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Study on biomass derived activated carbons for adsorptive heat pump application

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ABSTRACT

Biomasses are renewable resources and suitable precursors for synthesis of activated carbons (ACs). Two biomass sources: (i) Waste Palm Trunk (WPT) and (ii) Mangrove (M) are employed to synthesis activated carbons with huge surface area by chemical activation with potassium hydroxide (KOH). Thermophysical characteristics of the derived activated carbons namely thermal conductivity, particle size distribution, pore size distribution, surface area and pore volume are assessed. The total surface area of WPT-derived AC and mangrove-derived AC are found to be as high as 2927 $m^2\,g^{-1}$ and 2924 $m^2\,g^{-1}$, respectively. The adsorption capacities of the synthesized biomass-derived ACs for ethanol are evaluated for assorted temperature and pressure conditions. It is observed that WPT-AC shows an ethanol uptake of 1.90 $kg\,kg^{-1}$ whilst the M-AC can adsorb up to 1.65 $kg\,kg^{-1}$. The isosteric heat of adsorption associated with the present adsorbents/adsorbate (ACs/ethanol) calculated at different coverages showed only marginal difference. For a typical operating condition of adsorption heat pump, both biomass derived ACs showed similar net ethanol uptake which is significantly higher than the net uptake of commercially prevalent Maxsorb III AC.

1. Introduction

Sorption-based cycles have been successfully employed in various applications starting from separation, heating ventilation and air conditioning (HVAC), refrigeration and lately desalination [1–9]. Adsorption systems can significantly reduce the amount of environmentally harmful gases as it can be driven by waste heat at temperatures below 100 °C whilst the working pairs are benign to the environment [10–13]. Waste heat-driven adsorption cycles have been studied extensively for their performance at various operation conditions over the past decades [11,14–16] along with the solar-powered systems [17–20]. Alahmer et al. [21] proposed solar adsorption chiller under different climatic conditions. Adsorbed Natural Gas (ANG) systems have been developed for natural gas storage in automobiles [22–24]. Various types of materials have been applied as adsorbents whilst silica gel-, zeolite- and activated carbon-based adsorbents are popular choice [25–30]. Composite adsorbents and metal organic frameworks gained significant interest recently [31–36].

Among the various adsorbents, activated carbons (ACs) and carbon based composites are receiving continuous attention owing to high porosity and hence high adsorption uptake of refrigerant vapor which plays significant role for the performance improvement of adsorption heat pump systems. Some representative examples are presented here. El-Sharkawy et al. [30] used AC powder namely Maxsorb, supplied by Kansai Coke & Chemicals Co. Ltd., Japan, for application of adsorption cooling system. They reported that adsorption capacity can be as high as 1.2 kg of ethanol per kg of activated carbon. Akkimaradi et al. [37] presented a study of three types of ACs (Chemviron, Fluka and Maxsorb) + HFC-134a (1,1,1,2-tetrafluoroethane) system as a possible pair for refrigeration application. El-Sharkawy et al. [38] studied the characteristics

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Nomenclature

A	adsorption potential [kJ mol^{-1}]	R	universal gas constant [J mol^{-1} K^{-1}]
b_o	equilibrium constant [–]	Q	isosteric heat of adsorption [kJ mol^{-1}]
E	adsorption characteristic energy [kJ mol^{-1}]	T	temperature [K]
M	molar mass constant [g mol^{-1}]	t	heterogeneity factor [–]
n	exponent of D-A equation [–]	W	adsorption uptake [kg kg^{-1}]
P	equilibrium pressure [kPa]	W_o	saturated amount adsorbed [kg kg^{-1}]
P_s	saturated pressure [kPa]		

of ethanol adsorption onto two spherical phenol resin based ACs named as KOH4-PR and KOH6-PR. They found that adsorption capacity of KOH4-PR/ethanol is as high as 1.43 kg kg^{-1} whilst one kg of KOH6-PR able to adsorb nearly about 2 kg of ethanol. Precursor material of above mentioned and commercial ACs are usually various kinds of coal, coke and pitch [38,39].

Activated carbons can be synthesized from renewable sources in various ways. Recently, numerous researchers have been prepared ACs from different source of waste biomasses as it is renewable and cheap [40–43]. Yang et al. [41] prepared AC from coconut shell using activating agents such as steam, CO_2 and a mixture of steam-CO_2 with microwave heating. Results showed that BET surface area of activated carbons irrespective of the activation agent resulted in surface area in excess of 2000 m^2 g^{-1}. Kyzas et al. [42] investigated the use of ACs after pyrolysis of waste potato peels. The activation agent was phosphoric acid, whilst three different carbons were prepared based on the different activation temperatures (400, 600, 800 °C). Highest achievable surface area is 1041.43 cm^2 g^{-1}. Hao et al. [44] synthesized ACs from hydrothermally carbonized waste biomass for CO_2 capture from flue gas. Mahamad et al. [45] prepared AC from the pyrolysis (500 °C, 1 h) of pineapple waste biomass (leaves, stem, crown) impregnated with $ZnCl_2$ for dye removal. Resulting AC showed surface area as high as 914.67 m^2 g^{-1}. Other related articles can be found elsewhere [46–48].

Regardless of various studies on synthesis of biomass based ACs, fewer researchers have been achieved to prepare ACs with very high surface area from biomasses. In addition, there is no significant studies which focus on biomass based ACs for adsorption heat pump applications. Accordingly, the aim of this study was to synthesis very high surface area ACs and characterize of biomass (WPT and mangrove)-derived ACs for application to adsorption heat pump systems. Some momentous contributions in this paper are:

(1) Highly porous ACs have been prepared from biomasses namely waste palm trunk and mangrove wood by KOH activation.
(2) Textural characteristics, porous properties, thermal conductivity and particle size distribution of biomass-derived ACs have been studied in detail.
(3) Adsorption isotherms of ethanol as a refrigerant onto prepared biomass-derived ACs has been experimentally investigated.
(4) Dubinin Astakhov (D-A) and Tóth equations are employed to fit ethanol adsorption isotherms of assorted pairs and isosteric heat of adsorption has also been calculated from isotherm data.

2. Experimental

2.1. Synthesis of activated carbons (ACs)

Waste palm trunk (WPT) from Malaysia and Mangrove wood from Indonesia were used as biomass precursor materials for the preparation of activated carbons (ACs). ACs have been prepared by activation using potassium hydroxide (KOH) through carbonization of biomasses with physical mixing at ratio 1:6 (biomass: KOH). Preparation process can be explained as follows; biomasses are first crushed into a particle size less than 5 mm in order to perform homogeneous drying and carbonization. The crushing samples are then dried in air dryer and vacuum dryer at 100 °C for 48 h and 105 °C for 1 h, respectively, to remove water or moisture content. Carbonization process is carried out at 600 °C with a heating rate of 10 °C/min with N_2 flow rate at 100 cc/min for 1 h using vertical electric furnace, then cooled to room temperature. Carbonized samples are then powdered and sieved to mesh size 100 μm for adsorption heat pump application. Samples obtained are then mixed directly with a chemical activator i.e. solid potassium hydroxide (purity > 85.0%, Wako Pure Chemical Industries, Ltd.) at the fixed weight ratio (carbonized biomass/KOH = 1/6). The mixture has been placed in a nickel crucible (diameter 48 mm, length 100 mm), and then nickel crucible is put into stainless steel tube (diameter 60 mm, length 500 mm). The stainless steel container is placed vertically in the electric furnace. Afterward, mixture has been heated up to 900 °C at heating rate of 5 °C/min for one hour under N_2 flow rate at 100 cc/min. After completing activation process, remaining KOH and salts formed during the heat treatment are removed by washing with HCl solution for three times and deionized water once to adjust pH to be about 7. Finally, the collected ACs are dried in an air oven and vacuum oven at 100 °C for 3 h and 150 °C for 12 h, respectively. Synthesized activated carbons are denoted as WPT-AC for waste palm trunk and M-AC for mangrove. Activation yields of WPT-AC and M-AC are summarized in Table 1.

2.2. Characterization of activated carbons

Nitrogen adsorption is one of the standard procedures to determine the porous structure of carbonaceous adsorbents, which includes the surface area of pores, pore volume and pore size. The nitrogen (N_2) adsorption/desorption isotherm of prepared activated carbons has been measured at 77 K using volumetric adsorption equipment "Belsorp-Max-S" supplied by MicrotracBEL, Japan.

Porous structure and chemical nature of activated carbons depend on the raw materials used in its preparation, the activation method and conditions. Surface morphology of prepared biomass-based activated carbons namely WPT-AC and M-AC have been observed using field emission scanning electron microscopy (JEOL-JSM-6700F-SEM, JEOL, Japan) with accelerating voltage of 3.0 kV.

Laser Diffraction Particle Size Analyser, SALD-2300, which is supplied by Shimadzu Corporation, Japan, has been employed to determine the particle size distribution of synthesized ACs. Particle size distribution is calculated using the light intensity distribution pattern of scattered light that is generated from carbon particles when laser irradiates them. AC sample is mixed with distilled water in the dissipation bath of the analyser; after that it is circu-