**SEPARATION OF CO₂ FROM FLUE GASES BY CARBON-MULTIWALL
CARBON NANOTUBE MEMBRANES**

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ABSTRACT

Multiwalled carbon nanotubes (MWNT) were found to be an effective separation media for removing CO₂ from N₂. The separation mechanism favors the selective condensation of CO₂ from the flowing gas stream. Significant uptakes of CO₂ were measured at 30°C, 150°C and 300 °C over the pressure range 0.5 to 5 bar. No measurable uptake of nitrogen was found for this range of conditions. The mass uptake of CO₂ by MWNT was found to increase with increasing temperature. A packed bed of MWNT completely removed CO₂ from a flowing stream of CO₂/N₂, and exhibited rapid uptake kinetics for CO₂.

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EXECUTIVE SUMMARY

The feasibility of using a novel carbon-multiwall carbon nanotube membrane for separating CO₂ from the flue gas of a power generation plant is being studied. Such an innovative membrane system offers unique advantages over existing technologies: refractory carbon-carbon membranes are resistant to temperature and chemical attack, the multiwall nanotube derived pores in the membrane are mono-disperse, the pore size can be controlled, and the rapid kinetic and diffusion rates will yield high permeate fluxes. As the first step toward design and construction of a working carbon-carbon nanotube based membrane, specific goals have included evaluation of the separation mechanism, either diffusive or adsorptive, and a test to demonstrate proof-of-concept separation. Experimental work has determined uptakes and separation efficiencies for CO₂ and N₂ mixtures by open ended multiwall carbon nanotubes.

As-produced multiwall nanotubes (MWNT) are open at one end, but contain small particulate inclusions of iron catalyst blocking access to the core. We have found that a simple graphitization step (heating to 1800 °C in an inert atmosphere) removes this iron contaminant, greatly enhancing adsorption within the nanotube core. We have produced and graphitized 10 grams of MWNT, allowing for bench scale studies on these materials. Static adsorption isotherms for both N₂ and CO₂ have been measured on MWNTs. The MWNTs show little uptake of N₂ over the pressure range 0.5 to 5 bar. In contrast, the measured uptake of CO₂ on MWNT at 30 °C was found to be two orders of magnitude greater than for N₂ over the same pressure range. The MWNTs exhibit significant CO₂ adsorption capacities over this pressure range for operating temperatures in excess of 300°C.

A fixed bed containing 0.25g of the graphitized multiwall nanotubes was used to separate CO₂ from N₂ from a gas flow of 100 SCCM containing equal quantities of the two components. Prior to breakthrough, CO₂ was retained for 0.4 min, illustrating the efficacy of these materials for separating the two gases. Further refinements of bed separations at higher temperatures and pressures are being pursued, as is the fabrication of single-layer nanotube membranes.

Classical molecular dynamics simulations are used to investigate the diffusive flow of pure molecules and binary molecular mixtures. The simulations predict which binary mixtures separate as a result of this diffusive flow and which remain mixed. They also indicate how these results depend on the nanotube properties such as diameter and helical symmetry. The molecular dynamics simulations are based on the numerical integration of Newton's equation of motion. The potentials influencing the molecular interactions were broken into short-range interactions and long-range interactions. Short-range interactions (covalent potential, modeled as Brenner potentials) fix bonding energy, bond length and bond angle. Long-range interactions were comprised of Lennard-Jones potentials and Coulombic potentials. Long-range interactions affect macroscopic movements like diffusion and adsorption.

Finally, a bouncing flow (back and forth) flow was found to exist at the open end of the nanotube, with lots of CO₂ molecules diffusing into the core of the nanotubes. The CO₂ molecules that do diffuse into the core region of the nanotube progress through the nanotube axially following a spiral flow pattern along the core wall. Finally, molecules diffuse out the opposite end of the nanotube. This result also indicates that the core region of nanotubes can be used as an effective separation medium for CO₂ in gas streams.

EXPERIMENTAL

Production of MWNT

We have previously described the synthesis of MWNTs by reacting hydrocarbon vapor over a dispersed iron catalyst that is deposited *in situ* in a quartz tube reactor within a multi-zone furnace [1]. A xylene-ferrocene feedstock was continuously injected *via* syringe pump into a preheat section operated at ~ 250 °C. The xylene-ferrocene vapors were swept into the reaction zone of the furnace by an Ar/10% H₂ carrier gas that also maintained a partial pressure of 32 mbar carbon inside the reactor. The reaction zone was held at 725 °C, with an Ar/H₂ flow rate of 6 L/min (STP). The operating procedure was: the quartz tube and substrates were installed into the furnace and then purged with Ar gas; the preheater and furnace heaters were ramped up to achieve the desired stable temperatures; the liquid and gas feeds were started and run for the desired reaction times. The MWNTs grew on both the quartz tube wall and flat quartz plate added for additional surface area, forming thick mats of well-aligned nanotubes that could be readily harvested by brushing the surfaces.

Graphitization of MWNT

For graphitization, the bulk MWNT samples were centered within a horizontal electric resistance tube furnace. After purging the system with dry nitrogen (Air Products NF grade) and maintaining slightly above atmospheric pressure, the samples were heated from ambient to 1000 °C at 20 °C/min. Once 1000 °C was reached, the furnace was put under automatic control (optical pyrometer) and heated at 12.5 °C/min to the set point. Samples were treated to 2800 °C, and held at temperature for 45 min.

Mass Uptake of CO₂ and N₂ on Multiwall Nanotubes

The mass uptake of CO₂ and N₂ on graphitized MWNT was measured using the Hidden Intelligent Gravimetric Analyzer (IGA). The nanotubes were loaded into the sample side of the apparatus, and the chamber sealed and evacuated to 10⁻⁶ mbar. High purity CO₂ or N₂ was introduced into the chamber and the pressure raised in 500 mbar increments to a maximum of 5 bar. At each pressure step, the IGA waits for the sample mass to equilibrate and then records this value versus the samples initial value. This procedure was performed for both CO₂ and N₂ gases at 30 °C, 150 °C, and 300 °C. Mass uptake measurements were also taken for gas mixtures of N₂ and CO₂ ranging from 0 to 100% CO₂ at 150 °C.

Separation of Flowing Stream of CO₂ and N₂ on Packed MWNT Bed

A packed bed of nanotubes was used to separate a flowing stream of CO₂ and N₂. The gas composition was 50% CO₂ and 50% N₂ with a volumetric flow of 100 SCCM total. The bed consisted of 0.26 g of graphitized MWNT packed into a fixed column 6 mm in diameter and 80 mm long. A blank column of the same dimensions was installed as a bypass line, and the outlet from this system (diluted with a carrier stream of He) was sent to a mass spectrometer. Figure 1 shows a schematic of the fixed bed apparatus. Once a baseline spectra was determined by flow on the bypass side, the gas flow was switched to the MWNT bed, the mass spectrometer was used to detect CO₂, indicating breakthrough. After saturation of the bed, the flow was switched to the bypass, and the time taken to fill the empty bed was measured. The empty bed time was used to calculate the proportion

of time for CO₂ adsorption on the MWNT prior to saturation and the time due to simple flow dynamics. As the flow time on the empty bed would in actuality be longer than for a packed bed, the measured CO₂ uptake value on the packed bed should be considered a minimum value and could be higher than that measured.

The Molecular Diffusion and Dynamic Flow of CO₂, N₂ and O₂ through Carbon Nanotubes

The simulations were performed on a Compaq Alpha 64 Workstation. Molecular dynamics simulations, based on numerical integration of Newton's equation of motion, were used to predict diffusive behavior of molecules in the core region of nanotubes. Standard Lennard-Jones potentials are used to model the intermolecular interactions. Both H-terminated and C-terminated open nanotube ends have been considered. For the calculation of intermolecular potentials and total energy, Lennard-Jones potential parameters had to be obtained [2,3]. While parameters had been computationally compared with the bond lengths and bonding energies, and each other, we chose the best parameters.

In some studies these molecules are treated as single, spherical particles [5]. While this simplifies the simulation considerably, our previous work has demonstrated that molecular shape can have a significant influence on molecular diffusion through nanopores [6]. Therefore the approach that is being taken is one where the atoms are treated explicitly and the molecules are characterized with Coulomb and Lennard-Jones (LJ) potentials [7,8]. The atoms in the carbon nanotube walls are characterized with a many-body reactive empirical bond-order potential that is coupled to LJ potentials [9]. Simulations are based on an idealized (10,10) nanotube with one shell. This restriction exists due to the computational limits on the number of atoms that can be handled. It will have no effect on the predicted diffusion of molecules through the core and can be directly correlated to the diffusion of molecules through MWNT cores of similar size.

The modeling is described in detail in Results and Discussion section below.

RESULTS AND DISCUSSION

N₂ and CO₂ Adsorption on MWNT

The as-produced MWNT were graphitized prior to use to ensure removal of any blockages caused by residual iron catalyst from the core of the nanotubes. No significant mass uptake of N₂ was measured on the MWNT in either static or flowing mode. The mass uptake of nitrogen was unaffected by temperature (30°C to 300°C).

The mass uptake of CO₂ on MWNT was measurable at 30°C, 150°C and 300°C. As shown in Figures 2, the mass uptake was low (~3.5% by mass) but was significant. The uptake was higher at higher temperatures, indicative of a chemisorption mechanism. A screening study showed this uptake to be reversible, with full desorption isotherms measured to determine that the mass uptake is reversible. This finding will significantly affect the design of a MWNT membrane in future work. As shown in Figure 3, the mass uptake of CO₂ from mixtures of CO₂ and N₂ increased with increasing concentration of CO₂, indicative of a strong preference for sorption of CO₂ over N₂ and the supporting the conclusion that MWNTs are an effective separations medium for CO₂/N₂ mixtures.

The mass uptakes increased with increasing gas pressure (to 5 bar) as would be expected. The significant mass uptake of CO₂ onto the nanotubes at 5 bar and 300°C signifies that the MWNT are an effective medium for separation of CO₂ and N₂. The goal of this project was to determine what separation mechanism would be viable for the design of a nanotube membrane for CO₂ removal from flue gases, either diffusion driven or condensation driven. As the uptake of CO₂ is significant while the uptake of N₂ is negligible, the condensation mechanism appears to dominate.

A packed bed of MWNT was used to separate a flowing stream of 50 SCCM CO₂ and 50 SCCM N₂. The packed bed configuration was employed to provide a more realistic comparison of the behavior of a membrane based on MWNT. The packed bed also provides valuable data on the uptake kinetics relative to gas velocities and concentrations. The bed was able to take up all the CO₂ for 1.4 minutes (Figure 4), while the blank bed retained CO₂ for only 1 minute. Therefore the MWNT took up CO₂ prior to breakthrough for at least 0.4 minutes (see Experimental section as to why this is a minimum uptake value). This uptake value is in excess of 10% by mass and indicates that nanotubes are an effective separation media for removing CO₂ from N₂. While it would be outside the scope of this project, this result indicates that a satisfactory separation of CO₂ and N₂ could be designed around a simple packed bed of MWNT.

Modeling of Separation Mechanism

Classical molecular dynamics simulations are used to investigate the diffusive flow of pure molecules and binary molecular mixtures. The simulations predict which binary mixtures separate as a result of this diffusive flow and which remain mixed. They also indicate how these results depend on the nanotube properties such as diameter and helical symmetry. The simulations provide information about how the structure and size of the molecules in the mixtures influence the results. Molecules with non-spherical aspect ratios exhibit different behavior than spherical molecules that affects both their diffusion mechanisms and their separations in mixtures.

Classical molecular dynamics simulations based on the numerical integration of Newton's equation of motion were utilized:

$$U = \sum_i \sum_{i < j} \left[\underbrace{V_r(r_{ij}) - B_{ij} V_a(r_{ij})}_{\text{Short-range}} + \underbrace{V_{vdw}(r_{ij}) + V_{Coul}(r_{ij})}_{\text{Long-range}} \right]$$

Where U = Binding E

r_{ij} = Distance between atom i and j

V_r = Core-core repulsive E

V_a = Attractive E due to valence e^- s,

B_{ij} = Many-body empirical bond order term

Modulates valence e^- density

Depends on atomic coordination, bond angles

V_{Coul} = Coulombic potential

The potentials influencing the molecular interactions were broken into short-range interactions and long-range interactions. Short-range interactions (covalent potential, modeled as Brenner potentials) fix bonding energy, bond length and bond angle. Long-range interactions were comprised of Lennard-Jones potentials and Coulombic potentials. Long-range interactions affect macroscopic movements like diffusion and adsorption.

Brenner Potential

Brenner potentials are used to describe the short-range interactions, and adequately describe the covalent interactions between atoms. Figure 5 shows the covalent potential between carbon and oxygen in CO₂.

$$V_a = a_1 \cdot e^{-b_1 \cdot r_{ij}} + a_2 \cdot e^{-b_2 \cdot r_{ij}} + a_3 \cdot e^{-b_3 \cdot r_{ij}}$$

$$V_r = c_1 \cdot e^{-d_1 \cdot r_{ij}} \left[1 + \frac{c_2}{r_{ij}} \right]$$

	Bonding E [eV]	Bond Length [$\text{\AA}$]
O=CO	5.517	1.160
N $\equiv$ N	9.799	1.098
O-O	5.166	1.207

Lennard-Jones Potential

Lennard-Jones Potentials are used to describe long-range interactions between atoms. The form used was:

$$V_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right]$$

$$\sigma_{AB} = \frac{(\sigma_A + \sigma_B)}{2} \quad \epsilon_{AB} = \sqrt{\epsilon_A \cdot \epsilon_B}$$

	<u>Atomic #</u>	<u>Atomic Mass[g/mol]</u>	<u>ϵ/k_B [K]</u> *	<u>σ[Å]</u>
C	6	12.0	28.129	2.757 [2]
N	7	14.0	37.300	3.310 [3]
O	8	16.0	80.507	3.033

Coulomb interaction

Applying partially charged carbon dioxide, we have to added potentials due to Coulomb potential into total energy [4].

$$\begin{aligned} U_{qC*qC*} &= + 6.105/r_{C*C*} [\text{eV } \text{\AA}/\text{\AA}] \\ U_{qC*qO*} &= + 3.053/r_{C*C*} [\text{eV } \text{\AA}/\text{\AA}] \\ U_{qO*qO*} &= + 1.526/r_{C*C*} [\text{eV } \text{\AA}/\text{\AA}] \end{aligned}$$

The Lennard-Jones potentials and the coulombic potentials were combined to describe the long-range interactions between C-C, C-O, and O-O in the CO₂-nanotube system, Figures 6, 7 and 8.

Finally, a bouncing flow (back and forth) flow was found to exist at the open end of the nanotube, with lots of CO₂ molecules diffusing into the core of the nanotubes. The CO₂ molecules that do diffuse into the core region of the nanotube progress through the nanotube axially following a spiral flow pattern along the core wall. Finally, molecules diffuse out the opposite end of the nanotube. This result is also indicates that the core region of nanotubes can be used as an effective separation medium for CO₂ in gas streams.

CONCLUSIONS

MWNT have been shown to be an effective media for the separation of CO₂ from N₂. At 300°C and 5 bar pressure of CO₂, the mass uptake of CO₂ onto graphitized MWNTs was found to be 3.5%. The results indicate that these materials should be effective for separating CO₂ from flue gases at elevated temperatures and pressures. The data indicate that a MWNT membrane system could be designed based on the mechanism of CO₂ condensation within the pores of the nanotubes. As this uptake of CO₂ has been found to increase with temperature and CO₂ concentration in gas stream, these materials seem ideal for use at the elevated temperatures found in a flue stream. Concurrently, the use of a packed bed of MWNT has been show to be an effective separator for CO₂ from N₂ and does offer an alternative technology for performing this separation. Molecular dynamics simulations based on the numerical integration of Newton's equation of motion have shown that: (a) bouncing (back and forth) flow of molecules occurs around the open end of the nanotube; (b) lots of CO₂ molecules diffuse into the nanotube; (c) a similar number of molecules will diffuse out the opposite end of the nanotube; and (d), the molecules follow a spiral flow path along the inner wall of the nanotubes.

STUDENT SUPPORT

One graduate student, Ms Jenny Hilding, was supported on this grant at the University of Kentucky. Ms. Hilding is a PhD student in Chemical and Materials Engineering program under the advisement of Prof. Eric Grulke.

Due to Prof. Sinnott moving the University of Florida mid-grant period, another graduate student, Mr. Ki-Ho Lee, was also associated with the project. Mr Lee was not directly supported with grant funds, but did work on the project as part of his PhD program under Prof. Sinnott.

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Figure 1. Packed bed flow separation apparatus.

Figure 2. Mass uptake of CO₂ at 30 °C, 150 °C and 300 °C. Sample weight of 54 mg graphitized MWNTs. (VGB-S2).

Figure 3. Mass uptake of CO₂ at 150 °C for various mixtures of CO₂ and N₂. Sample weight of 54 mg.

Figure 4. Selective uptake of CO₂ on packed bed of MWNT. Gas composition: 50 SCCM N₂ and 50 SCCM CO₂. Packed bed: 0.26g of MWNT.

Figure 5. C=O Covalent Potential for CO₂.

Figure 6. Combination of Lennard-Jones and Coulomb Potentials for C and O of CO₂: C—C interactions.

Figure 7. Combination of Lennard-Jones and Coulomb Potentials for C and O of CO₂: O—O interactions.

Figure 8. Combination of Lennard-Jones and Coulomb Potentials for C and O of CO₂: C—O interactions.