Development of Novel Low-Cost Activated Carbon for Carbon Dioxide Capture

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Abstract—The increase in carbon dioxide (CO₂) emission into the atmosphere has become the key factors in an extend of the temperature rise, that eventually causes global warming and climatic change. Thus, low-cost coconut shell activated carbon was synthesized, and its applicability in CO₂ capture at 25°C and 1 bar was tested. Utilization of coconut shells as precursors for activated carbon production is economically viable. The pore structure of synthesized and commercial activated carbon was evaluated by using the nitrogen physisorption. In addition, comparability of the CO₂ sorption capacity with the commercial activated carbon proposes that better-quality adsorbents can be produced by a single activation process. This chemically-free process is favorable as it promotes a cleaner pathway on the activated carbon development. Besides, the equilibrium data for CO₂ adsorptions are well-fitted to Langmuir isotherm, with the maximum adsorption capacity is 49.75 and 70.42 cm³/g for both the synthesized and commercial activated carbon, respectively.

Index Terms—Activated carbon, carbon dioxide adsorption, Langmuir isotherm, waste biomass.

I. INTRODUCTION

The tremendous demand of energy in the world these days has caused the rising of greenhouse gases (GHG) emission, which is becoming the major concern by the public recently. Associated with that, carbon dioxide (CO₂) is labeled as the most important GHGs that contribute to the global warming through anthropogenic emission from power plant generation, transportation, and industrial sector [1]. Instead of adapting to the substantial effect of global warming, mitigation of the CO₂ emission is preferable. Therefore, immediate and continuous action should be taken to decrease the CO₂ concentration in the atmosphere. The CO₂ reduction can be done by some options such as an enhancement in combustion and energy efficiency, reduction in the use of fossil fuel, switch to non-carbon-emitting resources i.e. renewable energy, and to capture and sequester CO₂ (CCS) permanently. Amongst these options, CCS is considered as a useful technique, since it provides an ample time for the development of low-cost renewable energies and cleaner usage of fossil fuels resources during the transition period [2].

Among the possible technologies for CO₂ capture, solid adsorption is preferred due to low energy requirements, low capital and operating cost, together with limited secondary waste generation [3]. Activated carbon is one of the

promising solid adsorbents that can be utilized to capture CO₂ due to its numerous benefits, such as inexpensive, easy for regeneration, insensitiveness towards the moisture, high CO₂ adsorption capacity at ambient condition, high specific surface area, adequate pore size distribution, high mechanical strength, as well as low in energy requirement [4]. Based on the benefits possessed by activated carbon, it has been widely employed in various applications, be it in gas or liquid phase. However, exploitation of the activated carbons in capturing CO₂ has not been extensively evaluated. The potential of activated carbon in CO₂ capture depends on few criteria such as types of activation method and nature of starting materials, which in turn affects the porosity and surface chemistry of the synthesized activated carbon [5]. The chemical activation method includes the ammonia treatment and impregnation technique that have been extensively employed nowadays is uninvited as it imposes hazardous impacts towards the environment and also, results in pore blockage that may possibly lessen the adsorption capacity. Plaza *et al.* [2] proved that impregnation of activated carbon with amine-based compounds is not a suitable approach for CO₂ capture at room temperature, as it reduces the surface area and block the microporous structure that is accountable for physical adsorption process. Specifically, the impregnated activated carbon with polyethylenimine (PEI) solvents which had BET surface area of 90 m²/g can only capture CO₂ up to 4.9 wt%, as compared to virgin activated carbon that had total surface area of 1,762 m²/g and CO₂ adsorption capacity of 7.3 wt%. In addition, an incorporation of nitrogen functionalities i.e. ammonia heat treatment as proposed by Plaza *et al.* [3] is not very effective as the adsorption capacity is similar as the CO₂-activated carbon, which is about 9.7 wt%. Associated with that, physical activation technique with an absence of chemicals is utilized in this study.

Conventional approach of physical or thermal activation involves two steps, which is carbonization (temperature range of (400-850°C) and activation (temperature range of 600-900°C) processes. However, longer time and high energy consumption of the process is undesirable from the industrial point of view. Hence, one-step activation process is proposed in the study. Matos *et al.* [6] verifies that this approach is undeniably the simplest and the cheapest technique to obtain the carbon materials. The overall objective of this present work is to study the efficiency of manufactured activated carbons from one-step activation in CO₂ capture at ambient temperature and pressure, and its physicochemical properties.

II. METHODOLOGY

A. Preparation of Activated Carbon

In this study, coconut shell was utilized as starting material

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for the activated carbon production. The biomass feedstock was cleaned and oven-dried at 110°C for minimum of 12 hrs to remove the excessive moisture. The dried feedstock was crushed and ground to fine particles using a Fritsch Pulverisette 25/19 cutting miller, and was sieved to particle sizes of 250 µm. The biomass materials were stored in a dessicator until further use. The chemical compositions of the

feedstock were as tabulated in Table I. Referring to Table I, the feedstock that contains high amount of fixed carbon, and low in ash content is desirable in the activated carbon production. In addition, high volatile matter of the feedstock is significant as it contributes to large pore volume of the activated carbon.

Fig. 1. Schematic diagram of experimental setup.

TABLE I: CHEMICAL COMPOSITIONS (WT%) OF LIGNOCELLULOSIC FEEDSTOCK

Materials	Moisture	Volatile matter	Ash	Fixed Carbon ^a
Coconut shell	1.91	74.41	1.26	22.43

^aBy differences.

B. One-Step Activation Process

The biomass feedstock was physically activated under the presence of CO₂ flow in a vertical lab-scale reactor as shown in Fig. 1. The components in the experimental setup include the gas tank, reactor, thermocouple, together with the condenser. In each run, 20-30 grams of the biomass feedstock were put onto the retainer i.e. metal wire at the bottom part of sample holder, and placed into the reactor. Afterward, the reactor was flushed with nitrogen (N₂; 99.999% purity) for almost 30 min to ensure an inert condition prior to the experimental work. Then, one-step activation process was initiated by heating the samples to reaction temperature of 900°C, and at heating rate of 20°C/min, CO₂ gas (99.98% purity) flow rate of 150 cm³/min, and with residence time of 45 min.

C. Porosity Properties of Activated Carbon

N₂ physisorption process was carried out at -196°C (77K) using a Micromeritics ASAP 2020. N₂ adsorption-desorption isotherm were interpreted as a graph plot of volume of N₂ gas adsorbed versus the relative pressure (P/P₀), in which P₀ was taken at an atmospheric pressure. In addition, the following parameters i.e. Brunauer-Emmett-Teller (BET) surface area, total pore volume (V_{total}), total micropore volume (V_{micro}) and total mesopore volume (V_{meso} = V_{total} - V_{micro}), were determined. The BET surface area was estimated at P/P₀ of

0.00 to 0.10; with the correlation coefficient was found to be greater than 0.999. In addition, the cross-sectional area of N₂ gas was assumed to be 0.162 nm². The total volume was calculated by converting the amount of N₂ adsorbed at P/P₀ of 0.98, to equivalent liquid volume of the adsorbate [7]. Besides, t-plot method was used to calculate the micropore volume as well as the micropore area [8].

D. Carbon Dioxide (CO₂) Capture

Volumetric adsorption study of CO₂ was carried out using a High Pressure Volumetric Analyzer (HPVA II). Prior of the adsorption process, 0.3-0.4 g samples were out-gassed in degas port at temperature of 120°C overnight in order to eliminate the moisture and weakly-bounded volatiles. Once the degassing process completed, the samples were cooled down to ambient temperature, and were transferred to the analysis port. CO₂ adsorption was performed at room temperature (25°C) and at pressure interval of 0.1 bar, until it reached to 1 bar. During this process, reaction temperature was controlled by using a re-circulating Julabo water control bath. All data requisitions were recorded in a Comprehensive Data Analysis Package via Microsoft Excel macros (v.22.0.6) software. CO₂ adsorption capacity (wt%) for both the activated carbons is calculated as follows:

$$q_p = \frac{V_p \times MW \times 100\%}{V_{mol,STP}} \quad (1)$$

Referring to (1), q_p is the adsorption capacity in wt%, V_p is volumetric adsorption capacity in cm³/g, MW is adsorbate molecular weight (44.01 g/cm³), and $V_{mol,STP}$ represents the

molar volume of a gas at STP (22,414 cm³/mol).

III. RESULT AND DISCUSSION

A. Porosity and Surface Area Characteristics

N₂ adsorption isotherm of the prepared activated carbon with comparison to the commercial adsorbent is illustrated in Fig. 2. According to Fig. 2, volume of N₂ adsorbed that is increased during the lower part of relative pressure (P/P₀) and tend to reach a plateau at a higher P/P₀ indicates the filling of micropores. In addition, both the adsorbents are confirmed to demonstrate Type I BET adsorption isotherm, which belongs to microporous materials, in accordance to the International Union of Pure and Applied Chemistry classification [7], [8].

Fig. 2. N₂ adsorption isotherm at -196°C (AC = Activated Carbon).

In addition, BET surface area, pore size and pore volume as listed in Table II can be determined from the N₂ adsorption-desorption analyses. Based on Table II, the activated carbons have an average pore diameter of 1.6 nm, which indicates their suitability to be applied in gas phase adsorption. Besides, the surface area of the raw precursors is roughly 0.96 m²/g with predominantly macropores structures. The improvement in the surface area is attributed to the CO₂ activation process that will create new porosity, and simultaneously, remove the tarry products and non-carbon elements like hydrogen and oxygen. The releasing of these compounds then open the block pores, and develop the pore structure with large surface areas.

TABLE II: POROSITY AND SURFACE AREA OF SYNTHESIZED AND COMMERCIAL ACTIVATED CARBON

Properties	Synthesized activated carbon	Commercial activated carbon
BET surface area (m ² /g)	370.72	717.22
t-plot micropore area (m ² /g)	295.87	584.83
Micropore volume (cm ³ /g)	0.11	0.22
Total pore volume (cm ³ /g)	0.15	0.29
Micropore volume ratio (%)	72.67	74.32
Average pore diameter (nm)	1.63	1.64

B. Carbon Dioxide Adsorption Performance

The adsorption capacity of CO₂ that is measured at room

temperature and pressure is illustrated in Fig. 3. The maximum CO₂ sorption capacity that is exhibited by the synthesized and commercial activated carbon is 8.21 wt% and 10.66 wt%, respectively. The difference in CO₂ mass uptake of these solid adsorbents could be due to the value of surface area, as shown in Table II. The commercial activated carbons that have larger BET surface area are observed to adsorb more CO₂ molecules onto them, and thus, it implies that there are more surface sites for CO₂ adsorption process to take place.

Fig. 3. Weight uptake of CO₂ adsorption at 25°C (AC = Activated Carbon).

TABLE III: COMPARISON OF WEIGHT UPTAKE AT ROOM TEMPERATURE AND PRESSURE

Sample materials	Activation technique	BET surface area (m ² /g)	CO ₂ uptake (wt%)	Ref.
Olive stone char (GKOS)	N ₂ pyrolysis	43	5.8	[1]
GKOSA20 ^a	CO ₂ activation	613	8.9	
GKOSA40 ^a		909	10.5	
GKOSA50 ^a		1,079	10.7	
GKOSN400 ^b	Ammonia (NH ₃) treatment	152	6.8	
GKOSN600 ^b		232	7.1	
GKOSN800 ^b		390	8.6	
GKOSN900 ^b		442	7.3	
Commercial activated carbon (N)	H ₃ PO ₄ activation	1,762	7.3	[2]
N-DETA ^c	Wet impregnation	157	4.0	
N-PEHA ^d		170	4.8	
N-PEI ^e		90	4.9	

^a GKOSA20/40/50 = Represents CO₂ activation at different burn-off degrees (%).

^b GKOSN400/600/800/900 = Represents NH₃ heat treatment at different temperatures (°C).

^c DETA = Diethylenetriamine; ^d PEHA = Pentaethylenehexamine; ^e PEI = Polyethylenimine.

In addition, to examine the effectiveness of the synthesized activated carbon by one-step activation process in CO₂ capture at an ambience condition, a comparison study as have been tabulated in Table III is carried out. Referring to Table III, CO₂ adsorption capacity of the synthesized activated carbon in this present work is equivalent or significantly higher compared to the published data. Comparing the virgin and surface-modified activated carbon, it shows that the CO₂ uptake is improved for unmodified activated carbon. Surface area reduction of the modified-activated carbon weakly assists the physisorption process, and at the same time, chemisorbed amine compounds or nitrogen functionalities

with the activated carbon enhances the basicity of the adsorbent. Nevertheless, the chemisorption process is ineffective at lower temperature and thus, causes poor CO₂ adsorption capacity. The importance of the surface area in the physisorption process can be proved by comparing the sorption capacity of the prepared activated carbon in the study with the activated olive stone char [1]. Referring to the higher surface area possessed by the physically-CO₂ activated olive stone char with the synthesized and the commercial adsorbent used in this study; it contributes to more adsorption capacity than the utilized activated carbons in this work. Yet, the surface area might not be the sole factor in influencing the CO₂ adsorption on activated carbon [5]. Although chemically-treated activated carbon has the highest surface area in this comparative study, but the CO₂ mass uptake is still relatively lower [2]. Thus, it can be concluded that one-step activation process without the carbonization or chemicals treatment is adequate enough to produce superior adsorbents.

C. Isotherm Measurement

The CO₂ mass uptake onto the prepared and commercial activated carbon is evaluated by using the Langmuir isotherm. The Langmuir isotherm assumes that the adsorbent has finite capacity for the adsorbate, in which, no further adsorption can occur once the CO₂ molecules already occupied the surface site. In other words, it indicates the existence of a monolayer adsorption of the adsorbate on the outer surface of adsorbents. Besides, the Langmuir isotherm assumes that the sorption sites are all identical and energetically equivalent. The Langmuir isotherm can be represented as shown in (2) [9].

$$\frac{P}{V} = \frac{P}{V_m} + \frac{1}{KV_m} \quad (2)$$

Based on (1), P is the pressure (bar), V and V_m implies the total volume adsorbed and monolayer adsorption capacity (cm³/g), and K indicates the Langmuir constant that is related to the adsorption energy (1/bar). The adsorption plot of P/V against the saturated pressure of CO₂ adsorbed gives a straight line with slope and intercept is $1/V_m$ and $1/KV_m$ respectively, as shown in Fig. 4.

Fig. 4. Langmuir isotherm plot (AC = Activated Carbon).

The parameters that have been calculated from Langmuir isotherm model are summarized in Table IV. Based on Table IV, the closer R-squared values towards unity suggest that

CO₂ adsorption is well-described by the Langmuir equation.

TABLE IV: COMPARISON OF WEIGHT UPTAKE AT ROOM TEMPERATURE AND PRESSURE

Samples	Parameters	Values
Synthesized activated carbon	K [1/bar]	3.09
	V_m [cm ³ /g]	49.75
	R^2	0.99
Commercial activated carbon	K [1/bar]	2.29
	V_m [cm ³ /g]	70.42
	R^2	0.98

IV. CONCLUSION

In this study, exploitation of the lignocellulosic agricultural residues or by-product into low-cost adsorbents is attractive due to its abundance, eco-friendly properties, renewability, and economically feasible. In addition, the applicability of the solid adsorbent in acidic gas capture is significant, as it overcomes the problems caused by the amine scrubbing process that is the most acceptable technology used in industrial sector nowadays. The findings prove that the produced activated carbon from one-step CO₂ activation process is microporous and capable in CO₂ gas capture; with maximum sorption capacity to be roughly 8 wt%. Also, the experimental data is well-fitted to the Langmuir isotherm, which can be verified by the closer regression value to unity.

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