

PREPARATION OF ACTIVATED CARBON FROM PALM OIL SHELL BY CHEMICAL ACTIVATION WITH Na_2CO_3 AND ZnCl_2 AS IMPRENATED AGENTS FOR H_2S ADSORPTION

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ABSTRACT

Hydrogen Sulfide (H_2S , rotten-egg) is one of the major environmental pollutants having its sources in natural and anthropogenic activities. It's had smell gas produced by anaerobic digestion in acid condition from organic and inorganic compounds containing sulphur, presents dual problems of its toxicity and foul odour. One of methods of its removal is adsorption. Activated carbon is a widely used adsorbent in the treatment of air pollution. Adsorption type and capacity are primarily based on the physical properties of pores, namely the surface area. Conventionally, activated carbon is produced from biomass residues, wood coal and agricultural residues. Today, one promising approach for the production of cheap and efficient activated carbon is used of waste from palm oil mill industries, which is palm oil shell. Palm oil shell is available in large quantities of approximately 0.53 million tonnes annually in Thailand. Palm oil shell is a by-products of the palm oil industry and was used as a raw material in this study due to its high carbon content, high density and low ash content. Normally, H_2S in biogas, which is found the range between as low as about 50-10,000 ppm depending on the feed material composition to production, can cause corrosion to engine and metal substance via of SO_2 from combustion. H_2S must be removed from biogas product prior to further utilization. Therefore, in these research the usage of palm oil shell is especially important due to its high value added for produced activated carbon adsorbent for H_2S adsorption in biogas product. In this study, fixed bed reactor (stainless steel with 54.1 mm internal diameter and 320 mm length) was studied to observe the effect of char product: Chemical agent ratio (Na_2CO_3 and ZnCl_2 , 1:1 to 1:3), which there are activated at 700°C activation temperature for 2 h on the chemical and physical properties, BET surface area, the pore volume, micropore volume and hydrogen sulfide adsorption. The result showed that the BET surface area, BET surface area, the pore volume and micropore volume increased progressively with increasing the char product: Chemical agent ratio. The value of mean total pore volume of activated carbon increased with an increased char product: Chemical impregnation agent ratio (Na_2CO_3 and ZnCl_2) as is a 1:1 to 1:3, from 0.3743 to 0.4181 cc/g and 0.2877 to 0.3137 cc/g, respectively. The average micropore volume were 0.2224, 0.2411, 0.2270, 0.1721, 0.1686 and 0.1546 cc/g of AC_Na13, AC_Na12, AC_Na11, AC_Z13, AC_Z12 and AC_Z11, respectively. The results of yield, it was found that that the activated carbon for Na_2CO_3 agent is higher than activated carbon for ZnCl_2 agent. The highest of yield was 32.3% for AC_Na13. Moreover, the maximum BET surface area and H_2S adsorption was $743.71 \text{ m}^2/\text{g}$ and 247.33 ppm was obtained on AC_Na13. This gave H_2S adsorption more than commercial activated carbon (1%). Guideline for evaluation chemically activated carbon for potential application were suggested. The conclusion showed that AC_Na13 has good chemical and physical properties such as chemical content and surface area, which showed that the highest H_2S adsorption (247.33 ppm). The carbon content and BET surface area of AC_Na13 were 78.76 (wt%)

and 743.71 m²/g, respectively. Thus, chemical agent (Na₂CO₃) can be used effectively as an operating strategy to optimize surface area. The synthetics activated carbon with suggested BET surface area were in good agreement with those obtained with chemical activation by Na₂CO₃ impregnation. Moreover, activated carbon was used to the H₂S removal, it is also for environment benefit in which air pollution by H₂S emission and impact on human health could be potentially reduced.

Keywords: Activated Carbon, Palm Oil Shell, Chemical Activation, Impregnated Agents and Hydrogen Sulfide Adsorption

1. INTRODUCTION

In Thailand, palm oil is one of primary agricultural products and it generates a large volume of residues. Every year about 0.53 million tons of palm oil shell are produced as by product and inadequately disposed. Only a portion of this residues is used for limited practical applications, such as raw material for the production of fuel and feed stock for obtaining chemical compounds. Palm oil residues result in palm oil mill industry. It is an environmental problem that has been frequently discussed by several sectors of the society. One alternative to attack this problem is by using adsorbents to remove pollutants from several effluents. This has generated an increasing interest in the search for efficient and low cost materials to be used as adsorbents for the elimination of air pollutants.

Activated Carbons (AC) as microporous materials are of the most important adsorbents, which have been extensively used as adsorbents, catalyst and catalyst supports in a variety of industrial and environmental applications. AC is an extremely versatile material as an effective adsorbent with its high adsorptive capacity and high surface area (Şahin and Saka, 2013). AC has been considered for the capture and eventual recovery of metal ions in aqueous industrial discharges for many years and indeed has enjoyed some commercial application. Metal plating and fabrication industries stand to benefit from a fast and robust method of sizing activated carbon adsorption columns for pollution mitigation and/or metals recovery (Banjonglaidee *et al.*, 2008). Among the factors making the activated carbon application attractive are availability, environmentally friendly material, safe and very low cost of the starting materials coupled with its high surface area (Diya'uddeen *et al.*, 2013).

Production of activated carbon can either be through physical or chemical activation. The former involves primary carbonization of raw material (below 700°C) followed by controlled gasification at higher temperatures (>850°C) (Yorgun *et al.*, 2009). Physical

activation of AC consists of two steps (i) the first step is the elimination of most of the hydrogen and oxygen contents by pyrolysis of carbonaceous material at high temperature and inert atmosphere and (ii) the second step is to activate the chars at high temperature and in presence of steam or carbon dioxide as oxidizing gases. Carbon atoms are extracted by these agents from the structure of the porous carbon according to the following endothermic reactions (Arani-Niya *et al.*, 2011):



Chemical activation is impregnated with an activation reagent and heated in an inert atmosphere. The carbonization step and the activation step proceed simultaneously. By dehydration and oxidation reactions of the chemicals, pores are developed. Produced char then washed to rid it from residual impurities (Kılıç *et al.*, 2012). Chemical activation is the process that normally takes place at lower temperature and shorter time than those used in physical activation (Yorgun *et al.*, 2009). Moreover, the advantages of chemical activation are: its low energy and operating cost, higher carbon yields and large surface areas when compared with physical activation. Chemical activation also has better development of porous structure. Knowledge of different variables during the activation process is very important in developing porosity of carbon which is sought for given applications. Chemical activation is held in the presence of dehydrating reagents such as KOH, K₂CO₃, NaOH, ZnCl₂, H₃PO₄ and H₂SO₄ which influence pyrolytic decomposition and inhibit tar formation. These reagents can improve the pore distribution and increase the surface area of adsorbents (Kılıç *et al.*, 2012).

Activated carbons are produced from a variety of organic materials rich in carbon contents like coal, lignite, wood and some types of polymers. Due to increasing usage of AC, exploring the economical

supplies for production of AC is necessary. Although coal and wood are mostly used as precursor, agricultural waste products would be a better choice in some applications (Arami-Niya *et al.*, 2011). Due to high carbon and low ash contents, many of agricultural by-products are appropriate for use as precursors for AC production it is accepted that the differences in material composition, such as lignin, cellulose and holocellulose influence the pore structure and pore size distribution of AC (Arami-Niya *et al.*, 2010).

Hydrogen Sulfide (H₂S) is an extremely toxic and malodorous gas, which is harmful to human health and has detrimental effects on many industrial catalysts, as well as a major source of acid rain when oxidized to sulfur oxide. Many efforts have been focused on H₂S removal from gas as the restrictive emission standards are worldwide enacted. One of the major challenges for natural gas purification is the removal of H₂S. Amine scrubbing along with the Claus process is a dominant technology currently used in industry for H₂S removal in natural gas, especially for high concentration of H₂S removal. But this method loses its efficiency and economic advantage for low concentration of H₂S removal. Alkali-impregnated activated carbons are usually used as low concentration of H₂S oxidation catalysts, due to their high activity and fast kinetics of reaction (Chen *et al.*, 2011).

In this research, palm oil shell as by product palm oil mill industries, was used as a raw material for the production of activated carbon by chemical activation. Palm oil shell is a cheap and abundant agricultural solid waste in tropical countries (Thailand). Palm oil shells have been successfully converted into well-developed activated carbons used for removal of various gaseous pollutants (Guo *et al.*, 2007). On the other hand, they have been done on the utilization of palm oil shell as a raw material of AC production and it was reported that due to its high density, high carbon contents and low ash, this material can be used for the production of good quality AC (Arami-Niya *et al.*, 2010).

This research focuses on different impregnation agents and the ratio of impregnated agent as controlling for activated carbon production and also on its pore volume and removal of H₂S for biogas purification. The aim of this study to achieving the following: (i) Production of activated carbon by chemical activation with Na₂CO₃ and ZnCl₂ as impregnation agent using palm oil shell as a raw material, (ii) analysis of chemical and physical properties for activated carbon product is

performed by ultimate analysis, proximate analysis and surface area, (iii) Hydrogen Sulfide (H₂S) adsorption test.

2. MATERIALS AND METHODS

2.1. Materials

Palm oil shell was used as raw material in this research study. Palm oil shell was collected from Suratthani province, southern Thailand. This raw material was dried at 110°C for 24 h and then crushed with a cutting mill and sieved to a particle size in the range from 1-2 mm. was used for preparation of activated carbon by chemical activation. The standard activated carbon (Commercial grade; code No.CGC-11A) was supplied from C. Gigantic Carbon Co. Ltd. Zinc Chloride (ZnCl₂) and Sodium Carbonate (Na₂CO₃) were dissolved in distilled water to prepare a saturated solution.

2.2. Experimental Method

The preparations of the activated carbon were divided into two steps. The steps are as follows: (i) Carbonization process and (ii) impregnation process. The first step, carbonization process was the first step of the experiment. Palm oil shell was set in a reactor, which had fixed bed design of stainless steel with 54.1 mm internal diameter and 320 mm length, as shown in **Fig. 1**. This process was carried out under constant nitrogen flow (150 cm³/min) at a heating rate of 10°C/min up to 600 °C for 1 h. The second step, char product was directly impregnated with chemical agents, using Zinc Chloride (ZnCl₂) and Sodium Carbonate (Na₂CO₃) solution in three different weight as 1:1, 1:2 and 1:3 of char product: Chemical agent ratio (w/w) and were kept at 80°C for 10 h. The experimental design was reported in **Table 1**. The temperature of activation was raised at 4°C /min up to 700°C, which was maintained for 2 h. After activation, the excess of chemical agent (ZnCl₂ and Na₂CO₃) was removed with a 0.1 M solution of hydrochloric acid. Finally, the sample was then washed to remove excess reagent until there were pH about 6-7 and dried at 110°C for 3 h to obtain the final activated carbons. The samples were classified as AC_Z and AC_Na. The first two characters, AC, represents activated carbon and the third characters, Z and Na, represents ZnCl₂ and Na₂CO₃ impregnation, respectively. The experimental design was operated following condition in **Table 1**.

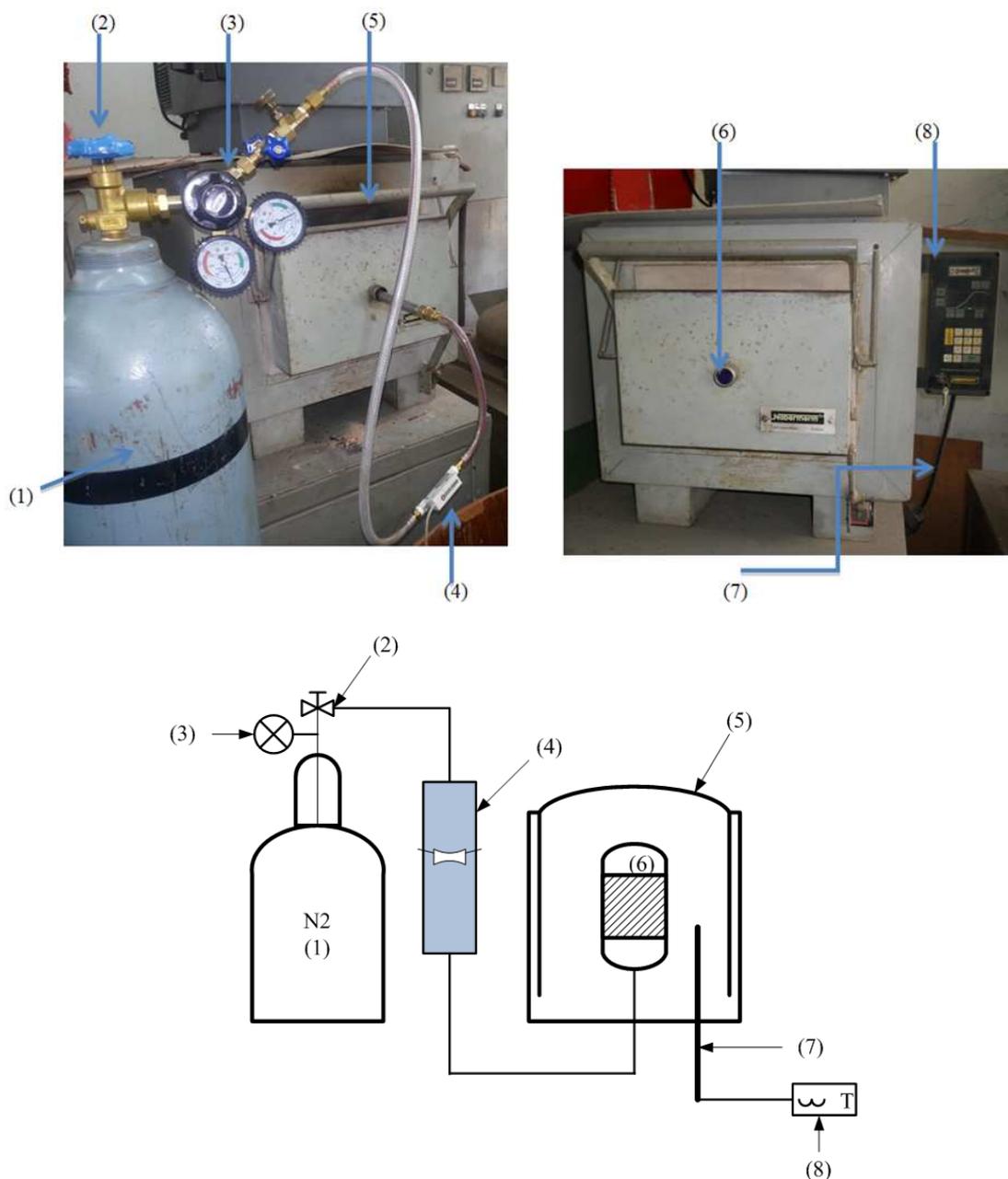


Fig. 1. Experimental set up for activated carbon production; (1) nitrogen gas cylinder, (2) regulating valve, (3) pressure gauge, (4) rotameter, (5) furnace, (6) reactor, (7) thermocouple and (8) temperature control

2.3. Characterization of Impregnated Samples and Standard Activated Carbon

An elemental analysis was carried out using a CHNS/O ANALYZER (PE2400 SeriesII). Gaseous products were freed by pyrolysis in high-purity oxygen

and were chromatographically separated by frontal analysis with quantitatively detected by thermal conductivity detector. Proximate analysis was conducted according to the American Society for Test in and Materials (1997) and the results were expressed in terms of moisture, volatile matter, ash and fixed carbon content.

Table 1. List of experimental design, the ratio of char: Chemical agent, activation temperature and retention time

Samples	Impregnate agent	Char: Agent ratio	Activation temperature (°C)	Retention time
AC_Na11	Na ₂ CO ₃	1:1	700	2
AC_Na12	Na ₂ CO ₃	1:2	700	2
AC_Na13	Na ₂ CO ₃	1:3	700	2
AC_Z11	ZnCl ₂	1:1	700	2
AC_Z12	ZnCl ₂	1:2	700	2
AC_Z13	ZnCl ₂	1:3	700	2

The surface areas of various samples were determined by gas adsorption and desorption (ICG, 2010). The specific surface areas of the samples were calculated using the Brunauer-Emmett-Teller (BET) single-point method. Approximately 0.01-0.03 g of the sample was placed in the sample cell, heated to 623 K and held at that temperature for 6 h under a N₂/He flow. The sample was then cooled to room temperature and dipped into liquid nitrogen. After the adsorption of nitrogen reached equilibrium, the sample cell was then dipped into a water bath at room temperature. The amount of nitrogen desorped was measured by a gas chromatograph (Hussar *et al.*, 2011). The specific surface area of the prepared activated carbons was estimated by the BET method using N₂ adsorption isotherm data.

Yield is usually defined as final weight of activated carbon produced after impregnation, washing and drying, divided by initial weight of raw material. The following relationship is used for calculating the yield of activated carbons (Kılıç *et al.*, 2012):

$$\text{Yield (\%)} = (W_{ac}/W_i) \times 100 \quad (3)$$

Where:

W_i = Mass of impregnated sample

W_{ac} = Mass of the dried carbon after washing

2.4 Hydrogen Sulfide (H₂S) Adsorption Test

Activated carbon with different microporous and mesoporous structure were presented and then impregnated with different content of ZnCl₂ and Na₂CO₃ to remove H₂S in the biogas product at low temperature of ambient temperature (about 30°C). The H₂S adsorption using small column test equipment was conducted on the adsorbents of the activated carbon product. Adsorbent (20 g) of the impregnated activated carbon was placed in a glass column 5 cm diameter, using biogas product (Saitawee *et al.*, 2014) as test gas with the total flow rate 15 cm³ min⁻¹. Biogas detector was used to analyze the concentration of H₂S in the inlet and outlet gases, as shown **Fig. 2**.



Fig. 2. Experimental set up for Hydrogen Sulfide (H₂S) adsorption test

3. RESULTS

3.1. Characteristics of Raw Material

The results of component characteristics of raw materials fed to reactor are summarized in **Table 2**. The ultimate proximate analyses of palm oil shell were as follows (dry wt basis%): Fixed carbon 24.1, moisture 4.2, ash 2.3, volatile 69.4, C 49.90, H 6.37 and N 0.46. A high carbon and low ash content of palm oil shell indicates that the precursor is suitable for activated carbon production. After carbonization process with the temperature of 600°C for 1 h, the volatile content of the chars decreased from 69.4 to 24.34% whilst the fixed carbon content increased from 24.1 to 70.65%. This phenomena was due to the release of volatile matter during physical process (with N₂ inlet during activation process), which subsequently caused an increase in carbon content.

3.2. Effect of Impregnated Ratio on Activated Carbon Product

The results of standard activated carbon and activated carbon product (AC, AC_Z11, AC_Z12, AC_Z13, AC_Na11, AC_Na12 and AC_Na13) samples characterization are presented in **Table 3**. The elemental analysis shows that the nitrogen and hydrogen contents are low.

Table 2. Ultimate and proximate analyses of palm oil shell and char product

Proximate analysis (wt.%)	Palm oil shell	Char product
Moisture	4.20	1.77
Ash	2.30	5.01
Volatiles	69.40	24.34
Fixed carbon	24.10	70.65
Ultimate analysis (wt.%)		
C	49.90	
H	6.37	
N	0.46	
HHV (cal/g)	4735.00	

Table 3. Characteristics of the standard activated carbon and activated carbon product (AC, AC_Z11, AC_Z12, AC_Z13, AC_Na11, AC_Na12 and AC_Na13)

Sample	C (%)	H (%)	N (%)
AC (Standard)	72.58	1.97	0.63
AC_Na13	78.76	0.38	0.77
AC_Na12	76.46	0.48	0.65
AC_Na11	75.19	0.88	0.09
AC_Z13	76.14	0.93	0.72
AC_Z12	75.42	1.32	0.79
AC_Z11	73.98	1.02	0.71

The impregnation process of char produces an increment in the carbon. The carbon content was increased with in increasing impregnate ratio of reagent. The high char product: Chemical agent ratio (1:3) in the AC_Na13 and AC_Z13 samples indicates a degree of aromaticity and suggests that during heating a polymerization takes place. It can be inferred that impregnation process of palm oil shell activated with Na₂CO₃ had carbon content higher than that of palm oil shell activated with ZnCl₂.

The impregnation ratio plays an important role on the yield of activated carbon, as seen in **Fig. 3**, which the yield percentage had been calculated from Equation 1-3. The yields of activated carbons were in the range of 32.3-19.1% for Na₂CO₃ and 25.1-15.2% for ZnCl₂ impregnated samples. It is shown that yield of carbon decreased as the impregnation ratio increases, due to promoting the gasification of char and increasing the total weight by excess chemicals (Kılıç *et al.*, 2012). Moreover, it is observed that the activated carbon for Na₂CO₃ agent is higher than activated carbon for ZnCl₂ agent. The activating agent in the interior of particles produces a dehydrating effect on the already transformed components during the heat treatment (700°C). It is very possible that cross-linking reactions are predominant in this step with the subsequent reduction in the exit of volatile matter and tars, leading to high active carbon yield observed (Yorgun *et al.*, 2009).

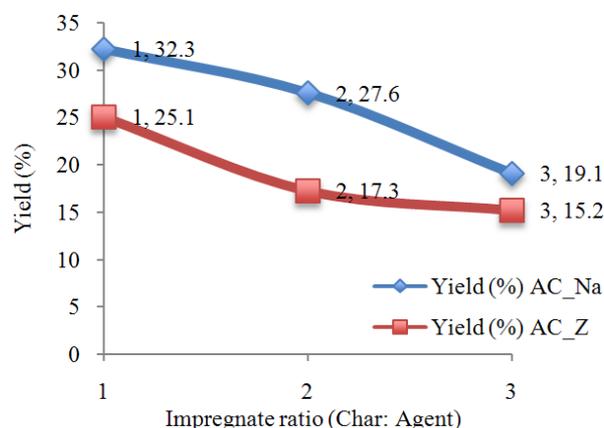


Fig. 3. The impregnation ratio on the yield of activated carbon

The surface area of powdered or porous solid can be calculated from the volume of gas absorbed onto the surface of the solid. In general, solids adsorb gases weakly bound due to Van der Waal's forces only, to cause sufficient gas to be absorbed for surface area measurement. The volume of gas absorbed increases with increasing pressure. The physical absorption of gases by solids increases with decreasing temperature and with increasing pressure. The process is exothermic, i.e., energy is released. The investigative procedure has first to establish what is known as an absorption (or desorption) isotherm. This, quite simply, is a measure of the molar quantity of gas n (or standard volume V_a, or general quantity q) taken up, or released, at a constant temperature usually T by an initially clean solid surface as a function of gas pressure P. Most frequently the test is conducted at a low temperature, usually that of Liquid Nitrogen (LN2) at one atmosphere pressure) (Hussar *et al.*, 2011). Convention has established that the quantity of gas adsorbed is expressed as its volume at standard conditions of temperature and pressure (0°C and 760 torr and signified by STP) while the pressure is expressed as a relative pressure which is the actual gas pressure P divided by the vapor pressure P₀ of adsorbing gas (called the adsorptive prior to adsorption and adsorbate afterward) at the temperature at which the test is conducted. Regardless of how the data are obtained and how manipulated thereafter, all analyses first must establish information in the form of quantity adsorbed (or desorbed) versus pressure; therefore the requirement that these measurements be of the highest quality cannot be overemphasized. These data, having been gathered at one temperature, constitute the adsorption (desorption) isotherm for the material in question. Plots of V_a as the

ordinate against P/P_0 as the abscissa reveal much about the structure of the adsorbing material (called adsorbent) simply from their shape.

N_2 -adsorption/desorption isotherms was using the adsorption process, as shown in **Table 4** and **Fig. 4**; the Brunauer, Deming, Deming and Teller (BDDT) theory, the basis of modern IUPAC classification, was used in this research to characterize the N_2 -adsorption isotherms. As can be seen from **Fig. 4** had very silimar shapes. The nitrogen uptake was significate only in the low pressure where $P/P_0 < 0.2$. At the higher relative pressure ($P/P_0 > 0.2$) had a nearly horizontal plateau, which no futher adsorption was observed and the adsorption curve reached equilibrium at P/P_0 about 0.2. This results indicating type I of isotherm based on the classification of IUPAC, which is characteristic of adsorbents having extremely small pores. On the other hand, in these material, the limiting uptake is controlled by accessible micropore volume rather than by the internal surface area (Diya'uddeen *et al.*, 2013).

Table 4. Adsorption/desorption isotherms of N_2 at 77 K on activated carbon product

AC_Na13		AC_Na12	
P/P0	Volume (cc/g)	P/P0	Volume (cc/g)
0.019971	191.3560	0.026455	196.1758
0.047770	208.8335	0.052620	209.0997
0.077522	219.2354	0.075646	216.0883
0.102370	225.2986	0.098278	221.0802
0.152800	233.5669	0.153870	229.1167
0.200530	238.7769	0.202410	233.6005
0.253250	242.8253	0.255300	237.0867
0.305260	245.9893	0.298650	239.3225
0.404460	250.2994	0.404480	243.5332
0.506110	253.4438	0.506810	246.4125
0.605440	256.1764	0.599140	248.5259
0.707870	258.5759	0.698990	250.5146
0.799140	260.5349	0.799020	252.3995
0.906560	263.0197	0.906320	254.8566
0.990560	272.1485	0.988100	262.2917
0.993380	274.6760	0.994160	267.5799
0.901630	264.8023	0.894140	256.6394
0.793940	262.5644	0.794350	254.6191
0.694080	260.5775	0.693780	252.9189
0.593910	258.6686	0.593590	251.3833
0.495920	256.1600	0.497340	248.7966
0.400110	250.5775	0.399600	243.6848
0.299120	245.9959	0.298380	239.6880
0.195940	238.6833	0.195040	233.3841
0.098881	225.0025	0.097423	221.3403
0.050665	210.6038	0.048466	207.9254
0.019532	191.7933	0.020161	191.7172

The adsorption curve of **Fig. 4** has rises more rapidly in the intermediate zone and shown a wide hysteresis loop instead of nearly retracing the adsorption curve. This behavior is typical of mesoporous and macroporous materials, such as, those that have pores with openings greater than 2 nm (20 Å) and 50 nm (500 Å), respectively. Therefore, pore are likely to have a wide range of sizes and shapes. There were closed in the pressure region near saturation. This shaps reveals that the adsorbing solid contains mesopores with an upper size restriction. For ease of comparison, activated carbon obtained at three different values of char product/chemical agent ratio (1:1, 1:2 and 1:3), when the char to agent ratio was increased by a factor of agent in the range of 1-3, it was found that a volume of N_2 gas adsorption increasing with increased char product: Chemical agent ratio. Frome above results, it was found that the highest volume of nitrogen gas adsorption of AC_Na13>AC_Na12>AC_Na11>AC_Z13>AC_Z12>AC_Z11 were 274.676, 267.5799, 246.6837, 205.6472, 197.4784 and 197.2957 cc/g, respectively. Which, the AC_Na13 and AC_Na12 had the highest volume of nitrogen gas adsorption more than standard activated carbon (AC, 254.7467 cc/g).

The results of mean the BET surface area, total pore volume and micropore volume from three methods are reported in **Table 5**. By obtaining triple measurements under the same experimental conditions, the experimental reponds are randomized. Mean surface area analysis was obtained from BET method, which this results shown that AC_Na13 had the highest mean BET surface area, as shown in **Table 5**. The mean surface area of AC_Na12>AC_Na11>AC_Z13>AC_Z12>AC_Z11 were 725.66, 671.31, 551.05, 533.68 and 523.05 m^2/g , respectively. The data show that surface area of activated carbons increased from 671.31 to 742.34 m^2/g when the char product: Na_2CO_3 ratio increased from 1 to 3; this is different from that char activated with $ZnCl_2$, which the mean BET surface area of standard activated carbon (comercial graded) is lower AC_Na13 and AC_Na12. However, investigating the activation mechanism and understanding this phenomenon are quite meaningful. The value of maen total pore volume of activated carbon increased with an increased char product: Chemical impregnation agent ratio (Na_2CO_3 and $ZnCl_2$) as is a 1:1 to 1:3, from 0.3743 to 0.4181 cc/g and 0.2877 to 0.3137 cc/g, respectively. The average micropore volume were 0.2224, 0.2411, 0.2270, 0.1721, 0.1686 and 0.1546 cc/g of AC_Na13, AC_Na12, AC_Na11, AC_Z13, AC_Z12 and AC_Z11, respectively.

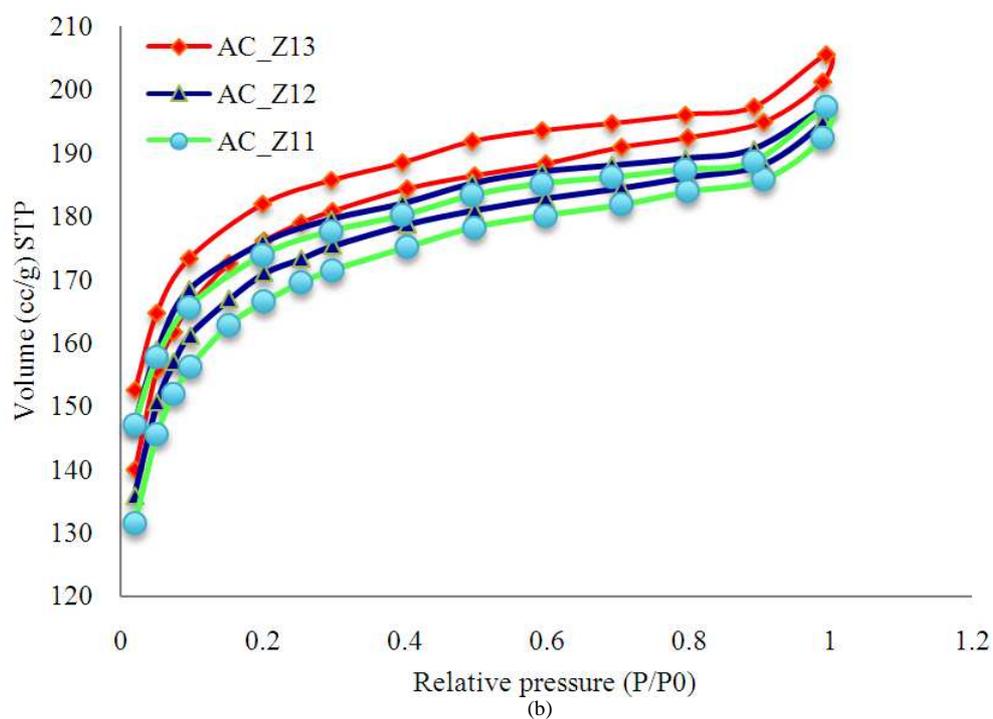
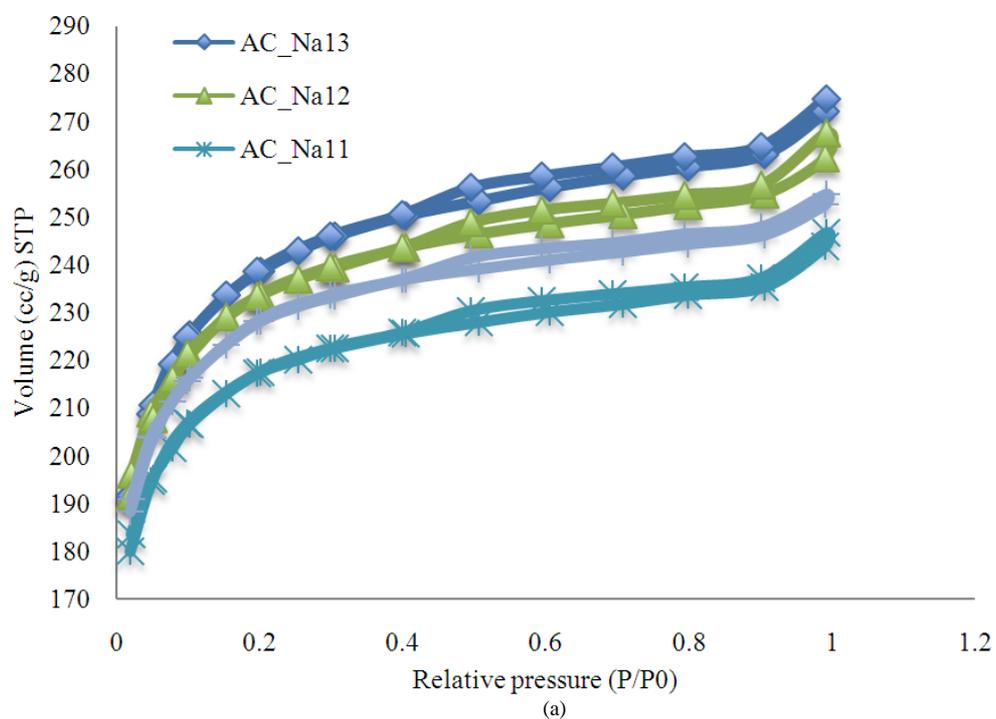


Fig. 4. Adsorption/desorption isotherms of N₂ at 77 K on activated carbon derived from palm oil shell by impregnation with (a) Na₂CO₃ and (b) ZnCl₂

Table 5. Surface area analysis on activated carbon derived from palm oil shell by chemical activation with Na₂CO₃ and ZnCl₂

Sample	BET surface area (m ² /g)	Total pore volume (cc/g)	Micropore volume (cc/g)
AC	707.10	0.3906	0.23890
(Standard)	705.99	0.3888	0.2229
	708.11	0.3967	0.23110
Average	707.07	0.3920	0.23090
AC_Na13	743.71	0.4210	0.23210
	740.11	0.4211	0.22250
	743.21	0.4122	0.21260
Average	742.34	0.4181	0.22240
AC_Na12	726.73	0.4057	0.24300
	725.72	0.3999	0.23900
	724.52	0.4061	0.24110
Average	725.66	0.4039	0.24100
AC_Na11	671.68	0.3774	0.23200
	670.99	0.3779	0.22910
	671.25	0.3677	0.21990
Average	671.31	0.3743	0.22700
AC_Z13	551.04	0.3112	0.17520
	550.99	0.3200	0.16990
	551.11	0.3099	0.17120
Average	551.05	0.3137	0.17210
AC_Z12	534.16	0.3014	0.16910
	533.88	0.3011	0.16800
	532.99	0.2999	0.16880
Average	533.68	0.3008	0.16860
AC_Z11	523.10	0.2976	0.15640
	522.99	0.2856	0.15810
	523.06	0.2799	0.14930
Average	523.05	0.2877	0.15460

The normality of the respond data is assumed. There were analyzed by using statistical software. The results of appying the analysis of variance are shown in **Table 6**, which it was found that a significant interaction the char product: Chemical agent ratio on BET surface area, total pore volume and micropore volume (Sig. <0.05).

The results of gas adsorption studies conducted utilizing a gas biogas on samples were shown in **Table 6**. Hydrogen Sulfide (H₂S) adsorption for AC_Na13 and AC_Z13 showed that the amount of H₂S adsorbed increased progressively with Na₂CO₃ impregnation. The total amount of H₂S adsorbed followed the order of AC_Na13>AC>AC_Z13. The average capacity of H₂S adsorbed by AC_Z13 was 241.67 ppm. While that of AC_Na13 was 247.33 ppm, which was better agreed with AC (245 ppm) as compared with other sample (as can seen in **Table 7**). These results show that the activated carbon could absorb the H₂S, but the adsorption capacity of impregnation ratio these result confirmed by pore

volume analysis, showing the increase pore volume with increased char product: Chemical agent ratio.

4. DISCUSSION

The results of this research showed that palm oil shell can be successfully converted into activated carbon with surface area properties. It was found that the amount of Na₂CO₃ and ZnCl₂ used for chemical activation controls the characteristics of the carbon contents including BET surface area, total por volume, micro pore volume and H₂S adsorption. Increasing the amount of chemical agent (Na₂CO₃ and ZnCl₂) used for chemical activation; char product: Na₂CO₃ and char product: ZnCl₂ ratio from 1:1 to 1:3 resulted in 9.69 and 5.07%, respectively, increase in the BET surface area. These findings are in agreement with the few reports in the orther hand that have addressed the possibility of using ZnCl₂ activation (Yorgun *et al.*, 2009). In particular, Arami-Niya *et al.* (2010) reported activation of palm oil shell with ZnCl₂, which chemically activated samples without extra heat treatment showed an increase in the surface area and pore volume with the increase in the mass ratio of ZnCl₂, methan adsorption did not improve at any ratio (less than 13 cm³/g). There are various methods of determing surface are of an adorment which include water and gas adsorption, inverse of iodine value and BET machine (Diya'uddeen *et al.*, 2013). The most reliable and recognized internationally results are those obtained from BET machines.

Moreover, Arami-Niya *et al.* (2011) was presented chemically ACs from palm oil shell as a precursor have been prepared using low concetration of zinc chloride or phosphoric acid as activating agent, which combined physical and chemical activation of palm shell revealed that H₃PO₄ impregnated samples attained better activation rates than those prepared using ZnCl₂ or physically samples.

Experimental results indicate that the suitable impregnated agent was Na₂CO₃ to prepare activated carbon. Which chemical activation is widely employed, mainly using the reagents ZnCl₂ or Na₂CO₃ as activating agents. Although the Na₂CO₃ has cation similar characteristics to ZnCl₂, in aqueous solution the Sodium cation (Na⁺) is bigger than the Zinc cation (Zn²⁺), which it is 99 and 83 pm, respectively. And this opens up the possibility of producing activated carbon with higher pore volume upon their activation. On the other hand, the zinc cation present in aqueous solution is a well-known pollutant (Oliveira *et al.*, 2009).

Table 6. ANOVA tables from BET surface area, Total pore volume and Micro pore volume respectively versus char product to chemical agent ratio

ANOVA	Sum of squares	df	Mean square	F	Sig.
BET between groups	168265.295	6	28044.216	29506.029	0.000
Within groups	13.306	14	0.950		
Total	168278.602	20			
Total between groups	0.052	6	0.009	301.294	0.000
Within groups	0.000	14	0.000		
Total	0.052	20			
Micro between groups	0.023	6	0.004	115.146	0.000
Within groups	0.000	14	0.000		
Total	0.023	20			

Table 7. The value of H₂S adsorption

Samples	Amount of H ₂ S from biogas before adsorption (ppm)	Amount of H ₂ S from biogas after adsorption with activated carbon (ppm)
AC	266.00	23.00
	267.00	22.00
	269.00	22.00
Average	267.33	22.33
AC_Na13	265.00	19.00
	268.00	20.00
	266.00	18.00
Average	266.33	19.00
AC_Z13	269.00	29.00
	268.00	26.00
	270.00	27.00
Average	269.00	27.33

As indicated by **Table 6** there were different the value of H₂S adsorption, due to different chemical impregnated char product. The different impregnated agent on char product for H₂S adsorption of AC_Na13 and AC_Z13 were the results of the distinguishably different of the surface area. For the AC and AC_Z13 the activities of H₂S dissolve and dissociation are refrained, which slows down the removal rate, due to the hydrophobic property of the carbon surface water film is difficult to be formed when the relative pressure of water is low. While, AC_Na13 an additional factor that Na₂CO₃ easily absorbs water should be considered. A basic solution film is formed on the surface of the AC_Na13, which promotes the dissociation. The present results in practice suggest that activated carbon production can be optimized if a impregnated with charproduct: Na₂CO₃ (1:3) can be used effectively as a means of higher surface area and H₂S adsorption.

5. CONCLUSION

The experimental study two contributions. First, it provides the palm oil shell from palm oil mill: As raw material in producing activated carbon by chemical activation. Activated carbon was prepared from char product of palm oil shell using Na₂CO₃ and ZnCl₂

impregnated for 1:1 -1:3 of char product: Chemical agent and there was activated at 700°C activation temperature for 2 h. Second, it is indicated that the activated carbon performance for removal Hydrogen Sulphide (H₂S). The results of these research showed that palm oil shell can be successfully converted into activated carbon with BET surface area, total pore volume and micropore volume. It was found that BET surface area, total pore volume and micropore volume were increasing with increased the char product: Chemical agent ratio (1:1 to 1:3). Moreover, AC_Na13 has good chemical and physical properties such as chemical content and surface area, which showed that the highest H₂S adsorption (247.33 ppm). The carbon content of AC_Na13 and AC (Standard activated carbon) were 78.76 (wt%) and 72.56 (wt%), respectively. The BET surface area of AC_Na13 and AC measured by N₂ adsorption at 77.4 K were found 743.71 and 707.10 m²/g, respectively. It indicated the activated carbon produced from palm oil shell lies in the range of commercial activated carbon. The impregnation with Na₂CO₃ results in the high concentration of Hydrosulfide Ion (HS⁻) and enhances the oxidation of H₂S (Xiao *et al.*, 2008). The high catalytic activity allows the pores to be fully utilized, which is the reason for the high sulfur capacity of AC_Na13. It had H₂S adsorption more than commercial

activated carbon (1%). However, the extra installation costs and process complexity in biogas purification system concept should be evaluated with the economic gain achieved due to extra biogas produced. Accordingly, the activated carbon produced from palm oil shell can be used as adsorbents for various environmental application including removing H₂S compound from industrial production, which this is the developing research in the future for developed purify system. Therefore, Na₂CO₃ was found more effective than the other agents as chemical reagent under same conditions in terms of high BET surface area, total pore volume, micropore volume and H₂S adsorption. In these case, H₂S adsorption was operated on lab-scale, due to there were used in biogas production on lab-scale. In future research, other impregnants and activated carbons will be used in studies similar to those described in this research. Moreover, H₂S adsorption will be operate in large scale for adsorption from source of biogas production on industrial.

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