PRODUCTION OF CARBON MOLECULAR SIEVES FROM PALM SHELL THROUGH CARBON DEPOSITION FROM METHANE

The possibility of production of carbon molecular sieve (CMS) from palm shell as a waste lignocellulosic biomass was investigated. CMS samples were prepared through heat treatment processes including carbonization, physiochemical activation and chemical vapor deposition (CVD) from methane. Methane was pyrolyzed to deposit fine carbon on the pore mouth of palm shell-based activated carbon to yield CMS. All the deposition experiments were performed at 800 °C, while the methane flow rate (100, 200, 300 mL min⁻¹ CH₄ diluted in 500 mL min⁻¹ N₂) and deposition time (30 to 60 min) were the investigated parameters. The textural characteristics of the CMSs were assessed by N₂ adsorption. The largest BET surface area (752 m² g⁻¹), micropore surface area (902.2 m² g⁻¹) and micropore volume (0.3466 cm³ g⁻¹) were obtained at the CH₄ flow rate of 200 mL min⁻¹ and deposition time of 30 min. However, prolonging the deposition time to 45 min yielded in a microporous CMS with a narrow pore size distribution.

Keywords: carbon molecular sieve; chemical vapor deposition; methane; microporosity; palm shell.

Carbon molecular sieves (CMSs) are porous skeletal structures able to discriminate molecules on the basis of their size and shape. They are supposed to be a special class of activated carbon with a substantial number of micropores. However, a narrow pore size distribution is not clearly the only distinction between activated carbon and CMS, as production of microporous activated carbon has been numerously reported. The main difference between these two carbonaceous structures may refer to their adsorption kinetics. The essential feature of activated carbon is separation of molecules on the basis of differences in the adsorption equilibrium constant. Whereas, carbon molecular sieve separates molecules through differences in the adsorption rate of molecules [1,2].

CMSs offer remarkable sieving properties which make them suitable for separation and purification of gaseous mixtures via pressure swing adsorption (PSA). They have been widely used for separation of nitrogen and oxygen from air stream [3-7], hydrogen from methane and also from ammonia, carbon dioxide and methane [1,8-11], propane and propylene [12], carbon disulfide from pentane, SO₂ from off-gas, benzene and cyclohexane and toluene from gaseous mixtures [13]. CMSs also have been explored for removal of water from alcohol, separation of olefins from isoprene and butadiene, removal of mercury from stack gasses and separation of polynuclear aromatics from hydrocracking product. Use of CMS as catalyst has been demonstrated in Fischer-Tropsch synthesis. They also have been applied for natural gas and refrigerant storage.

CMSs can be produced from any carbonaceous material with low inorganic compounds. Coal, pitch and polymers such as polyvinylidene chloride, polycyacrylonitrile and phenol formaldehyde have been used as carbonaceous raw material for CMS production [2,3]. Lignocellulosic biomass is also a cheap and abundant source of carbon which can be effectively used for fabrication of CMS. Many researchers have confirmed the high potential of lignocellulosic biomass for production of carbonaceous materials including activated carbon and CMS [14-17].
Malaysia, as the world’s leader in palm oil industry, generates significant amounts of lignocellulosic waste material, which has no specific use. Palm shell is one of these lignocellulosic by-products that can be utilized as a potential carbonaceous source for preparation of CMS. Use of such waste materials for production of adsorbents would be beneficial from both an economical and environmental point of view.

Generally, production of CMS from lignocellulosic biomass involves three consequent steps of (i) pyrolysis of the lignocellulosic material to obtain char, (ii) activation of the so prepared char and (iii) pore modification of the activated carbon to yield CMS [14]. Chemical vapor deposition (CVD) technique is typically applied at the final stage to modify the existing porosity of the activated carbon to obtain CMS. It deals with carbon deposition at the pore mouth and narrows the pore entrance to match the molecular size of the analyte. A variety of hydrocarbons including benzene [4,8,18–20], methylpentane [21] and methane [22] have been used as depositing agent for preparation of lignocellulosic-based CMS. Among various hydrocarbons applied for carbon deposition, benzene is by far the most employed one. Benzene does not generate intermediates during the cracking process, which makes the carbon deposition process controllable [23]. However, benzene suffers from disadvantages such as high toxicity and relatively high cost. Methane seems to be a suitable alternative as it is non-toxic abundant and low cost substance but it generates intermediate during the deposition process. During the heat treatment process, methane converts to hydrocarbons such as ethane, ethylene and acetylene. Ethane has a very short lifetime and converts to ethylene and consequently to acetylene. Ethylene and acetylene are both able to generate carbon directly [22]. Thus, the CVD process using methane should be carefully handled to achieve a well controlled deposition.

In this work, the possibility of CMS production from palm shell was investigated through physiochemical activation process followed by CVD of methane. The porous texture of the obtained CMS was characterized and the effect of methane flow rate and deposition time on microporosity development and pore size distribution was assessed.

EXPERIMENTAL

Raw material

Palm shells were obtained from a local palm oil mill, Nibong Tebal, Malaysia. They were dried, crushed and sieved to particle size of 1 to 2 mm. The ground palm shells were washed and oven dried at 110 °C for 48 h.

Preparation of activated carbon

Palm shell is kind of hard lignocellulosic biomass with a high lignin content of around 54% [24]. Lignin is a natural aromatic polymer found in the cell wall of woody biomass whose function is to cement the cellulosic structure of plants [14]. Because of the hard nature of palm shell, conventional physical or chemical activation process may not effectively convert it to highly porous activated carbon. Thus, in this study a combination of chemical and physical activation process was implemented to obtain activated carbon with large micropore surface area and high micropore volume before deposition step.

The experimental carbonization unit consisted of a stainless steel reactor (4 cm diameter and 40 cm length) equipped with a vertical tubular furnace as depicted in Figure 1. Batch experiments were conducted by loading 100 g of the raw palm shell in the reactor. The carbonization process was performed under a N₂ flow of 500 mL min⁻¹. The temperature of the reactor...
was increased at a rate of 15 °C min⁻¹ until the carbonization temperature of 900 °C was reached. The samples were pyrolyzed for 1 h, and then cooled down to room temperature under the N₂ flow. The carbonized samples were impregnated in NaOH (2 M) solution for 12 h. NaOH was used as a chemical agent that causes the swelling of the carbonized shells. It also creates some porosity inside the chars and inhibits particle narrowing during the next heat treatment process. The chemically activated shells were rinsed with distilled water until a neutral pH in the filtrate was achieved.

Then, the samples were oven dried at 110 °C for 3 h. In the next step, physical activation was carried out to develop the microporosity of the lignocellulosic char. This process was conducted while the chemically activated chars were reloaded in the reactor under a N₂ flow of 500 mL min⁻¹ until the temperature reached to 900 °C. Then, the N₂ flow was stopped and a CO₂ flow of 500 mL min⁻¹ was introduced into the column for 2 to 3 h. After that, the activated carbons were cooled down to room temperature under N₂ flow. The so prepared activated carbons were kept in a desiccator for textural characterization and deposition process.

Chemical vapor deposition

Deposition process was carried out by loading 10 g of the activated carbon in the pre-described column. Prior to deposition step, a N₂ flow of 500 mL min⁻¹ was passed through the column to flush out O₂ until deposition temperature of 800 °C was achieved. The deposition experiments were conducted at 800 °C under a diluted stream of CH₄ (100, 200, 300 mL min⁻¹ CH₄ diluted in 500 mL min⁻¹ N₂) for 30 min. Also, to investigate the effect of deposition time on microporosity of CMS, the suitable sample obtained from previous experiments was subjected to CH₄ deposition for 30 to 60 min. After deposition process, N₂ was introduced into the column to flush out residual CH₄ and cool the sample to room temperature.

Characterization

All carbonaceous samples were characterized in terms of surface area, total pore volume, micropore volume and pore size distribution by N₂ adsorption at 77 K in a Quantachrome Autosorb Automated Gas Sorption System. Brunauer-Emmett-Teller (BET) equation was used to measure the apparent surface area, \( S_{\text{BET}} \). The micropore surface area, \( S_{\text{DR}} \), was determined using Dubinin-Radushkevich (DR) equation because the adsorption mechanism in narrow pores is controlled by volume filling rather than surface layer formation [25]. Total pore volume, \( V_t \), was estimated from the liquid volume of N₂ adsorbed at a relative pressure of 0.95 for pores smaller than 48 nm (diameter). To calculate the micropore volume, \( V_{\text{mic}} \), and pore size distribution, PSD, non-local density functional theory (NLDFT) was applied [22].

The surface characteristic of the activated carbon was analyzed using a Hitachi TM-3000 tabletop scanning electron microscope (SEM). Transmission electron microscopy (TEM) was used to analyze the microporous structure of the CMS samples. A Philips CM12 TEM was used to attain high magnification micrographs of CMS.

RESULTS AND DISCUSSION

Characterization of the activated carbon samples

In this study, CMS samples were prepared by deposition of pyrolytic carbon on the surface of activated carbon to modify the existing porosity of the carbon samples. The porosity of the activated carbon samples was investigated in terms of micropore surface area and micropore volume to find the suitable sample for consequent deposition step. Table 1 shows the BET surface area, micropore surface area, micropore volume, total pore volume and microporous fraction of the two activated carbon samples. Comparing the textural characteristics of the two samples revealed that increasing the CO₂ activation time from 2 to 3 h, improved the micropore surface area from 157.8 to 569.8 m² g⁻¹ and the micropore volume from 0.1414 to 0.3130 cm³ g⁻¹. Such development in pore structure can be attributed to the opening of previously unreachable pores, formation of new pores and widening of the existing pores in the structure of activated carbon [22]. As a result, the micropore and total pore volume of the activated carbon (AC180) increased as the activation time was prolonged to 3 h.

Figure 2 shows the N₂ adsorption/desorption isotherm of the two activated carbon samples. As observed in this figure, the adsorption and desorption branches of the isotherm form a wide hysteresis loop which is associated with the mesopores. Such behavior implies that the confined N₂ vapor in the pores of activated carbon condenses at a relative pressure

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation time, min</th>
<th>( S_{\text{BET}} ) / m² g⁻¹</th>
<th>( S_{\text{DR}} ) / m² g⁻¹</th>
<th>( V_{\text{mic}} ) / cm³ g⁻¹</th>
<th>( V_t ) / cm³ g⁻¹</th>
<th>( V_{\text{mic}}/V_t )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC120</td>
<td>120</td>
<td>137.7</td>
<td>157.8</td>
<td>0.1414</td>
<td>0.2010</td>
<td>0.7031</td>
</tr>
<tr>
<td>AC180</td>
<td>180</td>
<td>476.8</td>
<td>569.8</td>
<td>0.3130</td>
<td>0.4607</td>
<td>0.6794</td>
</tr>
</tbody>
</table>

Table 1. Textural characteristics of activated carbons
higher than that of saturation pressure. This phenomenon is called “capillary condensation” which is a function of the size and shape of the pores as well as the strength of the interaction between the pore walls and adsorbate [26].

Based on IUPAC categorization of adsorption isotherms, four types of hysteresis loops (H1, H2, H3, and H4) may be observed in the sorption isotherms which are associated with the texture and geometry of the mesopores. The two branches of the isotherm may be nearly vertical (H1) or parallel (H4) or an intermediate between the two extremes may occur which represents types H2 and H3 [27]. The H1 hysteresis loop is generally obtained with spheric agglomerates or particles which show a narrow distribution of uniform cylindrical pores. Some materials with complex pore structure produce H2 type loop in which network and pore blocking effects are important. Particles containing slit-shaped pores or plate-like particles represent H3 and H4 hysteresis loops. These two types of hysteresis loop are not closed until the equilibrium pressure is very close or equal to the saturation pressure. In the case of H4 hysteresis loop, the pore size distribution is mostly in the micropore range [28]. The hysteresis loops generated by the activated carbon samples are very similar to H4 type indicating that micropores are dominant in the structure of adsorbents. Also, the slit-shaped pores as predicted by H4 hysteresis was confirmed by SEM image of the activated carbon (AC180) as depicted in Figure 3.

The pore size distribution of the activated carbon which is computed by NLDFT method is depicted in Figure 4. The sample AC180 which exhibited better microporosity and narrower PSD than AC120 was selected as the basis for further carbon deposition process.

Figure 2. N₂ Adsorption/desorption isotherms of activated carbons: for each isotherm, the lower branch represents the adsorption isotherm and the upper branch represents the desorption isotherm.

Figure 3. SEM image of the activated carbon prepared by CO₂ activation for 3 h (AC180).

Characterization of carbon molecular sieve

Efficiency of CMS is evaluated in terms of its selectivity and adsorption capacity. Adsorption capacity of CMS which is associated with the high micropore volume is developed during the activated carbon production. While, selectivity which is related to the tendency of CMS to adsorb one of the species from a mixture is provided by pore size distribution and is introduced by tailoring the pore entrance [14]. The induction of such properties in CMS is highly influenced by process parameters such as deposition temperature and time as well as depositing agent flow rate. In the current study, all the deposition experiments were carried out at 800 °C. Selection of such deposition temperature was based on the results of earlier works conducted by other researchers. Villar-Rodil et al. [23] prepared CMS cloth by CVD of methane over a polymer-based activated carbon cloth. They reported successful
deposition of carbon at 1098 K under either pure CH₄ or a diluted stream of CH₄ in Ar. In another investigation conducted by Vyas et al. [29], the possibility of CVD of CH₄ over indigenous bituminous coal-derived activated carbon was studied over a temperature of 750 to 780 °C. They obtained the best CMS sample at deposition temperature of 780 °C. However, Zhang et al. [22] failed to deposit methane over some commercial and sorghum grain-based activated carbons at 800 °C. Even increasing the methane concentration (5 to 30% in N₂) and deposition time (1 to 3 h) did not lead to carbon deposition. It was suggested that there might be some impurities on the surface of activated carbon which catalyze methane pyrolysis and lack of such impurities in their carbon substrate prevented CH₄ from deposition even after 3 h. The obtained results from the current study revealed that CH₄ was successfully deposited on the carbon surface due to the effective pore size reduction upon the CVD treatment in the all experimented conditions.

**Effect of methane flow rate**

The effect of CH₄ flow rate on microporosity development of CMS was studied while various streams of CH₄ (100, 200 and 300 mL min⁻¹) diluted in a flow of 500 mL min⁻¹ of N₂ were introduced into the reactor at 800 °C for 30 min. The result of such investigation is reflected in the values of textural parameters as tabulated in Table 2. The micropore surface area of the activated carbon pronouncedly improved from 569 to above 810 m² g⁻¹ upon CVD treatment while the total pore volume gradually decreased. Such obvious changes in the textural properties of activated carbon were probably due to the development of microporosity through deposition process as further confirmed by narrower PSD obtained in CMS samples. As the textural analysis shows, the BET and micropore surface area of the CMS samples improved by increasing the CH₄ flow rate from 100 to 200 mL min⁻¹ and then gradually reduced as the flow rate was increased to 300 mL min⁻¹. Such reduction in the BET and micropore surface area of CMS at a flow rate beyond 200 mL min⁻¹ could be attributed to the phenomena of pore blocking or excessive filling of pores. Similar trend was observed for micropore and total pore volume of this sample, increasing the CH₄ flow rate to 300 mL min⁻¹ caused the coating and blockage of the surface micropores and resulted in a reduced adsorption capacity.

Figure 5 depicts the N₂ adsorption/desorption isotherms of the three CMS samples prepared by CVD of CH₄ at 800 °C for 30 min. The flat-plateau isotherms (Type I) reveal the highly microporous structure of the CMS samples. As observed in Figure 5, increasing the CH₄ flow rate to 300 mL min⁻¹ caused some mesoporosity development. The narrow sorption hysteresis

![Figure 4. Pore size distribution of the activated carbon samples.](image)

### Table 2. Textural characteristics of CMS samples prepared at 800 °C and deposition time of 30 min

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gas flow rate, mL min⁻¹</th>
<th>S_{BET} / m² g⁻¹</th>
<th>S_{DR} / m² g⁻¹</th>
<th>V_{mic} / cm³ g⁻¹</th>
<th>V_{t} / cm³ g⁻¹</th>
<th>V_{mic}/V_{t}</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC180</td>
<td>-</td>
<td>476.8</td>
<td>569.8</td>
<td>0.3130</td>
<td>0.4607</td>
<td>0.6794</td>
</tr>
<tr>
<td>CMS100/500</td>
<td>100</td>
<td>664.4</td>
<td>813.7</td>
<td>0.2811</td>
<td>0.3230</td>
<td>0.8703</td>
</tr>
<tr>
<td>CMS200/500</td>
<td>200</td>
<td>752.0</td>
<td>902.2</td>
<td>0.3466</td>
<td>0.4280</td>
<td>0.8098</td>
</tr>
<tr>
<td>CMS300/500</td>
<td>300</td>
<td>673.0</td>
<td>839.7</td>
<td>0.3224</td>
<td>0.3968</td>
<td>0.8125</td>
</tr>
</tbody>
</table>
observed in this sample further confirms the difficulty of N₂ access to the pores. As a result, an irreversibility in the adsorption/desorption isotherms appears which originates from the similarity between the molecular size of N₂ and the dominant pore width in the adsorbent [23].

The PSD of the CMS samples is presented in Figure 6. Obviously, the CVD treatment significantly shifted the PSD of the carbonaceous material to the micropore region. As expected from earlier results, increasing the CH₄ flow rate to beyond 200 mL min⁻¹ caused the enlarging of micropores into mesopores.

The obtained results suggested that CMS200/500 which exhibited the largest micropore surface area and highest micropore volume among the three CMS samples was suitable for further deposition investigations. The TEM micrograph of this sample is shown in Figure 7. This image illustrates the amorphous structure of the CMS composed of carbon layer. The dark contrast layer corresponds to the deposited carbon on the amorphous structure and the bright sections are considered as undeposited hollow portions.

Effect of deposition time

In order to investigate the effect of deposition time on textural characteristics of CMS, deposition experiment was carried out on the best sample (CMS200/500) obtained from the previous experiment while the deposition time was varied from 30 to 60 min. Table 3 presents the obtained results from this experiment. As the deposition time was increased from 30 to 45 min, the micropore and BET surface area of the CMS as well as its adsorption capacity drastically decreased. This phenomenon probably refers to the excess carbon deposition on the walls and surface of the micropores. However, deposition of the pyrolyzed methane at the pore entrance for 45 min effectively tailored the mesopores to micropores and improved the
microporosity fraction of this sample to 87.46%. Prolonging the deposition time to 60 min, increased the total pore volume to 0.4607 cm$^3$ g$^{-1}$. A possible mechanism to explain such behavior may involve in some consequent processes: i) narrowing or blocking of the micropores while increasing the deposition time from 30 to 45 min which results in a reduced micropore surface area and volume, ii) conversion of some macropores (> 50 nm) to mesopores while prolonging the deposition time to beyond 45 min which increased the total pore volume (micropores and mesopores) and iii) tailoring some of the so created mesopores to micropores which improved the micropore surface area and volume. As a result of such process, the microporosity as well as mesoporosity of this sample (CMS200/500/60) was improved.

The N$_2$ adsorption/desorption behavior of the CMS samples is projected in Figure 8. It is observed that deposition times of 30 and 45 min resulted in highly microporous CMS as demonstrated by the type I plateau adsorption isotherm. The hysteresis behavior of the CMS200/500/60 may refer to the prolonged deposition process. The excess heating of this sample under CH$_4$ caused the destruction of the pore structure due to the sintering effect. Thus, the broad hysteresis loop exhibited by this sample which is not even closed at relative pressures below 0.4, may be attributed to the existence of large pores or presence of constrictions and narrow connecting pores inside the particles [30].

Figure 9 depicts the PSD of the CMS samples prepared under different deposition times. These results clearly show that effect of various deposition times on microporosity development of the CMS samples. Although extending the deposition time from 30 to 45 min reduced the adsorption capacity, but effectively narrowed the PSD of this sample. The TEM image of this sample is shown in Figure 10. The dark contrast region was extended in this micrograph in comparison to the CMS 200/500/30 which indicates the promoted carbon deposition and confirms the narrower PSD of this sample. Increasing the deposition time to 60 min

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deposition time, min</th>
<th>$S_{BET}$ / m$^2$ g$^{-1}$</th>
<th>$S_{mic}$ / m$^2$ g$^{-1}$</th>
<th>$V_{mic}$ / cm$^3$ g$^{-1}$</th>
<th>$V_t$ / cm$^3$ g$^{-1}$</th>
<th>$V_{mic}/V_t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMS200/500/30</td>
<td>30</td>
<td>752.0</td>
<td>902.2</td>
<td>0.3466</td>
<td>0.4280</td>
<td>0.8098</td>
</tr>
<tr>
<td>CMS200/500/45</td>
<td>45</td>
<td>408.9</td>
<td>484.7</td>
<td>0.1626</td>
<td>0.1859</td>
<td>0.8746</td>
</tr>
<tr>
<td>CMS200/500/60</td>
<td>60</td>
<td>470.2</td>
<td>607.0</td>
<td>0.273</td>
<td>0.4607</td>
<td>0.5929</td>
</tr>
</tbody>
</table>

Figure 8. N$_2$ adsorption/desorption isotherms of CMS samples prepared under a CH$_4$ flow rate of 200 mL min$^{-1}$ at 800 °C.
improved the mesoporosity and a wide PSD was obtained.

CONCLUSIONS

Preparation of CMS from palm shell was investigated through some consequent heat treatment processes including carbonization, char activation and CVD from methane. The effect of methane flow rate and deposition time as two important process parameters on microporosity development of CMS was examined. The textural analysis of the CMS samples explored the successful deposition of methane on pores of palm shell-derived activated carbon to yield a microporous CMS with a narrow pore size distribution.

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MAEDEH MOHAMMADI1,2

GHASEM D. NAJAFFPOUR2

ABDUL RAHMAN MOHAMED1

1School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia,Nibong Tebal, Penang, Malaysia

2Faculty of Chemical Engineering, Noushirvani University of Technology, Babol, Iran

NAUČNI RAD

DOBIJANJE UGLJENIČNIH MOLEKULSKIH SITA IZ PALMINE LJUSKE DEPOZICIJOM UGLJENIKA IZ METANA

Ispitvana je mogućnost dobijanja ugljeničnih molekulskih sita (UMS) iz palmine ljuske kao lignocelulozno otpadne biomase. Uzorci UMS-a su pripremljeni termičkom obradom, uključujući karbonizaciju, fizikohemijsko aktiviranje i hemijsku depoziciju (CVD) iz metana. Vršena je piroliza metana da bi se fini ugljenik deponovao u pore aktivnog uglja na bazi palmine ljuske pri čemu se dobijaju UMS. Svi eksperimenti depozicije su vršeni na 800 °C, pri različitim protocima metana (100, 200, 300 ml min⁻¹) koji je razblažen u azotu (500 ml min⁻¹ N₂) i vremenima depozicije (30 do 60 min). Teksturalne karakteristike UMS-a su određene na osnovu adsorpcije N₂. Najveće vrednosti BET površine (752 m² g⁻¹), mikroporozne površine (902,2 m² g⁻¹) i mikroporozne zapreminе (0,3466 cm³ g⁻¹) su dobijene pri protoku metana od 200 ml min⁻¹ i vremenu taloženja od 30 min. Pri tome, produženje vremena depozicije do 45 min dovelo je do stvaranja mikroporoznog CMS sa uskom raspodelom veličina pora.

Ključne reči: ugljenična molekulska sita; hemijsko depozicija u gasovitom stanju; metan; mikroporoznost; palmina ljuska.