorption (ppm)	H_2S content after adsorption with impregnated activated carbon (ppm)
AC	266.00	29.0
	268.00	23.0
	267.00	22.0
	269.00	22.0
Average K_2CO_3-AC	267.50	24.0
	266.00	22.0
	266.00	21.0
	268.00	20.0
	267.00	19.0
Average KI-AC	266.75	20.5
	269.00	21.0
	268.00	23.0
	270.00	22.0
	265.00	21.0
Average NaOH-AC	268.00	21.75
	268.00	27.0
	266.00	26.0
	269.00	28.0
	268.00	26.0
Average	267.75	26.75

4. DISCUSSION

Activated carbon produced from palm oil shell to be suitable for the removal of air pollutants. In this research, activated carbon prepared from char product of palm oil shell using $ZnCl_2$ activation (1:1 to 1:3 ratio of char product: $ZnCl_2$) were studied. It was found that the highest chemical content and surface area occurred in the ACZn13. One can see that the surface are incresed with increasing the ratio of char product: $ZnCl_2$ which it can be assumed that a large amount of activated agent expand the macro-pore entrance or open the empty surface area of the activated carbon. In the impreganated process, both chemical content, surface area, FITR band and SEM image indicate that impregnated activated carbon behavior depends on the alkaline impregnate agent, which there were K_2CO_3, KI and NaOH.

When chemical impregnated with K_2CO_3 was used, higher than of chemical content due to be release of volatile products as a result of intenifying dehydration and elimination reaction; it also indicated that activated carbon was gasified by K_2CO_3. On other hand studied the gasification of graphite by alkali metal and found that
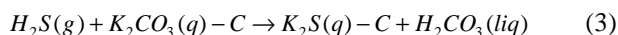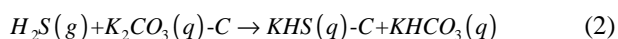
K_2CO_3 was redued in an inert atmosphere by carbon whereby activated carbon reacted with K_2CO_3 and then the later was removed during gasification. Therefore, the surface area and pore volume highest (Adinata *et al.*, 2007).

The H_2S adsorption performed of comercial activated carbon and impregnated activated carbon under ambient temperature were tested and the results are presented in **Table 7**. For impregnated activated carbon, after H_2S adsorption, the concentration of H_2S reached almost 20.5 ppm of K_2CO_3-AC, 21.75 ppm of KI-AC and 26.75 ppm of NaOH-AC. While the concentration of H_2S reached almost 24 ppm of comercial activated carbon. In this results showed that K_2CO_3-AC had slighly higher H_2S adsprprion than KI-AC and NaOH-AC were 3.26% and 8.8%, respectively. A reaction of H_2S adsorption occurs along with physical adsorption which there are two main reaction: The first, H_2S treanferred from the bulk stream into the pore or surface of the activated carbon; and the second H_2S adsorbed on activated carbon from which H_2S (g) and H_2S (ads) correspond to H_2S in gas and/or adsorbed phases (as can seen in Equation 1 (Sitthikhankaew *et al.*, 2014):

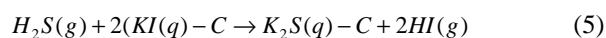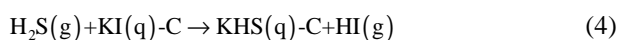$$H_2S(g) \rightarrow H_2S \ (ads) \tag{1}$$

The results of this research showed that H_2S adsorption on alkaline impregnated activated carbon (K_2CO_3-AC and KI-AC) had higher than comercial activated carbon. This positive effect is mainly due to the chemical reaction, which H_2S reacts with alkali at carbon surface to produce Alkali Hydrogen Sulfild (AHS) and alkali sulfide, from which alkali impregnated on the activated carbon covered by the water film generated by water produed from the reaction. The reaction of H_2S of three kinds of alkaline are showed in Equation 2 to 7:
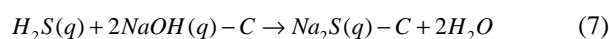
4.1. K_2CO_3 Impregnated Agent

$$H_2S(g) + K_2CO_3(q)\text{-}C \rightarrow KHS(q)\text{-}C + KHCO_3(q) \tag{2}$$

$$H_2S(g) + K_2CO_3(q) - C \rightarrow K_2S(q) - C + H_2CO_3(liq) \tag{3}$$

K_2CO_3 (q)-C is the K_2CO_3 impregnated on the activated carbon Equation 4.

4.2. KI Impregnated Agent

$$H_2S(g) + KI(q)\text{-}C \rightarrow KHS(q)\text{-}C + HI(g) \tag{4}$$

$$H_2S(g) + 2(KI(q) - C \rightarrow K_2S(q) - C + 2HI(g) \tag{5}$$

KI (q)-C is the KI impregnated on the activated carbon.

4.3. NaOH Impregnated Agent

$$H_2S(g) + NaOH(q) - C \rightarrow NaHS(q) - C + H_2O \tag{6}$$

$$H_2S(q) + 2NaOH(q) - C \rightarrow Na_2S(q) - C + 2H_2O \tag{7}$$

NaOH (q)-C is the NaOH impregnated on the activated carbon covered by the water film which was generated by produced water from Equation 6 and 7 (Sitthikhankaew *et al.*, 2011). It is note from this study that NaOH-AC shows lower H_2S adsoprtion than other impreganated agent (K_2CO_3-AC and KI-AC), which could possibly be due to the less residual water vapor content which it is block the carbon surface and it had effect on H_2S adsoption. Moreover, experimental results indicate that the suitable impregnated agent was K_2CO_3 to modified activated carbon, K_2CO_3 is not a hazardous chemical and not deleterious as it is frequently used for food additives (Adinata *et al.*, 2007)

5. CONCLUSION

The results presented in this research show that the potentials of palm oil shell as a raw material for the preparation of modified activated carbon for H_2S adsoption from biogas product (Saitawee *et al.*, 2014). There were four main experiment for activated carbon are as follows; (i) carbonization process which palm oil shell was carbonized in a muffle furnace at 600°C for 1 h under the flow of N_2 gas at 150 cm^3 min^{-1}; (ii) activation process which Activated carbon produced by chemical activation with zinc chloride ($ZnCl_2$) under conditions of activation 1:1-1:3 of char ratio: $ZnCl_2$ (w/w %), activation temperature 500°C for 2 h; (iii) modified activated carbon which the activated carbons were immersed 1:3 ratio in 500 mL of 1 N NaOH, KI and K_2CO_3 solutions and stirred for 30 min; and (iv) H2S adsorption. Hydrogen sulfide is among the pollutants effectively removed by activated carbon. The results showed that palm oil shell can be successfully converted into activated with surface area, total pore volume. It was found that surface area, total pore volume and micropore volume were increasing with increased the char product: Chemical agent ratio (1:1 to 1:3). ACZn13 has good chemical and physical properties such as

chemical content and surface area, which showed that the highest surface area (532.21 m^2/g) and total pore volume (0.2973 cc/g).

For modified activated carbon, it was found that the impregnation with K_2CO_3 results in the lower concentration of hydrosulfide (H_2S) (20.5 ppm) and enhances the oxidation of H_2S (Xiao *et al*., 2008) which is in high concentration of hydrosulfide ion (HS^{-1}). It had H_2S adsorption more than commercial activated carbon (8%). Factors affecting adsorption types are pore structure, surface chemistry and adsorbent properties. Among them funtional groups and chemical compositions play important roles in the adsorption mechanism and capacity. Moreover, alkali impreganated activated carbon (K_2CO_3-AC and KI-AC) had H_2S adsorption more than commercial activated carbon while NaOH-AC had H_2S adsorption lower than commercial activated carbon about 4% which could possibly be due to the less vapor water content effect of carbon surface (lower that other alkaline impregnated activated carbon) (Sitthikhankaew *et al*., 2014). Therefore, K_2CO_3-AC impregnated activated carbon in this study has these special characteristics and can be recommended as economical and environmentally friendly activated carbon.

Accordingly, in this case the activated carbon produced from palm oil shell are widely used as adsorbents of gases including removing H_2S compound, especially those which contitute an environmental hazard but there are limitation in the amount of biogas, which it was operated in laburatory scale effect to had operated small scale in H_2S adsorption. Therefore, in the further research, other alkalin impregnation, other ratio of impregnated ratios on activated carbon and the other method such as physical activated carbon for modified activated carbon will be used in studies similar to those described in this research. Especially, other gases adsorption such as CO_2 will be operate on modified activated carbon in the next research which use to industrial scale and evaluating the performace capacity of adsorption were suggest.

6. ACKNOWLEDGMENT

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