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.

Keywords: carbon dioxide capture; activated carbon; surface modification; Douglas fir; ammonium sulfate

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 extraneous 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 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 $((\text{NH}_4)_2\text{SO}_4)$ 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 to 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 Figure 1.

Figure 1 here

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 $7.5 \text{ K} \cdot \text{min}^{-1}$ 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 $\geq 99.0\%$, 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 $w_{(\text{NH}_4)_2\text{SO}_4} = 4.76\%$; $w_{(\text{NH}_4)_2\text{SO}_4} = 6.98\%$ and $w_{(\text{NH}_4)_2\text{SO}_4} = 9.1\%$ 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 μ m 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. Figure 2 shows the apparatus setup used for gas adsorption measurements.

Figure 2 here

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 sample elution through micro GC) until the carbon dioxide volume fraction in the outlet gas was greater than 9 % (approaching inlet carbon dioxide composition of 10 %), indicating that the adsorption capacity was close to being exhausted. The gas flow was switched off in between samples in order to ensure that the residence time of each gas sample packet was the same and to allow time for sample elution. Since the volume of stagnant gas present in the column between samples was less than 5 % of the gas volume passed through the system, gas diffusion effects

were neglected. The change in the carbon monoxide volume after passing through the column was very small ($< 5\%$), therefore the inlet volumes of the other gases were calculated based on the carbon monoxide volume and inlet gas composition. Relative volumes have been reported (outlet volume fraction/inlet volume fraction) in this work.

2.5 Regeneration

Regeneration was carried out for demonstration purposes on the best performing carbon, DF(3)10, by heating the used carbon sample in an oven at $105\text{ }^{\circ}\text{C}$ for 1 h [11]. After the 1 h regeneration, carbon dioxide adsorption tests were conducted as described in section 2.4. The regenerated carbon is referred to as DFR(3)10.

3. Results and Discussion

3.1 Commercial AC breakthrough

For preliminary observation of the effect of ammonium sulfate AC modification, breakthrough experiments were done on commercial AC (GAC 830 Plus, Norit Americas Inc., Marshall, TX, USA), modified with ammonium sulfate. Three modified samples were prepared with ammonium sulfate mass fraction loadings of 4.76% (C5), 6.98% (C7.5) and 9.1% (C10) respectively. Figure 3 shows the relative volume (ratio of outlet to inlet carbon dioxide volume fractions, $\phi_{\text{CO}_2\text{out}}/\phi_{\text{CO}_2\text{in}}$) of the packed AC tube over cumulative gas sampling times (breakthrough curves in this work) for the unmodified (C0) and modified commercial carbons (C5, C7.5 and C10).

Figure 3 here

The typical S-shaped breakthrough curves seen in Figure 3 are indicative of initial carbon dioxide adsorption and subsequent gradual occupation of AC active sites until exhaustion of the AC surface sites. In this work, the breakthrough time, t_B is defined as the time at which the ratio of outlet to inlet carbon dioxide volume fractions is greater than 0.1 ($\varphi_{CO2out}/\varphi_{CO2in} > 0.1$) and the exhaustion time, t_E is defined as the time at which $\varphi_{CO2out}/\varphi_{CO2in} > 0.9$.

As seen in Figure 3, there is an increase in t_E with increasing mass loading of ammonium sulfate on the AC. Although the unmodified commercial carbon, C0 initially adsorbs some carbon dioxide, as indicated by the low relative volume within the first 1 min, ($\varphi_{CO2out}/\varphi_{CO2in} = 0.11$; see inset image), its capacity was exhausted quickly within 4.5 min. This exhaustion time is however increased to 7 min, 10 min and 12.5 min upon the addition of 4.76 % (C5), 6.98 % (C7.5) and 9.1 % (C10) ammonium sulfate respectively. Also, the increase in relative volume over time is slower, for modified carbons with higher ammonium sulfate loading. Although all the C carbons reach breakthrough within 1.5 min, it can be seen in the inset figure, that the relative volume detected within this time, is lowered by modification with 9.1 % loading of ammonium sulfate (C10) from 0.11 (C0) to 0.08 (C10). These results indicate that there are a larger number of active sites for carbon dioxide capture on the modified ACs than on the unmodified AC and that these increase with increasing ammonium sulfate loading. This confirms that the modification of AC with ammonium sulfate increases its capacity to capture and hold carbon dioxide which can be attributed to the possible addition of nitrogen based functional groups to the AC due to ammonium sulfate treatment, similar to observations in previous work on ammonia and nitrogen AC modification [10,11,32].

3.2 Douglas fir AC breakthrough

Douglas fir biomass was used as a renewable precursor to produce AC by phosphoric acid activation and microwave pyrolysis. Modified samples were prepared with ammonium sulfate mass fraction loadings of 4.76 % (DF(1.5)5), 6.98 % (DF(1.5)7.5) and 9.1 % (DF(1.5)10). The effect of ammonium sulfate loading was studied using DF(1.5) ACs (Douglas fir AC produced with phosphoric acid to biomass impregnation ratio of 1.5:1) and the DF(3) AC (impregnation ratio 3:1) was modified with a mass fraction of 9.1 % ammonium sulfate (DF(3)10) due to insufficient yield. Figure 4 shows the breakthrough curves for the unmodified (DF(1.5)0) and modified carbons (DF(1.5)5, DF(1.5)7.5, DF(1.5)10 and DF(3)10).

Figure 4 here

It can be seen in Figure 4, that DF(3)10 has the best carbon dioxide adsorption of all the DF carbons. This carbon has a sustained relative volume of 0.03 to 0.04 for 2.5 min, indicating that 96 % to 97 % of the carbon dioxide entering the carbon column was adsorbed for 2.5 min consecutively. Among the DF(1.5) ACs, the carbon dioxide adsorption capacity of the unmodified AC, DF(1.5)0 is fairly low, as indicated by the large initial relative volume ($\phi_{\text{CO}_2\text{out}}/\phi_{\text{CO}_2\text{in}} = 0.46$ at 0.5 min). However, similar to the observation with the commercial carbons, the initial relative volume is lowered and exhaustion times are extended upon modification with ammonium sulfate. For example, by modification with 4.76 % (DF(1.5)5) and 9.1 % (DF(1.5)10) ammonium sulfate, the initial relative volume is lowered to 0.29 and 0.06 respectively. Also, t_E is more than doubled by a 9.1 % ammonium sulfate loading, from 3 min, to 7.5 min. Breakthrough as defined in this work, was not applicable to the DF(1.5)0, DF(1.5)5 and DF(1.5)7.5 carbons due to their high outlet carbon dioxide volume, however DF(1.5)10 had a breakthrough time, t_B of 1.5 min, the same as that of commercial carbon, C10. While the DF(1.5)

carbons did not match the performance of the C modified carbons, DF(3)10 had breakthrough and exhaustion times ($t_B = 3.5$ min and $t_E = 13.5$ min) comparable to and in fact better than that of C10 ($t_B = 1.5$ min and $t_E = 12.5$ min) and close to double the values for D(1.5)10 ($t_B = 1.5$ min and $t_E = 7.5$ min).

An increase in the exhaustion times and initial volume of carbon dioxide adsorbed in ammonium sulfate modified DF carbons indicates that there are far more active sites available for carbon dioxide capture in the modified carbons than in the original carbons. This implies that ammonium sulfate surface modification does indeed improve the carbon dioxide adsorption capacity of Douglas fir based ACs. AC produced with a higher impregnation ratio, DF(3)10, had carbon dioxide breakthrough curves comparable to commercially available modified AC implying that Douglas fir biomass is a suitable precursor for AC based carbon dioxide capture. The longer breakthrough time and exhaustion time of DF(3)10 imply that there is a slower decline in the adsorption capacity of DF(3)10 and it has a larger number of active sites available for carbon dioxide adsorption than DF(1.5)10. Several researchers have emphasized the importance of impregnation ratio as a primary parameter which effects the physico-chemical properties of the AC, specifically increasing the adsorption capacity of the carbon toward the target compound, by contributing to the porosity development [23,38,40,56,57]. Therefore, the higher adsorption capacity of DF(3)10 is presumably due to a more developed pore structure with higher impregnation ratio of phosphoric acid to biomass. The optimum conditions for AC production by microwave pyrolysis of Douglas fir is the subject of ongoing study in our group.

3.3 Carbon dioxide/methane selectivity

Selectivity of carbon dioxide over methane is important in natural gas and bio-gas purification applications where carbon dioxide is considered a contaminant [28,58,59]. In this work, it was found that all the ACs were selective to carbon dioxide over methane at all sampling times. While a small amount of methane was adsorbed, after 4 min of cumulative gas sampling time, all methane adsorption ceased completely and all the ACs were exclusively selective to carbon dioxide. The deviation in the volume of other gases after passing through the column was negligible. In order to understand the effect of ammonium sulfate modification on the methane adsorption of ACs, methane breakthrough in the 4 min time frame was studied. Figures 5a and 5b show the breakthrough curves of methane for the DF and C carbons respectively.

Figure 5 here

It can be seen in Figures 5 a and b that methane adsorption ceases within 4 minutes for both DF and C carbons, as the relative volume of methane ($\phi_{CH_4out}/\phi_{CH_4in}$) reaches 1 after this period. In the inset of Figure 5a, it can be seen that DF ACs modified with a higher loading of ammonium sulfate, adsorbed more methane as indicated by the low initial relative volume ($\phi_{CH_4out}/\phi_{CH_4in}$) and longer time of methane adsorption. For example, DF(1.5)0 adsorbed very little methane, however, at 0.5 min, the relative volumes of DF(1.5)5 and DF (1.5)10 decreased to 0.88 and 0.65 respectively (see inset of Figure 5 a). Of the DF carbons, DF(3)10 adsorbed the largest amount of methane from the inlet ($\phi_{CH_4out}/\phi_{CH_4in} = 0.54$) at 0.5 min with continued adsorption for 2 min. When compared with the results of carbon dioxide adsorption (Figure 4), it can be seen that DF ACs with higher carbon dioxide adsorption also adsorbed more methane from the mixed gas stream.

In Figure 5 b it is seen that the methane adsorption of the commercial carbons is not drastically effected by modification with ammonium sulfate. However, C10 adsorbed slightly more methane than the other commercial ACs as indicated by the lower relative volume over time. The commercial ACs adsorbed methane for 2 min to 3.5 min. When compared to the carbon dioxide adsorption in this time frame (see Figure 3 inset), it can be seen that C0, C5 and C7.5 all have similar curves of carbon dioxide relative volume ($\phi_{\text{CO2out}}/\phi_{\text{CO2in}}$) over time. C10, however has a slightly better carbon dioxide capacity indicated by its more gradual increase in relative volume. Similar trends are observed in methane adsorption, where C10 adsorbs slightly more methane than the other commercial carbons (C0, C5, and C7.5).

The above results indicate that ACs which have a higher carbon dioxide adsorption capacity adsorbed more methane than other carbons. This implies that a proportionate amount of methane adsorbing functional groups are also added to the AC surface along with carbon dioxide adsorbing functional groups. However, the methane sites are quickly depleted implying that there are a large number of functional groups which are selective to carbon dioxide over methane and that the competition for methane over carbon dioxide is low in this modification method. This point is illustrated in Figure 6. Figure 6 shows the carbon dioxide selectivity over methane (ratio of the total volume of carbon dioxide adsorbed to the total volume of methane adsorbed in 4 minutes) for the modified and unmodified C and DF carbons over 4 minutes, after which methane adsorption ceases.

Figure 6 here

It can be seen in Figure 6, that all the DF and C carbons have a selectivity greater than 3, indicating that they are all selective to carbon dioxide over methane. The DF carbons have a

much higher selectivity towards carbon dioxide than the C carbons. The unmodified carbon DF(1.5)0 has the highest selectivity of 17.6 which is more than 4 times that of C0. Although the selectivity of the DF carbons decreases with addition of ammonium sulfate it is greater in comparison to that of their commercial counterparts. For example, DF(3)10 has a selectivity of 5.27 indicating that 5.27 times more carbon dioxide is adsorbed by DF(3)10 than methane. All DF carbons have a selectivity above 5, comparable to the selectivity found in literature [28,59]. The results indicate that carbon dioxide adsorption is favored over methane adsorption in ammonium sulfate modified carbons and there is no competition for active sites between methane and carbon dioxide. Furthermore, AC produced by Douglas fir biomass precursor, is much more selective to carbon dioxide than its commercial counterpart implying that Douglas fir is a suitable precursor which can produce an activated carbon with high carbon dioxide selectivity.

3.4 Regeneration

For demonstration purposes, regeneration was carried out on the best performing carbon, DF(3)10. DF(3)10 was regenerated for 1 h. The regenerated carbon is referred to as DFR(3)10. The carbon dioxide and methane breakthrough curves of DF(3)10 and DFR(3)10 are compared in Figure 7 below.

Figure 7 here

It can be seen that the carbon dioxide breakthrough curve of the regenerated AC follows an S-shaped trend similar to the original carbon indicating gradual uptake of carbon dioxide by free active sites. While there is a slight decrease in t_B after regeneration, t_E is for both the carbons (17 min). The selectivity of the regenerated carbon over 4 min was calculated to be 3.93, whereas

that of the original carbon was 5.27, as discussed in Figure 6. This is possibly due to incomplete regeneration. The methane breakthrough curves for the regenerated and original carbons are almost identical. These results indicate that a majority of the carbon dioxide and methane were removed by exposure to heat at 105 °C for 1 h. While an optimum regeneration temperature and time are to be investigated in future work, the current conditions facilitate close to complete regeneration of the ammonium sulfate modified Douglas fir AC.

4. Conclusions

AC was produced from Douglas fir biomass by phosphoric acid activation and microwave pyrolysis. A low temperature modification method was tested using ammonium sulfate as a modification agent, in order enhance the carbon dioxide adsorption of AC. An increase in exhaustion time and breakthrough time after modification indicated that the modification of AC with ammonium sulfate enhances its capacity to capture and hold carbon dioxide. Douglas fir based AC, DF(3)10 had a sustained carbon dioxide adsorption of 96 % to 97 % for 2.5 min and a breakthrough time and exhaustion time comparable to that of commercial AC, C10 indicating that Douglas fir biomass is a suitable precursor for AC production and ammonium sulfate modification for carbon dioxide capture. Selectivity results show that there is no competition for active sites between methane and carbon dioxide before or after modification and that carbon dioxide adsorption is favored over methane adsorption in ammonium sulfate modified carbons. A 1 h exposure of used DF(3)10 to heat at 105 °C removed a majority of the carbon dioxide and methane on the carbon surface, facilitating regeneration. The results indicate that ammonium sulfate modified AC, DF(3)10, produced from Douglas fir biomass is a reusable technology

which can selectively adsorb carbon dioxide and offers promising solutions for carbon dioxide mitigation measures.

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6. References

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