

Using granular activated carbon prepared from oil palm shell by ZnCl_2 and physical activation for methane adsorption

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ABSTRACT

Granular activated carbons for methane adsorption have been prepared by impregnation of oil palm shell with various solutions of ZnCl_2 followed by heat treatment at 500°C under a flow of nitrogen. For this precursor, large micropore volume of micropores (with a very small volume of mesopores and macropores) was obtained with intermediate ZnCl_2 mass ratio. Methane capacity at 800 mmHg was in the range of $10\text{--}12\text{ cm}^3/\text{g}$. All the samples were further activated by reaction under a flow of carbon dioxide. Although such activation resulted in a decrease in the BET surface area, average pore width, micropore and pore volume (except very low impregnation ratio, $X_{\text{Zn}} = 0.15\text{ g/g}$), however, there was a 100% net increase in the methane capacity.

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1. Introduction

Activated carbon (AC) as a microporous material is one of the most important adsorbents commonly used in industries. Beside high surface area and micropore volume, favorable pore size distribution makes this group of adsorbents suitable for a variety of applications such as separation, storage and purification of gases and adsorption of solutes from aqueous solutions. Moreover, they are used as catalysts and catalyst supports [1].

A variety of carbonaceous raw materials are used for the production of ACs. Physical and chemical characteristics of the raw material and the preparation methods have significant effect on the quality and properties of ACs. 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, i.e. lignin, cellulose and hemicellulose influence the pore structure and pore size distribution of AC [2]. In this study, palm shell as by product of the palm oil industries, was used as a starting material for the production of AC. Many previous studies have been done on the utilization of palm shell as 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 [3–5]. Palm shell is abundantly available mainly in South East Asia (Malaysia, Indonesia and Thailand). For example in Malaysia, the world largest producer of palm oil, approximately 2 million tons

of palm shell produced annually. The lignocellulosic contents of oil palm shell that was determined by Daud and Ali [2], is shown in Table 1.

In addition, pore structure and adsorption properties of ACs are highly dependent on the activation process. Generally, there are two conventional methods to produce AC namely; chemical and physical activation. In the chemical activation process, impregnation of the precursors with a solution of the agent followed by conventional heat treatment. First the dehydrating agent (for example, zinc chloride, phosphoric acid or potassium hydroxide) influences the pyrolytic decomposition of the starting materials. The formation of tars occurs in the second stage, during the heat treatment (carbonization process) [6]. Therefore, the heat treatment influences the carbonization process, enhancing the yield of carbon and generating the porosity, which becomes reachable after the removal of the chemicals by washing [7,8]. Consequently, the alternation of the chemical/precursor ratio allows the adjustment of the porosity in the produced AC. Among the chemical agents zinc chloride is widely used for the production of ACs, especially for lingo cellulosic and cellulosic precursors [9–11].

Physical activation of AC consists of two steps: pyrolysis of carbonaceous material at high temperature and inert atmosphere to eliminate most of the hydrogen and oxygen contents followed by activation at high temperature and in presence of oxidizing gases. Carbon atoms are extracted by these agents (steam or carbon dioxide) from the structure of the porous carbon according to the following endothermic reactions [12]:



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Table 1
The lignocellulosic contents of oil palm shell (wt.%)^a.

Cellulose	Holo-cellulose	Lignin
29.7	47.7	53.4

^aDaud and Ali [2].

Common physical and chemical activation have been widely used for the preparation of high surface area AC. On the other hand, combination of chemical and physical activation is another technique to prepare AC. Production of ACs by chemical activation using zinc chloride, in an inert atmosphere such as nitrogen had been carried out by many researchers [11,13]; however, combination of this method with physical activation is rarely reported in the literature. Based on the observations in this field, there are scarce studies that use combination of these two methods [9,14] and to the authors knowledge, there is no information concerning the effects of using this method with oil palm shell as raw material.

The objective of the present study is to prepare microporous ACs from lignocellulosic materials with high surface area and narrow micropore size distribution (MPSD) for methane adsorption. The effects of different ratios of zinc chloride/precursor at the appropriate activation time on the pore structure and methane capacity of palm shell based AC were studied. In addition, the prepared samples were heated under CO₂ to investigate the changes in the surface morphology after additional physical activation. This is aimed at improving microporosity and controlling its pore size distribution to increase the methane adsorption of the produced AC.

2. Experimental methodology

2.1. Preparation of activated carbon

Raw oil palm shells were crushed using a grinder and sieved to a particle size in the range of 1–2 mm, then washed carefully with abundant amount of distilled water and dried at 110 °C for 24 h. For chemical activation the oil palm shell was first impregnated with a standard solution of chemicals (2 ml per gram of the precursor). The concentration of solution was tuned to provide the required ratio of zinc mass per gram of precursor that is indicated as X_{Zn} . A mixture of precursor and zinc chloride solution was stirred for 2 h at 85 °C and then the temperature was increased to the boiling point until complete dryness.

The resulting sample was placed in a vertical stainless-steel type 310 reactor (internal diameter of 63 mm) which was inserted in an electric furnace (Carbolite VST 12/900). The system can be operated to a maximum temperature of 1200 °C. A temperature controller with a K-type thermocouple is used to fix the temperature inside the reactor. The impregnated material with ZnCl₂ was heated up to 500 °C at a heating rate of 10 °C/min. The sample was activated at the desired temperature for a hold time of 2 h under N₂ (99.95% purity) flow rate of 100 ml/min and then cooled down to room temperature. The chemically produced AC was washed several times with abundant amount of distilled water to remove the excess activating agent and increase the pH over a value of 6. To increase the solubility of Zn, ACs were first washed with 0.1 N solution of HCl followed by distilled water washing until the absence of chloride ions in the washing water as indicated by its pH.

For additional physical activation, the products of chemical activation were first carbonized at 900 °C for 1 h with a heating rate of 10 °C/min in presence of nitrogen as inert gas (flow rate of 2 l/min) [2,15]. Following the carbonization, the resulting products were activated under a carbon dioxide stream in the smaller vertical reactor (25 mm internal diameter). AC samples of 40 g were heated up

to 850 °C (heating rate of 10 °C/min), then carbon dioxide stream with flow rate of 100 ml/min was used. To find out the best physical activation time, the chemically activated sample with a solution of $X_{Zn} = 0.25$ was heated 1–7 h to obtain ACs with different burn-off degrees and methane adsorption [9]. The burn-off degree of carbon, θ (wt.%) was calculated by Eq. (1) where W_0 is the initial weight and W_f is the final weight of the sample.

$$\theta = \frac{W_0 - W_f}{W_0} \times 100\% \quad (1)$$

Used CO₂ was preheated during physical activation, using a stainless-steel pipeline which passes through an oven (Heraeus D-6450) to heat the gas up to 850 °C and then fed to the reactor. The commercial granular palm shell based activated carbon was obtained from Bravo Green Sdn Bhd, a local manufacturer based in Sarawak, Malaysia. This activated carbon was first sieved to the desired particle size (1–2 mm) and then washed and dried at 110 °C overnight.

In order to make the description of the prepared systems easier, the following nomenclature is used. Z represents activated carbons prepared by chemical method using zinc chloride as agent. CZ resembles the chemically activated carbons in which activated again under CO₂ flow. Chemical ratio (ratio of zinc mass per gram of precursor) is displayed as a suffix for the two letters (example: CZ0.53 symbolizes the chemically activated sample with further activation under carbon dioxide in which the $X_{Zn} = 0.53$ g Zn/g precursor.)

2.2. Characterization

The characterization of AC samples was carried out using N₂ adsorption/desorption at –196 °C using Micromeritics ASAP 2020 surface area analyzer to assess the pore morphology of the produced activated carbons. The BET surface area, micropore and total pore volume, and pore size distribution were obtained by analyzing N₂ adsorption–desorption. The specific surface areas were determined according to the BET method at the relative pressure in the range of 0.05–0.30 [16]. Pore volume was directly calculated from the volume of nitrogen held at the highest relative pressure ($P/P_0 = 0.99$). The volume of micropore was estimated using the Dubinin–Radushkevich (DR) equation [17]. Pore size diameters were determined using the Dollimore–Heal adsorption pore distribution method.

Proximate analyses were carried out according to ASTM D 7582-10 and the results were expressed in terms of moisture, volatiles content, fixed carbon and ash contents. The sample was heated from room temperature to 110 °C under nitrogen atmosphere until complete dehydration for the determination of the moisture content. Then the temperature increased rapidly to 950 °C and held for 7 min. Volatile matters were determined from weight loss after dehydration. Then the temperature was decreased to 650 °C and the atmosphere was changed to oxygen gas. Weight loss during the oxidation stage shows carbon content. Ash constituted the remaining mass at the end of the analysis. Ultimate analysis was carried out using CHNS/O Analyzer model 2400 to determine fixed carbon, hydrogen, nitrogen and oxygen of the samples.

Adsorption isotherms of methane were recorded using a Micromeritics ASAP 2020 adsorption Analyzer at 30 °C and pressure range of 0–800 mmHg.

3. Results and discussion

3.1. Effect of activation time

Table 2 shows the surface area, micropore and pore volume of CZ0.25 samples prepared at different physical activation time.

Table 2

Preparing condition, production burn-off, surface area, pore volume and micropore volume of activated carbons.

Sample	Activation time (h)	Burn-off (%)	Surface area (m ² /g)	Pore volume (cm ³ /g)	Micropore volume (cm ³ /g)
CZ0.25	1	0	727.91	0.35	0.36
CZ0.25	3	7.2	736.84	0.36	0.38
CZ0.25	5	11.6	863.08	0.43	0.44
CZ0.25	7	12.61	1118	0.51	0.42

Although the CZ samples possess expected surface area values within the normal range, all of them show high relative micropore volume. The sample prepared after 5 h activation shows higher value of micropore volume compared to other samples in this series. As the time of activation increases from 1 to 3 h, micropore volume values show a small difference. However, there is an obvious increase in micropore volume values and BET surface area amount from 3 to 5 h of heat treatment under CO₂. It can also be observed that all of the products reveal low mesopore volume that can be because of the using carbon dioxide as activating agent. Larger mesopore volume could be produced if steam was used as the activating agent [18].

Fig. 1 shows the methane adsorption at pressures up to 800 mmHg and 30 °C on CZ0.25 activated under flow of CO₂ for different activation time. Less methane adsorption is expected when the adsorbent has low surface area and not enough well developed pores, as the case of 1 h activation. By increasing the activation time and burn-off up to 5 h there would be an increase in methane adsorption. Both 5 and 7 h cases attained same amount of adsorbed methane at low pressure. But they show different behavior at high pressure, when 7 h activated sample shows lower methane adsorption. This is mostly due to its lower micropore volume.

So, it can be concluded that the chemically activated sample (Z0.25) shows high surface area, pore volume and methane adsorption after 5 h of heat treatment under CO₂.

3.2. Effect of ZnCl₂ ratio

3.2.1. Nitrogen adsorption

Fig. 2 presents the N₂ adsorption isotherms for the chemically activated carbons. Similar to typical AC, Z0.15 shows Type I isotherm with a sharp “knee” form at the low relative pressure that has a tendency to turn into almost a horizontal plateau at higher relative pressure. The type I isotherm indicates highly microporous adsorbents with relatively small external surface at low relative pressure of <0.1 [19]. The commercial AC has a less steep Type I

isotherm with a slightly sloped-up plateau that is characteristic of an AC with a heterogeneous microporosity and a high fraction of mesoporosity. Evidently, Z0.15 is a microporous activated carbon, and presented here as a reference. At low concentration of zinc chloride (Z0.15 and Z0.28) the adsorption isotherms are similar and the difference is in the uptake at low relative pressure ($P/P_0 \leq 0.1$); indicating highly microporous materials with a narrow pore size distribution. The adsorption capacity increases with increasing chemical ratio and this is because of a widening of the microporosity. It is clear that Z0.4 adsorbs more nitrogen as compared to Z0.28, however their isotherms are similar except at low relative pressure. In addition, these two samples show very near adsorption isotherms compared to other samples, indicating almost a similar porosity.

At a higher ZnCl₂ concentration (Z0.53) the isotherm is analogous to previous isotherms at very low relative pressure and parallel at relative pressure above $P/P_0 = 0.4$. This means that the differences are in the large size micropores [11]. However, the increase in nitrogen uptake on Z0.65 is continued almost all over the entire pressure range, so the adsorption isotherms take a shape similar to the commercial AC. Large amount of nitrogen was adsorbed at low relative pressures indicating the character of Type I, and a gradual increase in nitrogen uptake at the other pressures showing the growth of small size mesoporosity. This development of porosity has been described for other lignocellulosic materials [20].

Another observation from Fig. 2 is that during activation, the zinc chloride acts as a dehydration agent for the impregnated samples. The movement of the volatiles through the pore passages is not hindered by ZnCl₂ impregnation and subsequently during activation volatiles will be released from the carbon surface. Increase of the ZnCl₂ mass ratio makes the release of volatiles matter easier and consequently results in a higher nitrogen adsorption of activated carbon. Similar results were reported in other studies on the production of ACs from lignocellulosic materials by chemical activation [21,22].

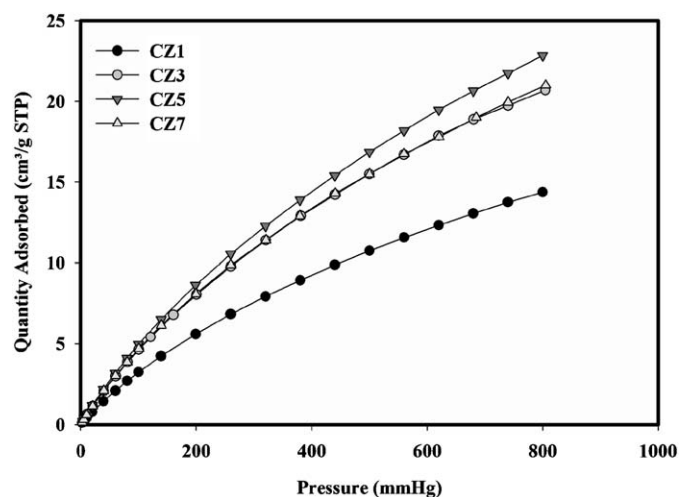


Fig. 1. Methane adsorption isotherms of CZ0.25 series with different activation time at different pressures.

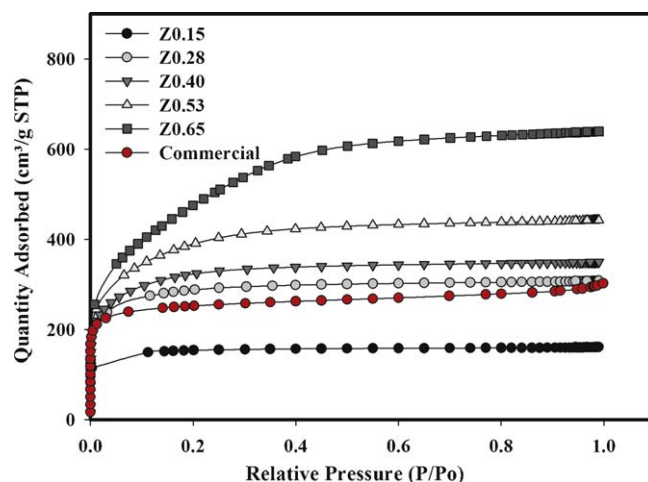


Fig. 2. Effect of ZnCl₂ to palm shell mass ratio on the N₂ adsorption isotherms of chemically activated carbons.

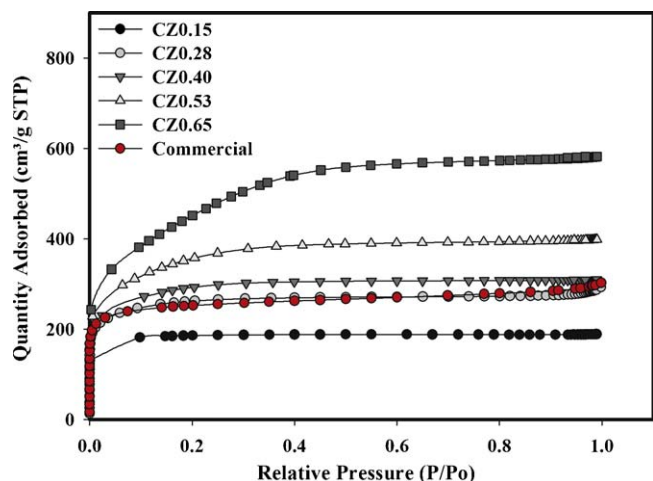


Fig. 3. Effect of ZnCl_2 to palm shell mass ratio on the N_2 adsorption isotherms of chemically activated carbons followed by extra physical activation.

Nitrogen isotherms of CZ series are depicted in Fig. 3. The curves trends for volume adsorbed are very similar to the Z series. All of the adsorption curves are Type I isotherms, implying that the carbon materials are highly microporous. The evolution of the isotherms shapes for this series is as follows: As the ZnCl_2 ratio was increased from 0.15 to 0.28 g/g, the adsorption capacity was increased as well, however, differences in the isotherms are noticed at very low relative pressure. The adsorption capacity increases with the mass ratio up to CZ0.65 for all relative pressures which indicates the widening of microporosity. Due to similar isotherms type for all of the CZ series, it can be concluded that all of these samples include micropores, however, the size of these micropores widens with the increase of the mass ratio. As the ratio increase from 0.4 to 0.65, three other samples show an increase in nitrogen adsorption especially at relative pressures lower than 0.4 and their isotherms become almost parallel at higher pressure range showing the differences in the large size micropores.

Within the range of mass ratios studied, the general trends for the two activation methods are quite similar. Increasing the mass ratio from 0.15 to 0.65 increases the nitrogen adsorption of the activated carbon in both methods. Comparing with the Z series, it is noticed that after extra physical activation, the capability of nitrogen adsorption for all the samples declines except for CZ0.15 which shows some increase in adsorption. Consequently, the gasification of volatiles under CO_2 activation was not so severe. The mechanism involved in physical activation depends on the trajectory that the carbon dioxide molecule takes to reach the internal carbon atoms and its ability for reaction at that site to remove carbon atoms [12]. Lua and Guo [23] pointed out that the best conditions for the physical activation of oil palm shell using CO_2 can be achieved at 850°C and gas flow rate of $100\text{ cm}^3/\text{min}$. Therefore, carbon dioxide molecules that can diffuse and reach to the internal carbon atoms are enough for the reaction. So it can be said that higher percentage of cellulose and holo-cellulose contents in Z0.15 (because of low proportion of chemical) causes the elimination of more volatile contents and the development of pore structure after thermal treatment. Putting another way, low cellulose and holo-cellulose contents of chemically activated carbons (except Z0.15) after the carbonization process and the lack of active sites for reaction with CO_2 are two main reasons that can describe the behavior of carbons after activation with CO_2 . Subsequently, further thermal activation causes pore shrinkage and the creation of small micropores. These observations are consistent with the analysis result of nitrogen adsorption in Figs. 2 and 3 at higher ZnCl_2 ratio. Comparison with the isotherms of Z0.65 and CZ0.65 especially at higher

relative pressure indicates that after physical activation, although total pore volume and mesopore percentage decrease, the sample is still microporous.

3.2.2. Textural characterization

The effects of ZnCl_2 ratio on the textural characteristics of activated carbons prepared with and without further physical activation are shown in Table 2. At each method of activation, as the mass ratio of ZnCl_2 increase, there is some increase in the BET surface area, micropore and nonmicropore volume. However the rates of change are not similar for different samples. The difference between micropore and pore volume can be assumed as nonmicropore volume while the percentage of micropore would be based on the total pore volume. The explanation for this increasing pore volume and surface area is similar to nitrogen adsorption isotherms in Figs. 2 and 3. So it can be said that increasing the amount of ZnCl_2 improves the removal of tar from the structure and raises the release of volatiles.

Changes in characteristics of activated carbons can be categorized into two different trends in both cases; the first one is from 0.15 to 0.53 g/g and the second one is from 0.53 to 0.65 g/g. Increasing the ratio from 0.15 to 0.53 g/g causes continuous increase in BET surface area, pore volume, micropore volume and average pore width for both methods. In this trend, because of weak inhibition of tar creation by ZnCl_2 , the release of volatiles from the carbon structure is lower. This is the reason for the restricted formation of nonmicropores and development of mostly micropores. From 0.53 to 0.65 g/g, it is observable that stronger inhibition of tar creation by ZnCl_2 causes higher volatile release and then considerable increase in the widening of the pores. Beside the creation of new micropores, some of the produced micropores would be converted to mesopores and even macropores. Therefore, in both methods as the micropore volume increases, the mesopore volume and average pore width increase rapidly as well. Similar results for the pore widening were reported by other researchers [22,24]. In general, the activated carbons produced with chemical ratios between 0.15 and 0.53 g/g are highly microporous though at higher rate, the micropore percentage decreases sharply (Table 3).

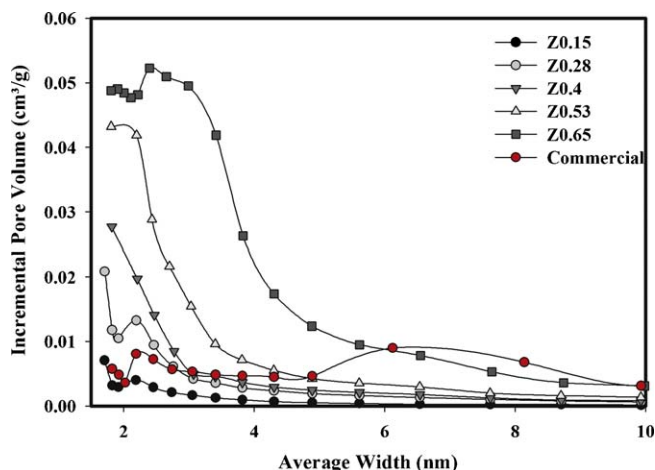
In evaluating the effects of ZnCl_2 ratio on the characteristics of the produced activated carbons, the chemically activated samples show higher BET surface area, average pore width and micropore and nonmicropore volumes in most of the cases than those treated with extra physical activation. As it was mentioned previously, for the chemical ratios between 0.15 and 0.53 g/g except CZ0.15, further thermal treatment of chemically activated samples in addition to the creation of small micropores, causes pore shrinkage. This initial decrease in surface area and pore volume in the final sample was also reported by Ahmadpour and Do [24]. They rationalized this effect due to the higher temperature of gasification compared to the temperature of carbonization in the chemical activation step. In the case of CZ0.15, although BET surface area and pore volume increase, average pore width decreases. This results show that at low concentration of ZnCl_2 , there are more active sites for the reaction of CO_2 as oxidizing gas. This is in good agreement with Prauchner and Rodríguez-Reinoso [9] study. They pointed out that using small proportion of ZnCl_2 creates an incipient narrow microporosity. Subsequent thermal activation allows to properly develop this initial pore structure.

It is noticeable in CZ0.53 and CZ0.65 that after physical activation, the BET surface area and micropore volume almost have the same values. On the other hand, the nonmicropore volume and average pore width increase. Hence, it can be assumed that after the mass ratio of 0.53 g/g there will not be any increase in surface area and moreover widening of the pores will occur.

Table 3

BET surface area, pore and micropore volume and average pore width of prepared activated carbons with and without physical activation.

Sample	Surface area (m ² /g)	Pore volume (m ³ /g)	Micropore volume (m ³ /g)	Average pore width (nm)	Average pore hydraulic radius (nm)
Z0.15	484.1	0.25	0.25	2.05	0.31
Z0.28	926.8	0.48	0.47	2.05	0.38
Z0.40	1078.2	0.54	0.54	2.06	0.39
Z0.53	1307.7	0.68	0.67	2.09	0.41
Z0.65	1671.6	0.99	0.87	2.36	0.49
CZ0.15	583	0.43	0.423	1.99	0.29
CZ0.28	869.9	0.45	0.425	2.02	0.34
CZ0.40	947.6	0.48	0.48	2.03	0.37
CZ0.53	1178.9	0.62	0.61	2.08	0.41
CZ0.65	1193.2	0.67	0.62	2.32	0.45
Commercial	837.8	0.47	0.4	–	0.3

**Fig. 4.** Effect of ZnCl₂ to palm shell mass ratio on the pore size distributions of the chemically activated carbons.

3.2.3. Pore size distribution

Generally, the pore size distribution is one of the characterizations of porous material that represents the structural heterogeneity and represents a model of the solid internal structure. Within the porous solid there are the complex void spaces constructed from an equivalent set of noninteracting and regularly shaped model pores [25]. The pore size distribution is defined as the degree of heterogeneity in structure of the porous material and closely related to both equilibrium properties and kinetics of these materials used in industrial applications. The pore size distribu-

tion of the samples was evaluated by Dollimore–Heal (DH) method using Harkins and Jura equation ($t = [13.99 / (0.034 - \log(P/P_0))]^{0.5}$). The DH pore size distribution of activated carbons without and with extra physical activation is shown in Figs. 4 and 5 respectively. It is apparent from Fig. 4 that the ZnCl₂ impregnation had significant effect on the pore structure of the produced ACs. Comparison between produced ACs and commercial AC shows that after chemical activation strong peaks are observed for all impregnation ratios used in the study while the commercial AC shows a heterogeneous pore size distribution. With the increase of impregnation ratio, creation of micropore and widening of micropore to mesopore also occurs. Fig. 4 shows that the activated carbons consists mainly of pore width around 2.05–2.09 nm, mostly micropores and some mesopores except for Z0.65. As it was noticed in Table 2, at Z0.65 the pore with size more than 2 nm (mesopore) is much more abundant.

For activated carbons produced with extra physical activation, pore size distribution is similar to the ACs without further thermal treatment at each chemical ratio (Fig. 5). However, predominant pore width shifts to smaller pore sizes and the average pore width decreases (as it was reported in Table 2). This indicates that the produced ACs with this method are more microporous in comparison with merely chemically activated series. At a mass ratio of 0.65 g/g, although there is widening in pores compared to CZ0.53, it still shows narrower pore size distribution than Z0.65.

3.2.4. Methane adsorption

Gas adsorption measurements for pure methane were conducted on Micromeritics ASAP 2020 adsorption Analyzer at 30 °C and pressure range of 0–800 mmHg. Results are presented for zinc chloride impregnated ACs and further physical activated samples in

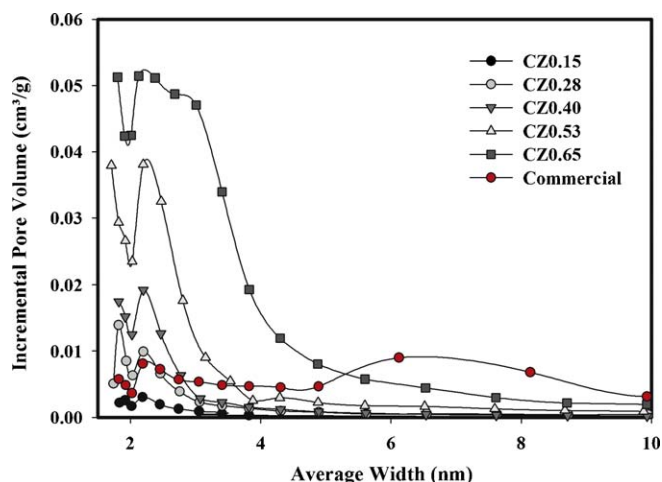
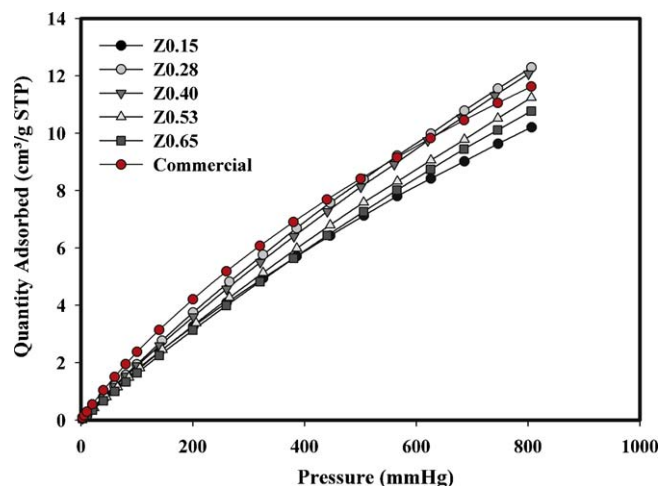
**Fig. 5.** Effect of ZnCl₂ to palm shell mass ratio on the pore size distributions of the chemically activated carbons followed by extra physical activation.**Fig. 6.** Methane adsorption isotherms of ZnCl₂ activated carbons at different pressures.

Table 4

Proximate and ultimate analysis of oil palm shell, chemically activated carbon (Z0.28) and chemically and physically activated sample (CZ0.28).

Sample	Proximate analysis (%)				Ultimate analysis (%)			
	Moisture	Volatile	Fixed carbon	Ash	C	H	N	O
Palm Shell	4.7	74.3	13.8	7.2	54.7	7.49	2.03	35.6
Z0.28	2.5	14	73.6	9.9	81.84	2.5	0.51	15.05
CZ0.28	2.5	10.9	76	10.6	83.4	0.46	0.43	15.67

Figs. 6 and 7, respectively. Due to the fact that methane adsorption consists of physisorption and chemisorption on the surface of activated carbon [26], both of these phenomena were analyzed for each sample. However, the analysis results from the ASAP 2020 analyzer showed that the adsorption and physisorption isotherms are similar, therefore it can be concluded that there is no chemisorption of methane on the surface of produced activated carbons. Initially, methane adsorption was measured for chemically activated samples at different mass ratios. Due to incomplete activation and low surface area, pore and micropore volume of Z0.15, it was expected to show the lowest methane adsorption. The highest methane adsorption was related to Z0.28 and Z0.40. Based on similarity of Z0.28 and Z0.40 in the BET surface area and pore characteristic, they show common methane adsorption behavior. Also, it can be seen that commercial activated carbon showed very similar methane adsorption results to Z0.28. This similarity could be due to the near textural form of this activated carbon that was shown in nitrogen adsorption results such as textural characteristics and pore size distribution.

In addition, it is noticeable that after the mass ratio of 0.28, increasing the ratio causes a decrease in methane adsorption. This decrease is due to the widening of micropores and the creation of mesopores. The sample Z0.65 shows the highest surface area and pore volume. Because of the high percentage of mesopores and wide micropores, the amount of methane adsorption is low. Therefore, methane adsorption in chemically activated carbons not only depends on the development in porosity, but also changes by width of micropores.

Fig. 7 shows the volumetric methane uptake for extra physical activation of the samples presented above. The value of methane adsorption depends on the micropore volume and micropore size distribution. The results show that, even though the values of methane uptake decrease with the mass ratio of zinc chloride, the optimum degree of activation corresponds to an intermediate chemical ratio of 28 g/g. A higher and lower ratio of ZnCl_2 gives a lower amount of methane adsorbed on a volumetric basis due

to pore size distribution that is too wide or not developed, respectively for this methane adsorption application. This leads to a higher or lower average pore width. The important effect of the micropore size distribution on methane adsorption is clear in this set of experiments.

By comparing the results presented in Figs. 6 and 7, it can be seen there is significant difference in methane adsorption between the samples prepared with and without extra physical activation. After the thermal treatment under CO_2 , the amount of methane adsorption of each sample shows an increase to around twice their corresponding values before physical activation. The highest adsorption level reaches a maximum of $27 \text{ cm}^3/\text{g}$ in CZ0.28. Although Z0.15 showed low amount of methane adsorption compared to other samples, this sample shows some increase in methane capacity after physical activation. Extra heat treatment in the physical activation stage induces the development of micropores. CO_2 activation made the structure of these samples more suitable for methane adsorption by affecting the micropore size distribution.

3.2.5. Proximate and ultimate analysis

Results of the proximate and ultimate analysis of the raw, chemically activated (Z0.28) and extra physically activated (CZ0.28) oil palm shell are given in Table 4. As it was mentioned before, the high fixed carbon and volatile contents of the palm shell make this material a good precursor for preparing activated carbon. After chemical activation with the ratio of 0.28, the volatile content of the chars decreased from 74.3% to 14% whilst the fixed carbon content increased from 13.8% to 73.6%. This behavior was due to the release of volatile matter during chemical activation process, which subsequently caused an increase in carbon content. However, extra physical activation marginally increases the carbon content.

4. Conclusion

Activation of oil palm shell with ZnCl_2 followed by extra physical activation under CO_2 stream proved to be an efficient method to prepare activated carbons for methane adsorption. This preparation strategy (at an intermediate impregnation ratio, $X_{\text{Zn}} = 0.28 \text{ g/g}$) leads to high volumes of micropores (around $0.425 \text{ cm}^3/\text{g}$) without any significant development of mesopores. Although chemically activated samples without extra heat treatment showed an increase in the surface area and pore volume with the increase in mass ratio of ZnCl_2 , methane adsorption did not improve at any ratio (less than $13 \text{ cm}^3/\text{g}$). Furthermore, the samples prepared without extra physical activation showed wider pore size distribution and average pore width compared to the samples with further CO_2 activation. After heat treatment under CO_2 , samples showed lower surface area, pore and micropore volume that indicates that further thermal activation causes a pore shrinkage and the creation of small micropores. However methane capacity increased two folds.

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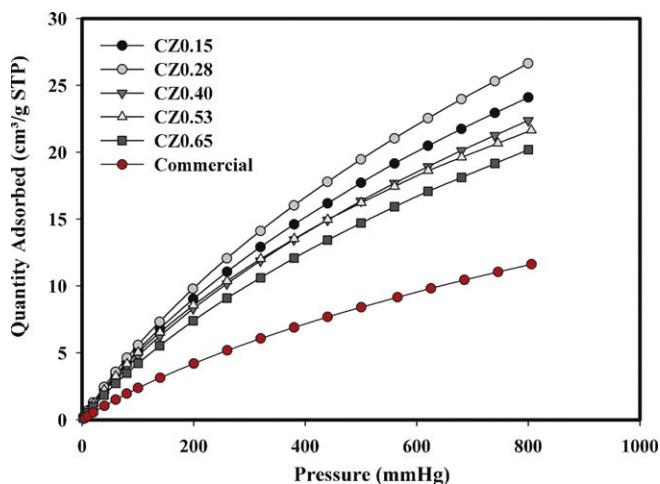


Fig. 7. Methane adsorption isotherms of ZnCl_2 activated carbons with further physical activation at different pressures.

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