

CARBON MOLECULAR SIEVES FROM CARBON DEPOSITION OVER PALM SHELL BASED ACTIVATED CARBON

M.A. Ahmad^{a,b}, W.M.A.W. Daud^a and M.K. Aroua^b

^a*Department of Chemical Engineering, University of Malaya,
50603 Kuala Lumpur, Malaysia*

^b*School of Chemical Engineering, Universiti Sains Malaysia, Seri Ampangan,
14300 Nibong Tebal, Penang, Malaysia*

ABSTRACT

Adsorption on carbon molecular sieves (CMS) prepared by carbon deposition (CD) has become an interesting area of adsorption due to its microporous nature and favorable separation factor on size and shape selectivity basis for many gaseous systems. Gas separation in PSA systems is their main industrial application. In the present work, the preparation of CMS by carbon deposition on palm shell based activated carbon has been studied. The activation temperature of 830°C using steam for 60 minutes produced the highest micropore volume of the order 0.407 cm³/g, which is used as precursor for CMS production. The best CMS for feed benzene entrance of 1.87 x 10⁻⁵ g/ml N₂ was produced at cracking time of 30 min. All the products were characterized by analysis of adsorption isotherm, BET surface area, micropore volume, and equilibrium isotherms.

INTRODUCTION

In 2001, the oil palm industry was found to have reached 3.2 million hectares and is expected to increase further due to the rapid expansion of the oil palm industry in Malaysia. Despite being the major producer of palm oil in the world, the industry has faced with environmental protection. Huge oil palm wastes especially palm shell have been created by the industry [1]. Currently, the palm shell has no specific technical uses and only a small portion is used as fuel to generate process steam in the palm-processing mill. The rest is wasted by pile burning in the open air and dumped in areas adjacent to the mill [2]. It is an added advantage to the oil palm industry if the excess palm shell can be turned into useful and valuable product. The high fixed carbon content in palm shell shows that it is a capable of yielding activated carbons with high surface areas and porosities, which can possibly be converted to carbon molecular sieves (CMS).

CMS is one member of the family of activated carbons (AC) with a homogeneous pore size distribution, having a pore size of several angstroms in diameter. This pore characteristic leads to selective adsorption property. Currently, the CMS is used for the separation of nitrogen from air by pressure swing adsorption (PSA) process. They separate O₂ from N₂ by allowing the smaller O₂ molecule to fill the micropores of the carbon before the N₂. Currently CMS was produced from coconut shell [3,4,5], nutshells [6,7], and coal [8,9]. There are different techniques that have been developed for CMS production i.e. controlled pyrolysis [4,10], coating method, and carbon

deposition (CD) method [3,5-8,11-13]. Among them, the CD approach has been found particularly suitable and has received considerable attention. The concept of this method is to control the narrowing process of the pore openings by carbon precipitation at the pore mouth [6]. CD allows for optimizing adsorption capacity and selectivity separately. Adsorption capacity of CMS is developed during the production of the activated carbon while selectivity is introduced by creation of constrictions at the entrances of pores by depositing carbon. Although a wide range of organic substances has been employed to generate the carbon deposit such as benzene [6,12,13], 3-methylpentane [7], acetylene [8], methane [11,16], cyclohexane [13], and isobutylene [3], benzene has been by far the most employed one. Benzene has high chemical stability and does not produce intermediate species in the cracking process, which makes deposition easier to be controlled. In this work, we study the preparation of CMS from palm shell based activated carbon. The activated precursors were modified by CD with benzene at different deposition time. The produced CMS samples are characterized in terms of adsorption isotherm, surface area, and pore volume by using adsorption of N_2 at 77 K. The CMS performance will be compared with commercial Carbotech (Germany) CMS in the separation of O_2 and N_2 at room temperature using adsorption equilibrium isotherms.

EXPERIMENTAL

Experimental set-up

The schematic diagram of the experimental setup is shown in Fig. 1. The main component of the system is a stainless steel reactor (6.9 cm ID) equipped with vertical tubular furnace and a pre-heater. The distributor, which is a perforated stainless steel plate covered with a fine stainless steel wire mesh is located at the center of the reactor.

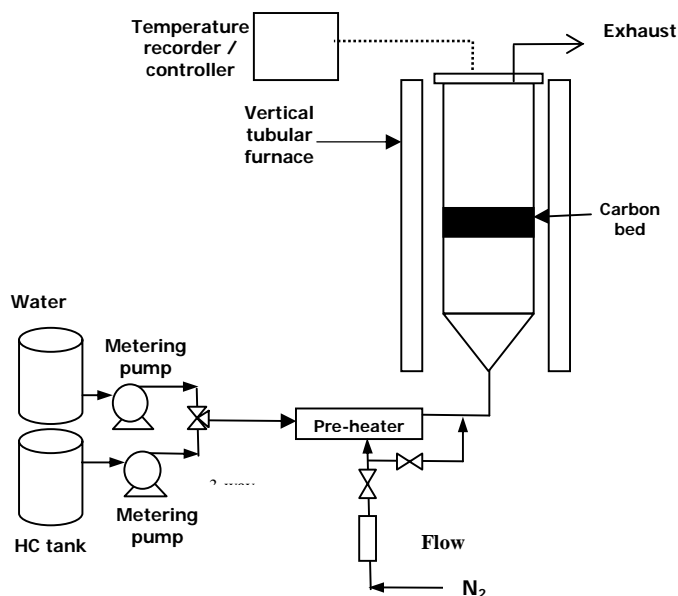


Figure 1: Schematic diagram of the experimental set-up.

The reactor is designed for batch operation and it is heated within an enclosing electric tube furnace. By regulating the 3-way valve, the pre-heater can be used to generate either steam during activation of char or benzene vapor during carbon deposition process. The temperature in the bed is precisely controlled by a Eurotherm furnace temperature controller and a K-type (chromel-alumel) thermocouple, which is lowered from the top section of the reactor and the tip of the thermocouple is positioned 5 mm above the distributor.

A batch of 500 g of the dried palm shell with an average size of 1.0-2.0 mm was charged into the reactor. The palm shell was carbonized in a N₂ flow at 900°C for 1 hour followed by steam activation for a period of 30-420 min to achieve burn-off falling in the range 0-60%. After the desired time elapsed, the reactor was cooled to room temperature under flowing N₂. Activated sample with the highest micropore volume was used for CD step. For CD step, 10.0 g of activated sample were charged into the same reactor and were heated to 800°C in flowing N₂. Benzene (Merck, analytical grade) was used as the carbon source for this study. The benzene concentration in the N₂ flow at the inlet to the reactor was held at 1.13×10^{-2} g/ml N₂ for all cracking experiments. The exposure time for cracking was ranged from 15 to 60 minutes after which benzene was switched off and the reactor was allowed to cool in flowing N₂. Samples prepared in this way will be referred to as Bt, where B will specify the benzene and t will specify the period of time (in minutes) of the deposition treatment. CMS supplied from Carbotech (Germany) was used to compare the performance of synthesized samples.

The activated and CMS samples were characterised by N₂ (77K) adsorption in a Micromeritics 2010 system. The BET surface area was measured from the adsorption isotherms using the Brunauer-Emmett-Teller equation. The Dubinin-Radushkevich (DR) equation was used to calculate the micropore volume over a range of relative pressure of 1.1×10^{-5} to 0.02. The total volume (V_t) was obtained at a relative pressure of 0.99 [15,16]. The weight gain was calculated as the difference between the sample weights after and before the CD treatment. The adsorption equilibrium isotherms studies for O₂ and N₂ (kinetics diameter 0.34 and 0.36 nm, respectively) at 298 K up to 760 mmHg were carried out using a Micromeritics ASAP 2010C analyzer which uses the static volumetric technique. This apparatus allows isotherms to be determined for the individual pressure steps. Prior to analysis, the samples were outgases to 180°C for 12 h to a residual pressure of 10^{-4} mmHg or less. The adsorbed amount (at STP) versus pressure was plotted and the uptake ratio was defined in this paper as the ratio of amount of O₂ and N₂ adsorbed at 760 mmHg [5].

RESULTS AND DISCUSSION

Activated samples

The micropore volume of an activated carbon increases with the extent of the activation treatment. In spite of this, the increase in the micropore volume is linked with the unfavorable growth of the pore size [6]. A large pore size distribution is formed in the advanced stage of activation, which is in contrast with the condition of a narrow microporosity required to produce a good CMS. Hence the aim of this step is to prepare

active carbon samples with a reasonably high adsorption capacity but at the same time a limited amount of larger micropores. Activation under steam atmosphere was chosen in our study because it produces activated carbons with greater micropore volumes [15]. Table 1 lists the activation times, burn-off, BET surface area, micropore volume, total pore volume, and ratio of micropore volume to total pore volume of six AC samples with different degrees of burn-off. The continuous development of microporosity takes place till exposure time of 250 min, beyond which the micropore volume decreases; indicating that the process of enlarging micropores into mesopores already begins as more carbon is removed.

Table 1: Properties of activated carbons

Sample	Activation time (min)	Burn-off (%)	S_{BET} (m^2/g)	V_{mi} (cm^3/g)	V_{t} (cm^3/g)	$V_{\text{mi}}/V_{\text{t}}$ (cm^3/g)
A30	30	16.1	576	0.2784	0.4728	0.5888
A90	90	31.3	655	0.3767	0.4931	0.7639
A160	160	45.1	980	0.3950	0.5038	0.7841
A250	250	53.2	1104	0.4067	0.5138	0.7915
A340	340	57.2	1302	0.3893	0.6266	0.6213
A420	420	58.7	1319	0.3397	0.7289	0.4660

Based on that, the AC obtained at 250 min (A250) is preferred as a base material for CMS production. According to Zhang et al. [16], a longer activation time causes micropores to widen because it destroys the walls between adjacent pores, thereby resulting in the enlargement of pores. This leads to a decrease in the fraction of micropore volume and an increase in the total pore volume. As can be seen from Fig. 2, the development of mesoporosity and multilayer adsorption of samples A340 and A420 occur at high relative pressure (approximately above 0.9).

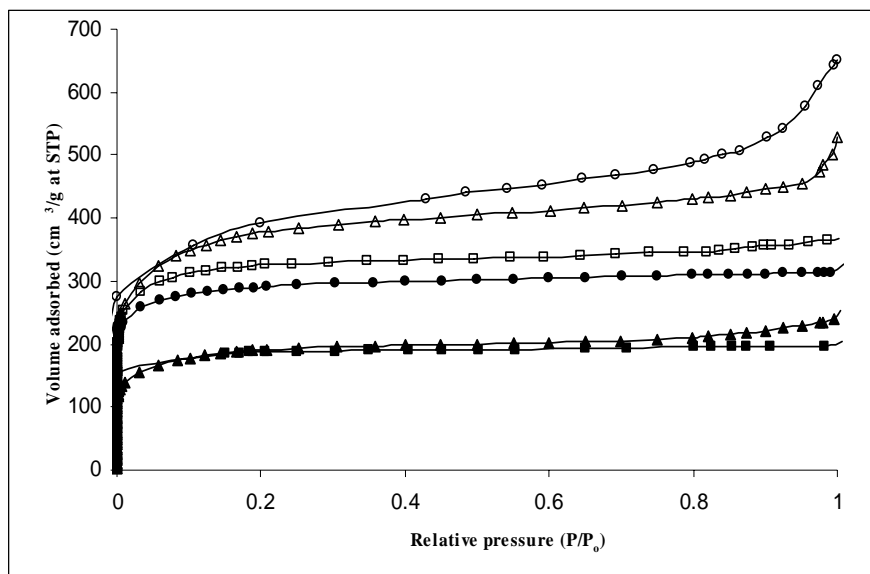


Figure 2: Adsorption isotherm of activated carbon with different degree of burn-off; 16.1% (■), 31.3% (▲), 45.1% (●), 53.2% (□), 57.2% (△), 58.7% (○).

Benzene cracking

Fig. 3 shows the weight gain during the carbon deposition step at cracking temperature of 800°C. An increase of weight of 412.5 mg/g within 30 min is the resulted from the benzene cracking on the wall or mouth of the pores, beyond which the increment become insignificant.

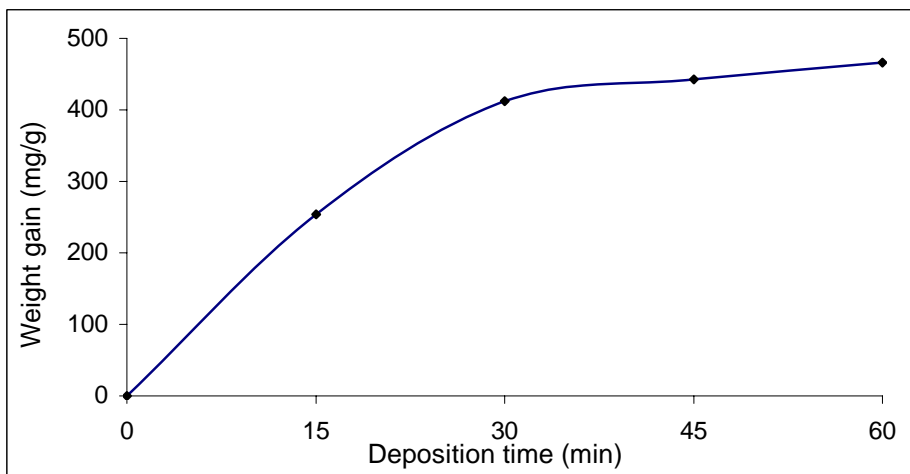


Figure 3: Carbon deposition from pyrolysis of benzene on A250.

Prolongation of the cracking time more than 30 min, pyrolysis produced no further gain due to the excessive carbon formation. The carbon deposition can occur at the pore mouths and on the interior surface of micropores when the micropores are still open. When all micropores become inaccessible to benzene molecules, carbon from cracking

reactions can only deposit on the external surface areas, resulting in a reduced surface area [6,7,12]. Table 2 shows the variation of micropore volumes during the deposition step. The O₂ and N₂ adsorption isotherms of samples B15, B30, B45, and B60 are shown in Fig 4. For comparison, a commercially manufactured Carbotech CMS was selected.

Table 2: Benzene cracked samples: Cracking temperature = 800°C, benzene entrainment = 1.13×10^{-2} g/ml N₂, nitrogen flowrate: 10 ml/s

Sample	Deposition time (minutes)	S _{BET} (m ² /g)	V _{mi} (cm ³ /g)	Uptake ratio of O ₂ /N ₂
B15	15	892	0.3860	3.85
B30	30	704	0.4120	9.76
B45	45	555	0.4076	9.41
B60	60	411	0.3291	8.13
CMS ^a	-	406	0.3087	9.32

^aCMS = Carbon molecular sieve (Carbotech).

The adsorption equilibrium isotherms of O₂ and N₂ at 298 K were almost linear. It is clear that all samples prepared are suitable for separation of O₂ and N₂ mixture. O₂ with molecular size 0.346 nm was preferentially adsorbed compared to N₂ with molecular size 0.364 nm. The uptake ratios calculated using equilibrium data are also given in Table 2.

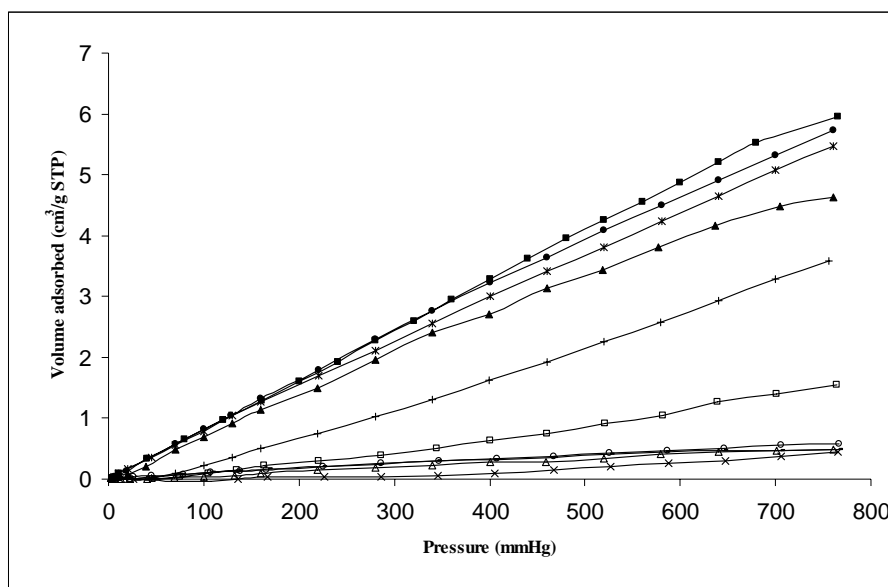


Figure 4: Adsorption isotherm of O₂ and N₂ for CMS samples with different deposition times (filled symbols: O₂; open symbols and ×: N₂); 15 min (■), 30 min (●), 45 min (▲), 60 min (+). Carbotech CMS is also shown (*: O₂; -: N₂).

The higher the uptake ratio indicates the better chances of separating individual gases from their mixtures. From the table, sample B30 exhibits the highest uptake ratio of 9.76 beyond which the ratio become decreasing. These CMS shows a better separation compared to the Carbotech CMS which produced uptake ratio of 9.32. The continuation of the cracking time more than 30 min led in fact to a reducing of the O₂ adsorption capacity.

CONCLUSIONS

Palm shell can be used to prepare CMS since its derivative carbon possesses a well-developed micropore system. The proposed method of sequential treatment, (1) carbonization, (2) activation, (3) carbon deposition, appears to be applicable for the CMS preparation. The activated sample of burn-off 53.2% gives the highest micropore volume of 0.4067 cm³/g was used as precursor for CMS production. CMS produced at 30 min deposition time gives the highest uptake ratio of 9.76 between O₂/N₂. This process is found to depend on the deposition time.

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