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

**Semi-Annual Technical Progress Report
for Period September 2000 thru February 2001**

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March 2001

**Prepared for
The U. S. Department of Energy
Under Contract No.
DE-FG26-00NT40825**

**Submitted by
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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 and 150°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 150°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.

Computational modeling was used to assess the interaction between various gas molecules and the carbon nanotubes. In this study, classical molecular dynamics simulations were used to investigate the diffusive flow of pure molecules and binary molecular mixtures through carbon nanotubes. Standard Lennard-Jones potentials were used to model intermolecular interactions. Both H-terminated and C-terminated open nanotube ends have been considered. The specific molecules and binary systems that are being examined include nitrogen, oxygen, carbon dioxide, nitrogen/oxygen, nitrogen/carbon dioxide and oxygen/carbon dioxide. These simulations predict which binary mixtures separate as a result of this diffusive flow and which remain mixed. Nanotube properties such as core diameter and helical symmetry are also accounted for in the simulation results. The simulations provide information about how the structure and size of the molecules in the mixtures influence the results. For example, n-butane and

isobutane are predicted to have significantly different separation behaviors when they are mixed with methane molecules. In addition, molecules with non-spherical aspect ratios exhibit different behavior than spherical molecules that affects both their diffusion mechanisms and their separation in mixtures. The study includes individual nanotubes and nanotubes in bundles and the degree of separation predicted depends on whether the nanotubes are retained as cohesive bundles.

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 and 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. The key components of work completed or underway to satisfy the modeling requirements are:

(1) Searching Lennard-Jones parameters

For the calculation of intermolecular potentials and total energy, Lennard-Jones potential parameters of newly applied atoms, i.e. nitrogen and oxygen, had to be obtained. While parameters had been computationally compared with the bond lengths and bonding energies, and each other, we chose the best parameters.

	<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

(2) Coulomb interaction

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

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

(3) Covalent potentials

The parameters for covalent potentials (Rebo potentials in this simulation) of N₂, O₂, and CO₂ are not prepared yet. Until the parameters for the gases will be obtained experimentally or calculated by trial-and error, we use the parameters assumed to be the same values as those for H₂.

(4) Modification to existing code

In addition of some parameters, we are modifying our program for new elements because the currently used program is adjustable for the simulation of hydrocarbon system that consists of just two atom types.

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 or 150 °C).

The mass uptake of CO₂ on MWNT was measurable at both 30°C and 150°C. As shown in Figures 2 and 3, the mass uptake was low (~3% by weight) but was significant. The uptake was higher at higher temperatures, indicative of a chemisorption mechanism. A screening study showed this uptake to be reversible, therefore full desorption isotherms will also be measured to determine if this mass uptake is reversible or not. This finding will significantly affect the design of a MWNT membrane in future work.

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 150°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. However, full desorption isotherms at higher temperatures and continued modeling of the system are required to fully understand the operating limitations of this system and to verify that condensation is the controlling mechanism.

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.

Further work in this area will address the need for data at still higher temperatures (to 300°C) and the reversibility of the gas uptake. Further work on the packed bed of nanotubes will also be undertaken at higher temperatures to determine the uptake kinetics for these materials at varying gas flow rates and CO₂ concentrations. Such information, combined with diffusion modeling, will allow for design of a membrane system in Phase II of this project.

Modeling of Separation Mechanism

Classical molecular dynamics simulations are used to investigate the diffusive flow of pure molecules and binary molecular mixtures. Standard Lennard-Jones potentials are used to model the intermolecular interactions. Both H-terminated and C-terminated open nanotube ends have been considered. The specific molecules that are being examined include methane, ethane, nitrogen, oxygen, carbon dioxide, methane/ethane, methane/n-butane, methane/isobutane, nitrogen/oxygen, nitrogen/carbon dioxide and oxygen/carbon dioxide (nitrogen/carbon dioxide are specifically considered for this project). 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. For example, n-butane and isobutane are predicted to have significantly different separation behaviors when they are mixed with methane molecules. In addition, molecules with non-spherical aspect ratios exhibit different behavior than spherical molecules that affects both their diffusion mechanisms and their separations in mixtures. The study includes individual nanotubes and nanotubes in bundles and the degree of separation predicted depends on whether or not the nanotubes are in bundles.

Sinnott and her graduate student, Mr. Ki-Ho Lee, are working to incorporate the appropriate potential for characterizing N_2/CO_2 mixtures into their molecular dynamics program. 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 will be characterized with a many-body reactive empirical bond-order potential that is coupled to LJ potentials [9]. We are currently working to merge the two types of approaches and expect to validate and begin the diffusion simulations soon.

CONCLUSIONS

MWNT have been shown to be an effective media for the separation of CO₂ from N₂. 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, 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 shown to be an effective separator for CO₂ from N₂ and does offer an alternative technology for performing this separation.

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Figure 1. Packed bed flow separation apparatus.

Figure 2. Mass uptake of CO₂ at 30 °C. Sample weights of 37 mg (VGB 42) and 54 mg (VGB-S2).

Figure 3. Mass uptake of CO₂ at 150 °C. 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.