

Novel Low-Cost Activated Carbon from Coconut Shell and Its Adsorptive Characteristics for Carbon Dioxide

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Abstract. The objective of this research is to synthesize the microporous activated carbon and test its applicability for CO₂ gas capture. In this study, coconut shell-based and commercial activated carbon is used as the solid adsorbent. Based on the findings, it shows that the gas adsorption capacity is correlated to the total surface area of the materials. In addition, reduction in the adsorption capacity with respect to temperature proves that the physisorption process is dominant. Higher carbon dioxide (CO₂) adsorption capacity in comparison to nitrogen (N₂) capacity contributes to higher CO₂/N₂ selectivity, and confirms its applicability in the post-combustion process. Utilization of abundance agricultural wastes and one-step physical activation process is attractive as it promotes a cleaner pathway for activated carbon production, and simultaneously, reduces the total operating cost.

Introduction

In current practice, the activated carbons have been extensively acknowledged as possible adsorbent for carbon dioxide (CO₂) removal, particularly at an ambient temperature and pressure. The activated carbon can be manufactured from any carbonaceous materials. In Malaysia, the abundance of coconut plantation (*Cocos nucifera*) offers good opportunities for activated carbon production. Coconut is the fourth most important crop after oil palm, paddy and rubber, and is estimated to generate about 3,960 metric tonne of wastes, in which the fronds and shells are the major representatives [1]. Aside from its wide availability, applicability of the coconut wastes as the precursors is due to its low cost, high durability, and resistant towards the attrition [2]. At present, the wastes are disposed through open burning or just dumped in the field. Due to the environmental problems caused by waste disposal, re-use of the wastes are preferred. Therefore, in this research study, coconut shell has been used as the starting materials for the activated carbon production.

Apart from the nature of the carbonaceous materials used, the features of the activated carbon rely on the technique of the activation. Basically, two types of activation technique have been utilized by the researchers, which is physical and chemical activation processes. In physical activation, two stage processes involve the carbonization at the temperature of 400-850°C, and activation of the produced char under the presence of oxidizing agent such as CO₂ and steam at temperature range of 600-900°C [3]. Unlike physical activation, chemically-activated carbon normally operates at lower temperatures around 400-700°C, and thus, contributes to higher percentage yield. Yet, the consumption of chemicals is unattractive as it may cause waste disposal problems. In addition, activation agent such as zinc chloride is unpleasant as it causes corrosion problems, and washing stage results in an acidic wastewater consisted of the left over activation agent [3]. Due to double steps of physical activation process, it consumes higher energy and operating time. Therefore, a new activation method has been proposed in the research work. The one-step CO₂ activation method which has received less scientific research involves a single activation technique under the CO₂ flow, without undergoing the carbonization process under an inert atmosphere. The CO₂ in this process serves dual purposes, as a

purging gas to remove all the volatile substances and as an activation medium to react with the carbon structures and develop the porosity afterwards. Aside from thermal and textural properties, the influence of temperature towards adsorption capacity of gas is also discussed in this work.

Research Methodology

Preparation of Activated Carbon. Coconut shell was ground using a cutting miller, and the product was sieved to particle size of 0.25 mm. The sample was used as raw precursors. Prior to the experimental work, the materials were stored in a dessicator to avoid contact with moisture.

One-Step Activation Process. The one-step physical activation under presence of CO₂ flow (99.8% purity) was performed using a vertical tubular furnace. The apparatus used for the activation process consisted of three parts, which are the gas inlet, tubular reactor, and condenser, as illustrated in Fig. 1. In addition, the sample size of 20 to 30 grams was used for the activation process. To maintain an inert condition, the furnace was flushed with highly purified nitrogen (N₂; 99.999% purity) prior to the activation process. The activation process was accomplished at temperature of 900°C with heating rate of 20°C/min, CO₂ flow rate of 150 cm³/g, and residence time of 45 min.

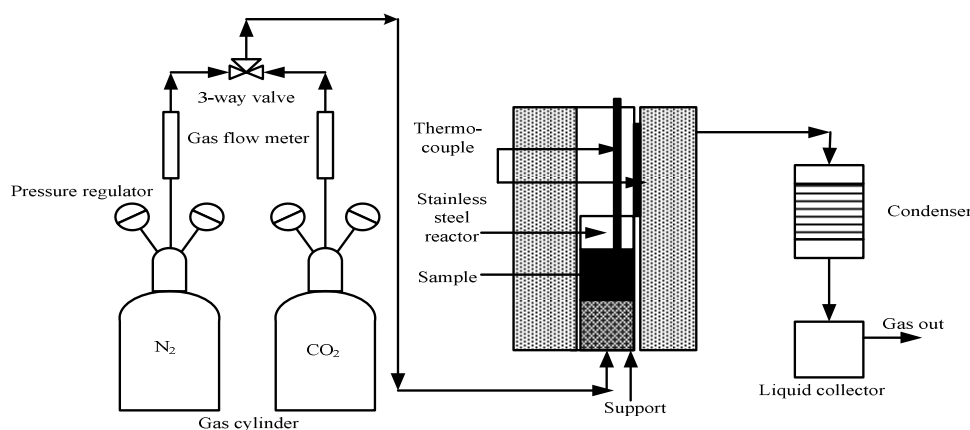


Fig. 1: Schematic diagram of experimental setup

Characteristics. The weight change of the coconut shell with respect to temperature was studied using an EXSTAR TG/DTA 6300 thermal gravimetric analyzer. The samples were heated from 25°C to 900°C at heating rate of 10°C/min and under N₂ flow of 10 mL/min. In addition, the pore structure of the activated carbons was analyzed using the N₂ adsorption-desorption at -196°C. The analysis was studied using the Micromeritics ASAP 2020. Before the analysis, the samples were first degassed at temperature of 120°C under vacuum to eliminate all the impurities presents. In particular, the surface area was calculated using the Brunauer-Emmett-Teller (BET) equation at relative pressure of 0.00 to 0.10, and the regression coefficient exceeded 0.9999. The total volume was determined at P/P₀ of 0.98. The t-method was used to estimate the micropore volume and area. Meanwhile, the mesopores volume and mesopores area were calculated by subtracting from the total pore volume and total surface area, respectively.

Gas Adsorption Analysis. Volumetric adsorption studies of CO₂ and N₂ on synthesized activated carbon were measured using a HPVA II analyzer. Prior to the adsorption measurement, 0.3-0.4 grams samples were degassed in a degas port. Then, the samples were transferred to the analysis port for gas adsorption analysis. The adsorption was repeated at three different temperatures (25°C, 50°C and 100°C), with a pressure interval of 0.1 bar, until it reached the specified pressure of 1 bar. At lower reaction temperature (e.g. 25°C and 50°C), a Julabo re-circulating water bath was employed to control the temperatures, whilst at an elevated temperature such as 100°C, a furnace was used. The data was stored in Microsoft Excel macros. In addition, the commercial activated carbon of the same size was used for comparative study.

Result and Discussion

Characterization. Fig. 2 illustrates the TG-dTG curve of raw coconut shell that corresponds to three different stages of thermal decomposition process. The first stage from 25°C to 100°C represents a 1.57 wt% mass loss caused by an evaporation of excess moisture. Then, the second stage from 200°C to 400°C shows a weight loss of 62.86 wt%, and is related to the release of volatile matters such as hemicellulose, cellulose and lignin content. According to the dTG curve, major weight loss is observed in this temperature range. It is due to the fact that the biomass typically built up of mainly volatiles, around 70 wt%. The weight loss in the third region which is beyond 600°C is not as significant as that observed in the second region. Abdullah *et al.* [4] reported that during this period, the left over elements which is lignin is decomposed firmly due to its high stability.

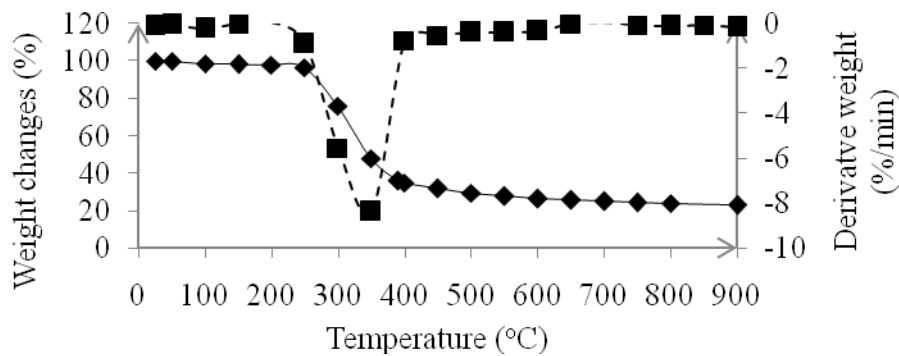


Fig. 2: TG-dTG curve of raw coconut shell (◆: Weight changes; ■: Derivative weight)

In addition, pore characteristics of the activated carbons are also investigated in this research work, and the N_2 adsorption isotherm of the activated carbons is as illustrated in Fig. 3. According to the International Union of Pure and Applied Chemistry (IUPAC) classification, the plot for graph shown in Fig. 3 is indicative of Type I isotherm, that corresponds to the microporous materials. In addition, the sharp increase of N_2 adsorbed in the lower relative pressure region is due to the micropore filling and plateau is a sign of type I BET isotherms. The micro-porosity in the activated carbon is very useful for gas adsorption process, given that the gases molecular diameter is within the range of 0.4-0.9 nm [5].

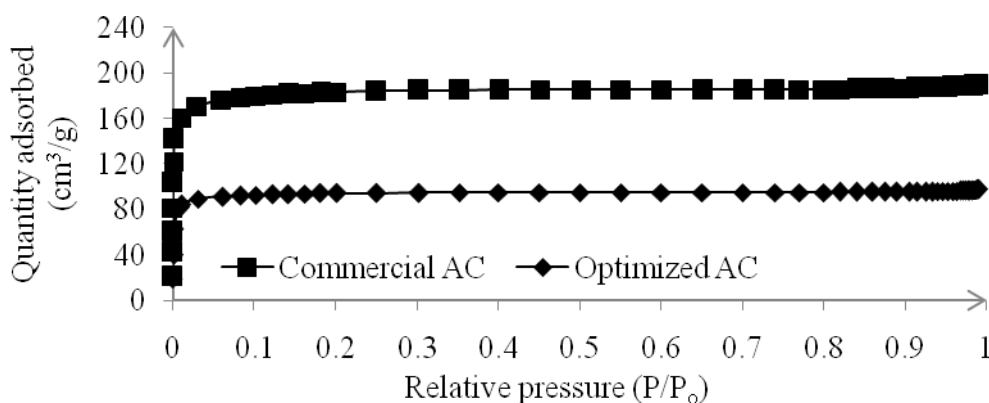


Fig. 3: N_2 adsorption isotherm at -196°C

Type I isotherm data is evaluated to acquire the BET surface area, pore volume, and average pore diameter, and the findings of the porosity for both activated carbons are as tabulated in Table 1. The improvements of BET surface area compared to the as-received coconut shell (0.96 m²/g) can be attributed to the activation process that form new microporosity, and removal of tarry and non-carbon products [6]. Besides, the micropores formation is also caused by thermal stress of the cellular structure on the raw coconut shell, and results in development of crack, crevice, slit, fissure and all types of openings in the carbon matrix [7]. Further, the average pore diameter of the activated carbon

is also inter-related to the carbon burn-off, as claimed by Martín-Martínez *et al.* [8]. His findings shows that there are three consecutive stages on the development of microporosity, in which (i) burn-off of less than 35 wt% develop small micropores of < 0.5 nm, (ii) medium micropores of size 0.5-1.0 nm are developed at burn-off of 35 to 60%, and (iii) at burn-off of > 60%, the large micropores of size 1 to 2 nm is produced. The widening of porosity depends on the extent of CO₂ activation process that will further react with carbon structures, and cause external burning of the particles and collapse of the pores, and thus, widen them [9]. In this study, the results are in agreement with the findings obtained by Martín-Martínez *et al.* [8], in which a burn-off of 72% results in average pore diameter of 1.6 nm.

Table 1: Porosity and surface area of synthesized and commercial activated carbon

	Coconut-shell activated carbon	Commercial activated carbon
BET surface area [m ² /g]	370.716	717.224
Micropore area [m ² /g]	295.874	584.828
Mesopore area [m ² /g]	74.842	132.396
Total pore volume [cm ³ /g]	0.150	0.292
Micropore volume [cm ³ /g]	0.109	0.217
Mesopore volume [cm ³ /g]	0.041	0.075
Porosity [%]*	72.667	74.315
Average pore diameter [nm]	1.634	1.640

*Porosity is the ratio of micropore volume to the total pore volume.

Gas Adsorption. Based on Fig. 4 and Fig. 5, the reduction in the CO₂ and N₂ adsorption capacity with respect to temperatures implies that the physisorption process is dominant. Basu *et al.* [10] reported that at an elevated temperature, the adsorbed molecules on the carbons' surface attain an ample energy to overcome the van der Waals bonding, and to migrate to the gas phase again. Also, it is clearly observed that the N₂ adsorption capacity is significantly lower than the CO₂ capacity, irrespective of the adsorption temperature. The preferential of CO₂ adsorption instead of N₂ suggests the suitability of these adsorbents to be used in post-combustion process, which normally consists of CO₂ and N₂. The greater CO₂ adsorption capacity compared to the N₂ is attributed to the ease of accessibility of the gas molecules towards material's porosity. The CO₂ that has smaller molecular diameter around 0.33 nm allows for better diffusivity into the porous network in the samples, compared to N₂ that has the molecular dimension of 0.364 nm [11]. In addition, higher adsorption capacity of the commercial activated carbon compared to the synthesized activated carbon can be explained based on surface area. The coconut-shell activated carbon has surface area of 48% lesser than the commercial adsorbent, thus, limited surface sites are available for the gas adsorption process to occur.

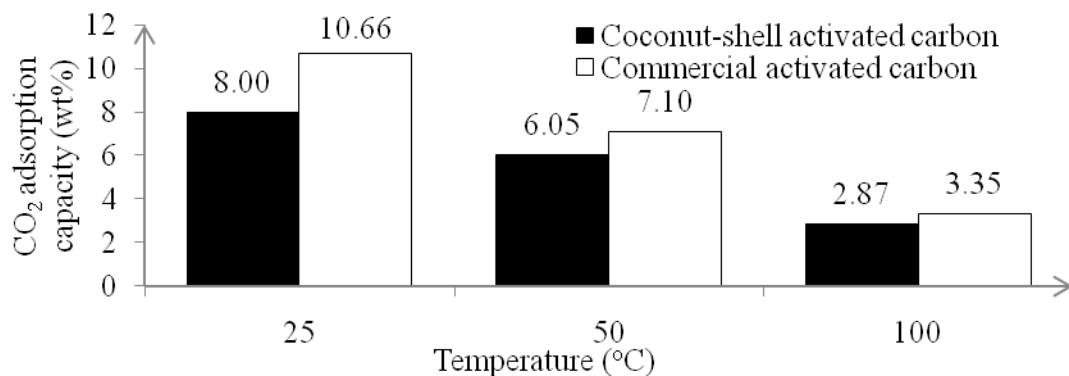


Fig. 4: CO₂ adsorption capacity at 1 bar

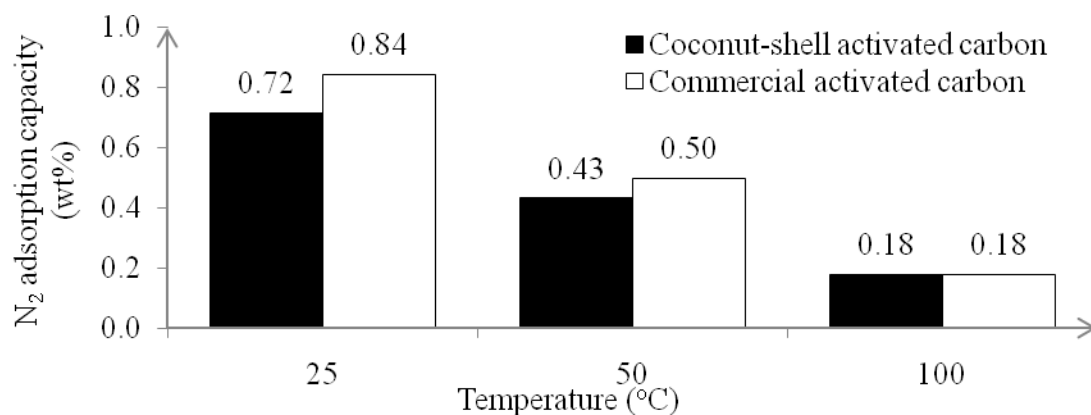


Fig. 5: N₂ adsorption capacity at 1 bar

Summary

In this study, an exploitation of the discarded coconut wastes in activated carbon production is greatly significant due to its environmental-friendly properties and economic viability. Regardless of lower BET surface area of the synthesized activated carbon in this work, the comparability of the adsorption capacity and gas selectivity with the commercial adsorbents proves that one-step physical activation technique has commercial potential. The utilization of the solid adsorbent as an alternative to the absorption process is preferred, as the existing problems encountered in amine scrubbing process e.g. corrosion and high energy penalty can be overcome.

Acknowledgements

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