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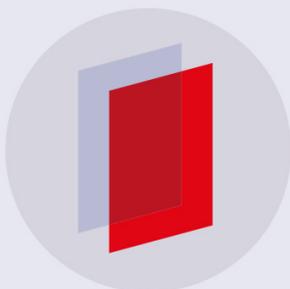
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Activated carbons from oil palm shell for hydrogen storage

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Abstract. Activated carbons (ACs) with controlled microporosity have been developed from oil palm shell and their H_2 storage performances been have tested at 77 K. Such adsorbents are the natural agricultural by-products of chemically activated with KOH. N_2 adsorption-desorption at 77 K was used to investigate the pore structure of the ACs produced with different weight ratio of KOH/oil palm shell charcoal. The results showed that the developed oil palm shell ACs achieved surface areas (S_{BET}) as high as 3508 m^2/g and micropores volumes (V_{DR}) as high as 1.10 cm^3/g. Outstanding storage capacities of hydrogen, as high as 6.8 wt.% have been obtained at 4 MPa and 2.86 wt.% have been obtained at 1 bar for some of these adsorbents at 77 K. These values of hydrogen adsorption are among the best that ever published so far, which well above those of some reference commercial materials, e.g. Maxsorb-3, and also the ACs from the open literature.

1.   Introduction

Hydrogen is a renewable energy, which holds the potential to be a means of providing clean, safe, affordable, and secure energy in the future because it is a renewable energy source that generates no carbon emissions [1]. It is frequently proposed as an alternative to the current fossil fuel-based energy system to solve problems pertaining to energy distribution and environmental issues. However, one of the greatest problems of hydrogen arises from its supercritical nature under standard conditions (Tc = 33.19 K, Pc = 1.296 MPa), giving it a very low density: only 90g m^{-3} at 1 bar and 273 K. The US Department of Energy (DOE) set new targets for hydrogen storage systems in light-duty vehicles in 2009, which correspond to reversibility, a gravimetric density of approximately 5.5 wt.%, and consideration of the entire storage system [2]. The methods for hydrogen storage include traditional compressing and liquefying hydrogen, but also with different materials by physisorption or chemisorption [3-6]. However, there is no method can reach the new targets at room temperature, even at 77 K. Since stationary applications are not limited by their weight and therefore technical solutions could be available in a shorter time.

The success of any future hydrogen economy depends on the development of inexpensive materials with sufficiently high hydrogen-storage capacity. Among all the materials, porous and high-surface area activated carbons (ACs) are among the most important candidates to store efficiently hydrogen due to their advantages of being reversible, having a high specific surface area and pore microstructure, being light weight (low density), being stable for large scale production, and having fast kinetics. The other important reason is for the stationary applications, in which the weight and

volume are not limiting factors. ACs can be prepared from the precursors of carbonaceous materials having a high carbon content and moderate inorganic contents, such as coal, peat, polymeric materials, wood, bamboo, and various agricultural by-products [5-8]. Among them, previous research reported that oil palm shell consisting of 26.4 % fix carbon which indicated as a good source as raw material for preparation activated carbon [9]. Meanwhile, oil palm shell is a common low-cost agricultural waste in Malaysia, more than 4.7 million tonnes produced in 2007 [10]. All above mentioned make that the oil palm shell is a suitable precursor for activated carbons production. Some studies have reported that using the activated carbon from oil palm shell for CO_2, chromium (VI), phenol, and methylene blue dye adsorption [9-11]. Efficient utilization of oil palm shell, in particular for high value-added applications, has yet to be explored.

This research presents the development of activated carbons using KOH as the activation agent from oil palm shell, which combine low cost, low ash content and an ideal microtexture for getting a tunable nanoporosity, for hydrogen storage application. The impact of the weight ratio of KOH/oil palm shell charcoal (OPC) on pore structure and hydrogen storage performance has been investigated. The best lab made AC was also compared with well-known commercial activated carbon Maxsorb-3 and also the ACs from open literatures [23].

2.   Experimental

2.1   Materials

The oil palm shell was selected as a char precursor was obtained from Malaysia by Chinalight Guangzhou Co., Ltd. (China). All reagents were of analytic grade and used without further purification or treatment. The commercial AC Maxsorb-3 (formerly AX21) from Kansai Coke and Chemicals Co., Ltd. (Japan) was used for the sake of comparison.

2.2   AC's synthesis

The precursor of the ACs investigated here was oil palm shell. It was first washed with water to remove oil and dirt attached on the sample then it was dried under sunlight for few days. The dried oil palm shell were put into a horizontal tubular furnace under a pure nitrogen environment and subjected to a gradual increase in temperature (5 °C/min) from room temperature to 650 °C, at which they were kept for 1 h. The flow rate of the nitrogen was 500 mL/min. After the furnace had been cooled down to room temperature under nitrogen atmosphere, the oil palm shell charcoal (OPC) was finally produced. The OPC was then ground and sieved in order to collect the grains having an average size within the range 100 – 200 μm. The OPC powder was mixed with KOH with different weight ratio of (W) of KOH/OPC. The resultant mixture was then introduced into a nickel crucible and heat-treated in a muffle furnace (KDF, 80-plus) at a constant heating rate (3 °C/min) up to the final activation temperature (T=800 °C), which was maintained for 2 h. The crucible was then allowed to cool down to room temperature. The whole process was conducted under a stream of nitrogen with a flow rate of 300 mL/min. Finally, the activated product was washed, first with distilled water (for the recovery of the rudimentary KOH), then with HCl (1 M), and finally, with distilled water again until the pH of the rinse had stabilized. After being dried in an oven for 12 h, a very pure activated carbon (AC) material was obtained. The developed AC was stored in a vacuum desiccator for subsequent pore texture characterization and hydrogen adsorption experiments.

2.3   AC's characterisation

2.3.1   Pore structure. N_2 adsorption isotherms were obtained at 77K using an automatic adsorption apparatus (Micromeritics ASAP 2020, USA). The samples were outgassed for 48 h under vacuum at 523 K prior to N_2 adsorption. Surface areas, SBET, were determined by the BET calculation method [12] applied to the adsorption branch of the isotherms. SBET and pore volumes were estimated with a

typical, maximum, uncertainty of 3 %.The pore-size distributions (PSD) were calculated by application of the DFT model [13] supplied by Micromeritics software, considering slit-shaped pores.

2.3.2 H_2 adsorption. The H_2 storage properties both at low pressure and high pressure at 77 K for the ACs were determined. The ASAP 2020 HD88 from Micromeritics in USA was used for the low-pressure measurements (up to 1 bar) and the gravimetric analyzer HPVA-100 (VTI Corporation of TA Instruments, USA) was used for the high-pressure measurements (up to 8 MPa). For both sets of measurements, the samples were outgassed under a primary vacuum at 350 °C for 24 h before any sorption measurements were taken. Repeatability was always found to be very satisfactory, leading to errors lower than 3% on each measurement.

3.   Results and discussion

3.1   Pore structure

All the ACs prepared were labelled as AC_x. In this nomenclature, the "x" at the end corresponds to the different weight ratios. Table 1 listed the textural characteristics that reflected the N_2 adsorption-desorption at 77 K for the OPC and all ACs. The result shown that the oil palm shell after carbonization presented a very low S_{BET} (198 m^2/g). During the activation process, the redox reactions between the potassium compounds and carbon can result in an increase in the value of the specific surface area [1]. After the activation with different weight ratio, W, from 2 to 6, the S_{BET} first increased from 1600 to 3503 m^2/g and then decreased to 3183 m^2/g, the V_{DR} increased from 0.63 to 1.1 cm^3/g, and the $V_{0.99}$ increased from 0.7 to 1.68 cm^3/g. As the previous studies reported, the weight ratio is the most important parameter in the KOH chemical activation process [1, 14]. It is interesting that the surface area and micropore volume were not increased with the W linearly. AC4 sample with weight ratio 4 achieved the highest S_{BET} and V_{DR}, then both the S_{BET} and V_{DR} decreased when W further increased to 6. The proportion of microporosity to total porosity was expressed as $V_{DR}/V_{0.99}$, which varied from 60 to 90 %, means these developed ACs were essentially microporous. The average micropore diameter (L_0) was in the range of 0.74 to 1.41 nm.

Table 1. Textural characterization of all the ACs.

Sample	W	T ($^{\circ}$C)	S_{BET} (m^2/g)	$V_{0.99}$ (cm^3/g)	V_{DR} (cm^3/g)	EA (kJ/mol)	Lo (nm)	$V_{DR}/V_{0.99}$	Vmeso (cm^3/g)
OPC	N	N	198	0.91	N	N	N	N	N
AC2	2	800	1600	0.70	0.63	25.98	0.74	0.90	0.07
AC3	3	800	3201	1.51	1.01	20.01	1.25	0.67	0.50
AC4	4	800	3503	1.68	1.10	20.24	1.22	0.66	0.58
AC6	6	800	3183	1.71	1.03	19.05	1.41	0.60	0.64

N_2 adsorption and desorption isotherms at 77 K consisting of both the linear and logarithmic patterns were shown in Figure 1. According to the IUPAC classification, all AC samples presented were type I isotherms with no hysteresis cycle [15]. When the W increased, the amount of nitrogen adsorbed increased and showed a more extensive widening isotherm 'knee' at a low relative pressure. It is well known that the sorption behavior at low pressures corresponds to nitrogen adsorption in the micropores, where a much steeper increase means more micropores. Accordingly, as the W increased from 2 to 6, the knee of the isotherm widened, indicating both the broadening of the micropore width and development of the mesoporosity.
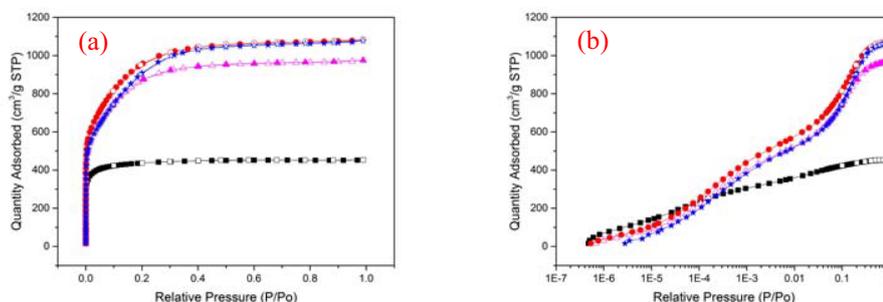
Figure 1. N_2 adsorption (solid symbols) and desorption (hollow symbols) isotherms on both (a) linear and (b) logarithmic scales (■ W=2, ▲ W=3, ● W=4, and ✷ W=6).
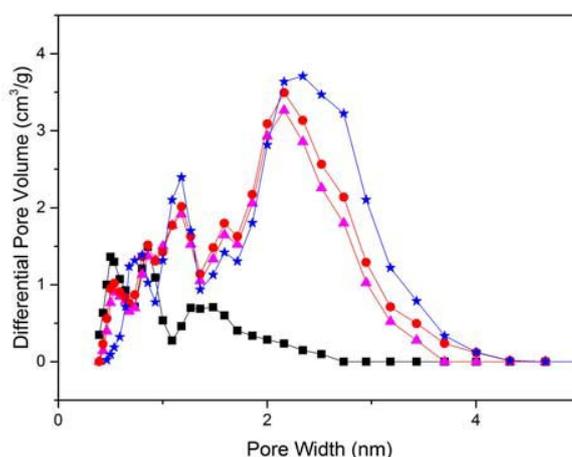
Figure 2. Pore size distributions from N_2 adsorption-desorption for all
the ACs calculated by DFT (■ W=2, ▲ W=3, ● W=4, and ✷ W=6).

The PSD was calculated using computer software by application of density functional theory (DFT) (Figure 2). The development of surface area by KOH activation is always accompanied of pore widening. The results shown that PSDs shifted to wider pores with higher W. The result also reinforced and confirmed the aforementioned finding that the micropores were the major component of the AC structure, coexisting with a few mesopores.

    In one word, the weight ratio plays the most important role, the optimum W may change with the precursors used. The reason why the surface area increased with W and then dropped could be explained by the fact that during KOH activation, the formation of mesopores and pore widening are two main mechanisms of the development of porosity, and in general the process of pore widening occurred at high Ws, which may damage the pores structure.

3.2   Hydrogen Storage Performance
Based on the previous experiments that the hydrogen storage capacities at 77K has linear relationship with surface area and micropore volume [1, 5], only AC4, which has the highest S_{BET} and V_{DR} were considered for hydrogen storage analysis. The hydrogen adsorption isotherms up to 1 bar and up to 8 MPa of the BC and ACs are given in Figure 3a and 3b. There was no hysteresis cycle. For low pressures up to 1 bar, the isotherms increased continuously, as shown in Figure 3a. Meanwhile, it is

clearly shown that under high pressure (8 MPa), a clear plateau can be found for all the isotherms, as show in Figure 3b. The results shown that the hydrogen storage capacity as high as 6.7 wt.% at 4 MPa, and 2.86 wt.% at 1 bar were obtained at 77 K. The US DOE target for 2010 was 5.5 wt.% for hydrogen storage systems (AC + tank). The hydrogen adsorption obtained in this study was still far from the US DOE target.
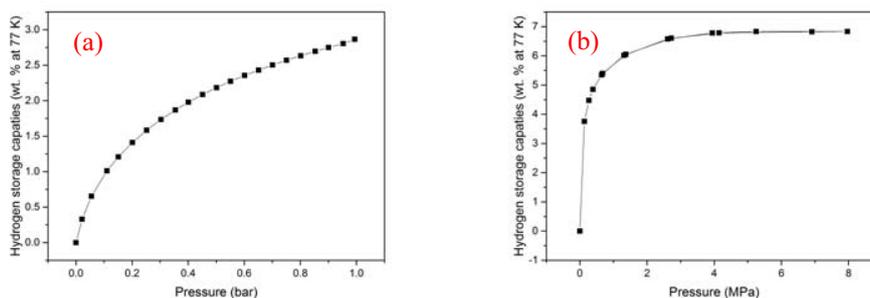

Figure 3. H_2 storage isotherms (wt. %), (a) low pressure up to 1 bar;
(b) high pressure up to 8 MPa

3.3   Comparison with Maxsorb-3 and Open Literature

The hydrogen storage capacities of the lab made sample was also compared with the well-known commercial activated carbon Maxsorb-3 (3203 m^2/g), which is one of the ACs frequently used for hydrogen storage. Both the lab made ACs and Maxsorb-3 prepared by activation with alkali hydroxide, but different precursor that the lab made sample AC4 used the biomass material oil palm shell, and the commercial sample maxsorb-3 used the petroleum coke. Maxsorb-3 has been claimed to adsorb about 6 wt. % of hydrogen at 77 K and 5 MPa, 5 wt. % being already reached at 2MPa [16]. Other results on the same material are about 3 wt. % at 80K and 10MPa [17]. Our lab-made AC reached 6.8 wt. % and 2.86 wt. % whereas Maxsorb-3 reached "only" 5.8 wt. % and 2.1 wt.% at 4 MPa and 1 bar. Our lab-made AC has a better hydrogen storage performance because it has higher S_{BET} than Maxsorb-3: 3503 and 3203 m^2 g^{-1}, respectively. But this is not the only reason. The reason of the higher performances of our lab-made AC is also based on its PSD shifted towards narrower pores, as shown in Figure 4.

Table 2 summarize the hydrogen adsorption data at 77 K but different pressure for AC produced from different precursors in the open literature and compared with the ACs prepared in this study for H_2 adsorption. However, the performances reached in this study are among the best reported by the latest reviews [18, 19] and recent literature in general, e.g. [1, 20-21]. Therefore, it can be seen that the activated carbon produced by the oil palm shell shows that our experimental results were among the best of the activated carbons from others.
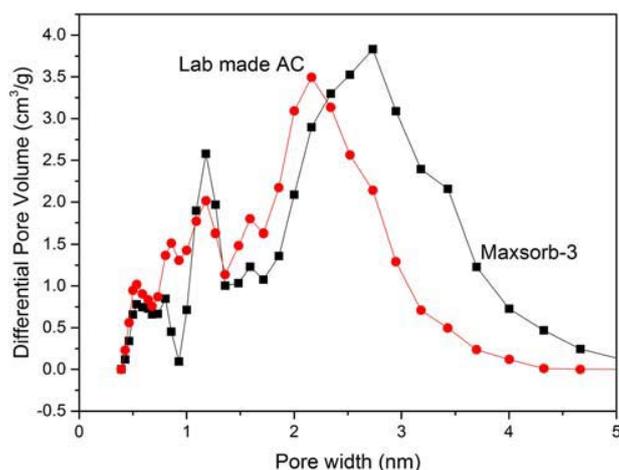
Figure 4. Pore size distributions from N_2 adsorption-desorption calculated by DFT for Mawsorb-3 and for our best lab-made AC.

Table 2. Comparison of activated carbons by KOH activation for H2 storage

Feedstock	Surface area (m^2/g)	H_2 uptake (wt.%)	Ref.
Oil palm shell	3503	6.7 (77K, 40bar) 2.86 (77K, 1bar)	This work
Bamboo	3208	6.60 (77K, 40bar) 2.74 (77K, 1bar)	1
Carbon precursor	2386	2.94 (77K, 1bar)	20
Chitosan	3100	5.6 (77K, 40bar)	21
Corncob	3708	5.8 (77K, 40bar)	22
Anthracites	3220	6.6 (77K, 40bar)	23
Carbon aerogels	1980	4.3 (77K, 20bar)	24
Bark	3170	4.08 (77K, 10bar)	21

4.   Conclusions

We have prepared a series highly microporous ACs from oil palm shell by activation with KOH due to the uniform pore structure and higher surface area from chemical activation. ACs with S_{BET} values as high as 3503 m^2/g and V_{DR} values as high as 1.10 cm^3/g were developed, representing a very promising material for hydrogen storage, which showed outstanding performances for hydrogen storage at 77K. The hydrogen storage capacity as high as 6.7 wt.% at 4 MPa, and 2.86 wt.% at 1 bar were obtained. These performances are well above those of the well-known commercial AC Maxsorb-3 and also the ACs from open literatures. Such exceptional hydrogen storage capacities may be ascribed to a higher surface area and volume of micropores of our ACs.

Acknowledgements

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