



Research paper

Carbon dioxide capture using ammonium sulfate surface modified activated biomass carbon



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ABSTRACT

Activated carbon (AC) was produced by phosphoric acid activation and microwave pyrolysis of Douglas fir biomass. A low temperature activated carbon surface modification method was tested using ammonium sulfate. This method successfully enhanced the carbon dioxide adsorption capacity of Douglas fir biomass based activated carbons. The activated carbon produced, was comparable to commercial grade modified carbon in terms of breakthrough time and adsorption capacity. All modified carbons were selective to carbon dioxide over methane. Activated carbon produced by a phosphoric acid impregnation ratio of 3:1, and modified with an ammonium sulfate mass fraction of 9.1%, had the highest breakthrough time and exhaustion time of 3.5 min and 13.5 min respectively. This carbon adsorbed 97% carbon dioxide from the inlet stream containing methane and other gases with a carbon dioxide over methane selectivity of 5.27. A 1 h exposure of the used carbon to a 105 °C regeneration removed a majority of the carbon dioxide and methane on the carbon surface, facilitating regeneration.

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1. Introduction

The impact of anthropogenic carbon dioxide emissions on environmental problems such as global warming is currently of major concern [1–5]. With fossil fuel fired power plants being a contributor to 85% of the world energy demand and 40% of total carbon dioxide emissions [5], a 50% increase in carbon dioxide emissions is predicted from fossil fuel fired power plants alone by 2030 [3].

Various global efforts are being made to reduce carbon dioxide emissions which include: improving energy efficiency, promoting the use of low carbon fuels and renewable energy, reforestation and carbon dioxide capture and storage (CCS) [6]. Among these, CCS (separation of carbon dioxide from exhaust or fuel, and subsequent storage or reutilization) is capable of reducing up to 90% of carbon dioxide emissions from sources such as power plants [7]. Technologies for carbon dioxide capture constitute a large portion of the total cost of CCS and therefore much effort is focused on reduction of energy penalty and operation cost [6–8]. Owing to the extra-neous effort required to incorporate these technologies into existing power plants, technologies which can be retrofit to existing

power plants are preferred (post combustion capture) [6,9].

The most mature carbon dioxide capture technology currently used commercially for post combustion capture, is absorption using liquid amines. While they have been used in industrial scale carbon dioxide capture technologies for many decades, liquid amines pose several shortcomings for operation such as the corrosion of equipment, energy intensive regeneration and generation of volatile degradation compounds [4,10–12]. Solid adsorption technologies such as activated carbon [2,13,14], metal organic frameworks (MOFs) [15–17], and zeolites [18–20] have been investigated as alternatives to liquid amine absorption. Among these, activated carbons (ACs) have the potential to address the shortcomings of liquid amines, by their robustness and stability [4,14], low energy and cost of regeneration [2,3,10,21,22]. They also present more feasibility for industrial scale application than contemporary solid adsorption technologies such as MOFs and zeolites [2,3,22,23]. The use of renewable materials for the production of AC as a cost-effective alternative to non-renewable fossil fuel based precursors is of increasing interest [2,23–26]. In this context, Douglas fir biomass, an abundant species in western North America [27], was used as an AC precursor in this work.

While ACs have been found to present some challenges such as low adsorption capacity at high temperatures and poor selectivity to carbon dioxide, these can be overcome by chemically modifying the AC surface to capture the target compound [28–31]. Carbon

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dioxide is a weak Lewis acid [11,14,22], therefore introduction of basic nitrogen containing functional groups [11,14,32] enables the surface to interact strongly with carbon dioxide thus enhancing the adsorption capacity of the AC [22,32]. Ammonium salts are nitrogen containing reagents, frequently used in synthetic fertilizers [33,34]. Modification of AC surfaces with nitrogen containing reagents such as ammonia [35,36], amines [32,37] and nitric acid [11,14] are a methods widely explored for carbon dioxide capture however, to our knowledge, no previous work has been reported using ammonium salts as a nitrogenous modification agent. To explore this possibility, ammonium sulfate salt ((NH₄)₂SO₄) was used as a novel and alternate nitrogen containing modification agent.

The objective of the present study was to prepare Douglas fir based AC and to determine the effect of ammonium sulfate salt as a novel surface modification agent on the carbon dioxide adsorption and selectivity of biomass based AC. AC was produced by phosphoric acid activation [38–47] and microwave pyrolysis [42–45,47–49] of Douglas fir biomass. The carbon was modified with various amounts of ammonium sulfate using a low temperature heat treatment and the adsorption of carbon dioxide by each carbon was analyzed over several sampling times using a packed column setup and micro gas chromatograph (3000 Micro GC, INFICON Inc., USA).

2. Materials and methods

2.1. Commercial AC

Commercial AC (GAC 830 Plus), was purchased from Norit Americas Inc. (Marshall, TX, USA). The carbon is an acid-washed granular AC (1 mm–2 mm diameter particles) produced by steam activation of coal.

2.2. Preparation of AC from renewable biomass

Douglas fir sawdust pellets (Bear Mountain Forest Products Inc., Cascade Locks, OR, USA) were used as feedstock to produce AC by phosphoric acid activation [38–47] and microwave pyrolysis [42–45,47–49]. Approximately 40 g of Douglas fir pellets (6 mm average diameter, 13 mm average length, 7% moisture mass fraction) were soaked at room temperature (25 °C) in phosphoric acid solution (85% mass fraction aq. soln., ACS, Alfa Aesar, USA) at a mass ratio of acid (dry basis) to biomass of 3:1 [42,44,46,47] for about 48 h [40,42–44]. The mass ratio of acid to biomass is referred to as the impregnation ratio [38,39,44]. After soaking, the biomass was air dried for about 24 h and then fed into a 500 cm³ quartz reactor flask and placed in a Sineo MAS-II batch microwave oven (Shanghai Sineo Microwave Chemistry Technology Co., Ltd., Shanghai, China). The outlet of the reactor was connected to a condenser system with 1.8 °C cooling water flow. The temperature of the reaction was measured by an infrared sensor enclosed in a sealed end quartz tube penetrating to the center of the flask. The reactor setup was sealed and purged with nitrogen gas for approximately 30 min to remove oxygen in the reactor before pyrolysis [48,49]. A schematic of the setup is shown in Fig. 1.

Pyrolysis was carried out at a power setting of 700 W [27,42,48,49]. After reaching the desired reaction temperature, the microwave reactor, equipped with automatic temperature/power control, used a minimum power (e.g. 0–100 W) to maintain the desired reaction temperature.

The temperature increased at an average rate of 16 K min⁻¹ for 20 min and was thereafter maintained at an average temperature of 450 °C [46,50,51] for 3 min [42,45]. The solid carbon product was rinsed with water to remove residual phosphoric acid and

thereafter magnetically stirred in 100 mol m⁻³ hydrochloric acid for 4 h to remove any metals in the form of ash clogging the pores of the carbon [52,53]. The carbon was then washed 4 times with 50 mL of distilled water and dried in an oven overnight at 105 °C. The Douglas fir AC samples contained both powdered particles of approximately 0.1 mm diameter and charred pellets of 6 mm diameter by 8 mm length. The charred pellets were broken to smaller pieces before modification, for easier handling, but were kept in pellet form.

Due to experimental constraints in activation using an impregnation ratio of 3:1 (the glassware became brittle and cracked due to the use of excess acid at high temperature) and depletion of the AC sample due to low yield, a larger quantity of a second carbon was also produced at an impregnation ratio 1.5:1 [38–41,45] by the method discussed above at 700 W power. 100 g of Douglas fir pellets were used to produce this carbon. The temperature increased at an average rate of 7.5 K min⁻¹ for 50 min and thereafter was maintained at an average temperature of 410 °C [46,50,51] for 20 min [49,54] for carbonization.

2.3. AC surface modification

100 g of unmodified AC was mixed with a saturated solution (25 °C) [55] of ammonium sulfate salt (BioXtra ≥99.0%, Sigma Aldrich, USA) prepared using 5 g, 7.5 g and 10 g of dry ammonium sulfate. The corresponding mass fractions of ammonium sulfate in these AC/ammonium sulfate mixtures were $w_{(NH_4)_2SO_4} = 4.76\%$; $w_{(NH_4)_2SO_4} = 6.98\%$ and $w_{(NH_4)_2SO_4} = 9.1\%$ respectively. The mixtures were placed in an oven at 105 °C for 24 h in 25 mL Erlenmeyer flasks and covered with aluminum foil, leaving a pinhole for gas escape. Thereafter, the modified carbons were thoroughly washed 3 times with 50 mL of distilled, dried overnight in an oven at 105 °C and stored at room temperature for gas adsorption measurements.

The Douglas fir based ACs are referred to herein as DF(x)y where x is the impregnation ratio of phosphoric acid to biomass and y is the mass of ammonium sulfate used for 100 g of unmodified AC. For example DF(1.5)5 is the Douglas fir carbon produced by an impregnation ratio of 1.5:1 and modified with 5 g ammonium sulfate in 100 g of AC. Similarly the commercial AC is referred to as Cy.

2.4. Carbon dioxide adsorption measurement

Approximately 1 g of AC was packed into a vertical 316 stainless steel tube (6.35 mm diameter and 150 mm length; Swagelok, Richland, WA, USA). The tube was closed on both ends with fiberglass wool plugs and a brass in-line particulate filter (15 μm pore size; Swagelok, Richland, WA, USA) was connected to the outlet side (top) of the tube to prevent small carbon particles from escaping the tube and entering connected equipment. The inlet of the tube (bottom) was connected to a gas cylinder containing the following gas composition by volume fraction: 10% carbon dioxide, 50.01% carbon monoxide, 10.01% methane, 19.96% hydrogen and 10.02% nitrogen (OXARC Inc., Pasco, WA, USA). The outlet of the tube was connected to a micro gas chromatograph (3000 Micro GC, INFICON Inc., USA). Copper tubing (ACE Hardware, Richland, WA, USA) and 316 Stainless steel nuts and ferrules of 3.18 mm diameter (Swagelok, Richland, WA, USA) were used for all connections. 316 stainless steel reducing unions (reduction from 6.35 mm diameter to 3.18 mm diameter) were used to connect the column to the tubing. Fig. 2 shows the apparatus setup used for gas adsorption measurements.

The inlet gas was allowed to pass through the AC for the sample injection time of the micro GC (30 s). Multiple such gas packet samples were run through a single AC at intervals of 36 s (to allow

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