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Project Title: **PREPARATION OF CARBON MOLECULAR SIEVES FOR OXYGEN SEPARATION FROM AIR**

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ABSTRACT

Carbon molecular sieves (CMS) have become an increasingly important class of adsorbents for use in gas separation and recovery processes. The overall objective of this project was to produce Illinois coal-based CMS suitable for producing an enriched oxygen stream of >85% from an air feedstock.

Theoretically, there are two ways to recover enriched oxygen, either as the high pressure product of adsorption or the low pressure product of desorption in a pressure swing adsorption (PSA) process. The high pressure product involves altering the surface chemistry of the char making the CMS selectively adsorb nitrogen. This is a novel approach that attempts to take advantage of nitrogen's higher quadrupole moment. The low pressure product of desorption involves the traditional CMS, which selectively adsorbs oxygen. Using carbon deposition (CD), generating a narrow pore size distribution (PSD) in the 3-4 Å range will be attempted. This range is based on the kinetic diameters of 3.46 Å for O<sub>2</sub> and 3.68 Å for N<sub>2</sub>. Char preparation techniques included pyrolysis, activation, and CD with benzene, or surface treatment with nitric acid, calcium, or ammonia.

Our initial CMS research used IBC-102 coal pellets, since commercial CMS is pelletized for use in PSA processes. However, to increase experimental productivity, it was decided to switch to granular coal as the raw starting material. The best CMS pellet produced thus far had an O<sub>2</sub>/N<sub>2</sub> selectivity of 3.36 with an O<sub>2</sub> capacity of 6.88 cc/g. However, selectivity was well below the goal of 20. One granular CMS sample produced an O<sub>2</sub>/N<sub>2</sub> selectivity of 29.5. During the five minute adsorption experiment, this same CMS demonstrated a selectivity as high as 58; however, capacity was extremely small. The best surface treated sample attained an O<sub>2</sub>/N<sub>2</sub> selectivity of 0.91 and an oxygen purity of up to 36%. However, these were well below our goals of a selectivity of 0.2 and >85% O<sub>2</sub> purity.

Future research recommendations include varying percent burn-off during activation, further study of the two-step hydrocarbon deposition process, and further surface treatment with calcium, chlorine, and possibly hydrogen to make a more N<sub>2</sub> selective CMS.

## EXECUTIVE SUMMARY

### Background

Gas separations are a major production cost in the chemical industry today. Production of industrial gases by pressure swing adsorption (PSA), is expected to grow much faster than by the conventional method, cryogenic distillation. Commercial interest in carbon molecular sieves (CMS) is growing and these materials are currently being used to replace less efficient adsorbents (e.g., zeolites) in industrial gas separation processes.

Carbon molecular sieves are microporous materials having pore size dimensions similar to the critical dimensions of the gas molecules to be separated. CMS separate gases based on kinetic adsorption. The pore surface area of CMS is usually less, and the pore size distribution narrower than that of typical activated carbons. Commercial CMS, used in nitrogen recovery, preferentially adsorb oxygen from air. The challenge is to produce a CMS which produces >85% oxygen purity. Most CMS made thus far at ISGS can produce an enriched nitrogen stream (90-95%) from an air feedstock, while a different CMS was able to produce an oxygen enrichment of approximately 40%.

### Goals and Objectives

By either producing CMS that preferentially adsorbs nitrogen or CMS with high oxygen adsorption capacity, we believe that it is possible to produce a gas separation system that could produce up to 90% oxygen. We outlined an experimental approach to develop these CMS.

The proposed research consisted of 5 tasks.

- Task 1. Chars were prepared from IBC-102 coal under specified heat treatment and activation conditions. The pore structure and surface chemistry of the chars were tailored for oxygen separation using chemical activation, carbon deposition, and surface treatment.
- Task 2. The kinetics of O<sub>2</sub> and N<sub>2</sub> adsorption and desorption on chars were measured at 25°C.
- Task 3. The physical and chemical properties of the CMS products were evaluated to gain additional insight into the fundamentals of preparation and properties of CMS.
- Task 4. A process flowsheet for oxygen recovery with Illinois coal-based CMS was developed.
- Task 5. Technical and management reports were prepared and submitted to the ICCI.

## Experimental and Results

Efforts this past contract year have focused on producing and evaluating O<sub>2</sub>/N<sub>2</sub> selectivity and capacity. A high selectivity is desirable for increased purity, while high capacity gives a high recovery of the product. There are two ways to recover oxygen. One is by preferential adsorption of O<sub>2</sub>, which involves carbon deposition and recovery of the low-pressure O<sub>2</sub> product in a PSA process. If a highly selective CMS with good capacity can be made, both high purity oxygen and nitrogen could be developed from the same CMS. The second method is by preferential adsorption of N<sub>2</sub>, which involves altering the char surface chemistry causing the resulting CMS to behave more like a zeolite, which preferentially adsorbs nitrogen.

The major steps for traditional CMS production involved pyrolysis, activation, oxidation, and carbon deposition or surface treatment. A 2 inch ID fluidized-bed reactor and a fixed-bed reactor were used for pyrolysis, activation, carbon deposition, and surface treatment. Our initial CMS research used raw IBC-102 pellets binded with cornstarch and preoxidized for two years under atmospheric conditions. Since finding a prospective CMS is a highly iterative process, it was decided to work with granular activated carbon instead of pellets to increase productivity in manufacturing and testing prospective CMS materials. IBC-102 coal, grinded to -24 to +48 mesh and pre-oxidized for two hours in oxygen at 225°C, was used as the starting raw material. Larger quantities of coal were pyrolyzed and CO<sub>2</sub> activated to provide a large number of samples of activated char as the starting material for carbon deposition (CD) or surface treatment.

Pyrolysis and activation resulted in char (both pellets and granular) that exhibited no molecular sieving effects. It is desirable to produce a char with a narrow pore size distribution (PSD) in the 3-4 Å range. This range is based on kinetic diameters of 3.46 Å for oxygen and 3.68 Å for nitrogen. To accomplish this task, CD was employed. The CD procedure was done using a two-step hydrocarbon deposition process with a single hydrocarbon, benzene in this case. The procedure was to deposit carbon on to the activated char under relatively high hydrocarbon concentrations for a short amount of time, then dilute the hydrocarbon concentration and deposit carbon for a longer period of time. This allowed a more precise way of controlling the pore size of the CMS. We deposited carbon on to the activated pellets using benzene for various times, and at various temperatures and concentrations. The best CMS pellet produced thus far had an O<sub>2</sub>/N<sub>2</sub> selectivity of 3.36 with an O<sub>2</sub> capacity of 6.88 cc/g. However, selectivity was still well below the goal of 20. While the two step process seemed to work well in maintaining capacity and improving O<sub>2</sub>/N<sub>2</sub> selectivity slightly, the process did just the opposite for the granular samples. While there was significant increase in selectivity, capacity was very low. One granular CMS sample produced an O<sub>2</sub>/N<sub>2</sub> selectivity of 29.5. During the 5 minute adsorption experiment, this same CMS demonstrated a selectivity as high as 58; however, capacity was extremely small. This CMS would perhaps have potential for nitrogen generation, but not for oxygen generation. The reason(s) for such a difference between granular and pelletized samples is unknown at this time. Our goal for traditional CMS produced by CD is an O<sub>2</sub>/N<sub>2</sub> selectivity greater than 20 and minimum O<sub>2</sub> capacity of 6 cc/g. A higher selectivity gives a higher purity product, while high capacity increases product recovery.

Traditional CMS production, as described above, results in a CMS that is more oxygen selective. To create a CMS which is more nitrogen selective, the surface chemistry of the activated char must be altered. Since alteration of surface chemistry is not well known in the scientific community, it is hard to say what selectivity requirements are needed for surface treated carbons. However, based on commercial zeolite data, an  $O_2/N_2$  selectivity of 0.2 seems to be a good candidate. Capacity requirements are unknown, but are probably on the same order as traditional CMS. In preparing a more nitrogen selective CMS,  $CO_2$  activated char was oxidized with  $HNO_3$  to add surface oxygen groups to the prospective CMS. The next surface treated CMS involved depositing nitrogen on the surface of a KOH activated char by heat treating with ammonia. Another surface treatment technique was impregnating the  $HNO_3$  oxidized char with calcium by ion exchange. The resulting surface treated chars were all evaluated for selectivity. Efforts thus far have produced marginal results, with three of the four samples exhibiting nearly no significant selectivity. However, the  $HNO_3$  oxidized char became slightly more nitrogen selective ( $O_2/N_2 = 0.94$ ) from its parent  $CO_2$  activated char ( $O_2/N_2 = 0.99$ ). Treating the surface further by ion exchange with  $Ca^{2+}$  made the oxidized char even more  $N_2$  selective ( $O_2/N_2 = 0.91$ ). This selectivity was still well above an  $O_2/N_2$  selectivity of 0.2.

### **Recommendations for Future CMS Research**

The importance of pore size distribution (PSD) has been stressed in literature and it is stressed here. It is desirable to start with a char that has a narrow PSD and high micropore volume, especially for making traditional CMS by carbon deposition. This is true since CD is a uniform treatment of the activated char. It is obvious that an activated char with a uniform PSD will be narrowed down uniformly and still have a narrow PSD except the pores will be smaller. A good CMS has a narrow PSD in the 3-4 Å range. If the PSD is wide, CD treatment will narrow the pores; however, the pore size distribution will still be wide and this is not good for a CMS. The narrow PSD for an activated char can potentially be obtained by activating under the right conditions and with the right gas. The starting coal may also have an impact, but that is currently not known. We were unable to characterize our chars' PSD since our adsorption instrument (Quantachrome Autosorb-1) was not operating correctly for seven of the 12 project months. It is recommended that pore size distributions be characterized for starting chars to gain more insight on the effect of PSD on making an effective CMS.

Activation of our chars resulted in approximately a 23% weight loss or burn-off. Past research showed that maximum micropore volume occurred at approximately 35% burn-off. Burn-off in the 8-10% range also showed molecular sieve properties around the 5-6 Å range. For future work, it is recommended that activating char to 8-10% and 35% burn-off be looked into. If a char activated to 8-10% burn-off results in a narrow micropore distribution, this could be a very good candidate for carbon deposition, particularly using the two-step hydrocarbon deposition process. 35% burn-off should give us the maximum micropore capacity attainable with IBC-102 coal pellets; however, the PSD will need to be characterized to determine how effective carbon deposition will be.

Our best results were obtained using the two-step hydrocarbon deposition process. The first step involved depositing carbon using a concentrated stream of hydrocarbon for a short period of time which closes the pore openings on the CMS. The second step involved using a dilute hydrocarbon stream to carefully reduce the pore opening to suitable dimensions to separate oxygen. It is desirable to characterize the porosity of the activated char and resulting CMS after CD. This can give information on the type of process required for carbon deposition and can determine its affect. It is recommended that the two-step hydrocarbon deposition process be further explored since it has good potential. However, it is still emphasized that a starting char with a narrow micropore size distribution will have the best results after CD.

As mentioned, the results of surface treating carbons have been marginal at best. Ammonia treatment seems to have no effect on O<sub>2</sub>/N<sub>2</sub> selectivity and decreases capacity at longer treatment times. Calcium treatment by ion exchange does seem to have only a slight positive effect on selectivity. Past research indicates O<sub>2</sub>/N<sub>2</sub> selectivity can be decreased by outgassing the sample at higher temperatures. However, this may not be feasible for commercial PSA processes. It is recommended that calcium treatment be further studied by increasing treatment time and/or the amount of calcium used. To take advantage of nitrogen's higher quadrupole moment, it is recommended for future work that hydrogenation to remove surface oxygen groups and chlorine (a polar molecule) be used to treat the carbon surface.

Upon producing a suitable O<sub>2</sub> or N<sub>2</sub> selective CMS, the laboratory scale PSA process designed for this project should be used to evaluate product purity. Currently, our laboratory scale PSA process adsorbs at 1 atm and desorbs by pulling a vacuum and heating the CMS. It is recommended that the process be modified slightly to adsorb under 5 to 10 atm and desorb at 1 atm by acquiring a very fine metering valve. This slight modification will allow our laboratory scale PSA process to operate under conditions more similar to a commercial scale PSA process.

## OBJECTIVES

The overall objective of this project was to produce Illinois coal-based CMS suitable for producing an enriched oxygen stream of >85% O<sub>2</sub> from an air feedstock. Low grade oxygen (less than 95% O<sub>2</sub>) has many industrial and medical uses, including feed to a gasifier in an IGCC plant. We believe that it was possible to produce an oxygen recovery system that would produce >85% oxygen using CMS and we outlined an experimental approach to develop these CMS.

The proposed research consisted of five tasks.

- Task 1. Chars were prepared from IBC-102 coal. Pelletized and granulated coal were pyrolyzed at 600-1000°C in a horizontal tube furnace for small samples and a 2-in. ID batch fluidized-bed reactor for large samples. Process conditions that were varied include: heat treatment temperature, heating rate, hold time and flow rate. The pore structure of the char was modified to optimize molecular sieving behavior for an oxygen recovery process. Chars were activated to different levels of conversion in 100% carbon dioxide at 850-900°C. Coals were also chemically activated with potassium hydroxide to enhance surface area development and increase adsorption capacity of the char. Different techniques of loading potassium onto the coal were investigated, e.g., physical mixing, ion exchange and impregnation to incipient wetness. Coals were impregnated with calcium using ion exchange and chars hydrogenated to remove surface oxygen groups in an effort to produce carbon surfaces that will preferentially adsorb nitrogen rather than oxygen. Carbon deposition, using suitable hydrocarbons such as isobutane and benzene as the cracking gas, was used to further tailor the pore structure of the activated chars to improve selectivity and capacity.
- Task 2. The molecular sieve properties of the chars prepared in Task 1 were evaluated. Kinetic studies were performed to determine volumetric adsorption capacity and selectivity of prepared chars for oxygen recovery from air. An O<sub>2</sub>/N<sub>2</sub> selectivity >20 (carbon deposition) or <0.2 (altering surface chemistry) and capacity above 6 cc/g was considered suitable for commercial use. Carbon-bed breakthrough curves were measured using a laboratory scale adsorption column/gas chromatography system. Analysis of breakthrough curves yielded valuable information on the kinetics of oxygen recovery with the various types of CMS produced. Breakthrough times gave an indication of the efficiency of the CMS in separating and recovering oxygen from air. Results were compared with commercially available zeolites.
- Task 3. The chemical, physical and morphological properties of the products prepared in Task 1 were determined to provide additional information on the fundamentals of preparation and properties of CMS. Tests performed included: measurement of total surface area (N<sub>2</sub>-BET and CO<sub>2</sub>-DR), density (helium and bulk), and

ultimate and proximate analyses.

- Task 4. If a suitable CMS product was identified to recover oxygen from air, the technical and economic feasibility of manufacturing it on a commercial scale was evaluated. Based on the results obtained in Tasks 1-3, a process flow sheet for the production of CMS from Illinois coal was developed.
- Task 5. Technical and management progress reports were prepared quarterly, and a final report at the end of the 12 month project. The quarterly reports provided information about progress to date as well as plans for the upcoming quarter. These discussions included any variance from cost and scheduling projections.

## INTRODUCTION AND BACKGROUND

Gas separations are a major production cost in the chemical industry today. Production of industrial gases by non-cryogenic methods, e.g., pressure swing adsorption (PSA), is expected to grow much faster than the conventional method, cryogenic distillation. Although there is room for improvement in the design and operation of PSA processes for gas separation, most gains in process efficiency will likely come about from the development of new and improved adsorbent materials. Carbon molecular sieves have become an increasingly important class of carbonaceous adsorbents for application in the separation of small gas molecules and are currently being used to replace less efficient adsorbents (zeolites) in commercial gas separation processes.

The particular separation examined in this research, separation of oxygen from air, is usually performed with zeolites, membranes, or cryogenic distillation. With a Type 5A zeolite, it is possible to produce an oxygen stream containing 85% O<sub>2</sub>, but that concentration is sustained for only a short time. It is the goal of this project to produce an Illinois coal-based carbon molecular sieve that performs as well or better than Type 5A zeolite. Preliminary studies by showed that HSA char (KOH impregnated) was capable of producing oxygen concentrations up to 40%, depending upon time and flow rate<sup>1</sup>.

Different surface treatments on carbon and how they affected the adsorption of oxygen and nitrogen have been examined<sup>2</sup>. It was noted that Saran carbon adsorbs more N<sub>2</sub> than O<sub>2</sub> at 25°C due to stronger interactions of the larger N<sub>2</sub> molecule with the adsorbent pore walls and due to the interaction of the nitrogen quadrupole moment with the electrostatic field gradient. Expanding on previous work, which observed that the adsorption of molecules having high quadrupole moments is increased on cation exchanged silica-alumina, Ehrburger examined the adsorption of N<sub>2</sub> on calcium-exchanged carbon and found an increase in N<sub>2</sub> adsorption<sup>3</sup>. Other research included treating CMS with hydrogen to remove oxygen that was chemically bound to the carbon and found that the diffusion rate of O<sub>2</sub> into CMS was reduced<sup>4</sup>. Thermal desorption of the char at 925°C can also remove oxygen from the char surface. Treating CMS with hydrogen or through ion exchange shows promise for producing CMS suitable for oxygen recovery and will be investigated in this research.

A German company manufactured carbon molecular sieves from coal for the purpose of oxygen recovery. They evaluated different methods for producing CMS from coal and found that most of the CMS produced oxygen enriched gas streams of up to 40-50% O<sub>2</sub> from an air feedstock. However, they found one CMS that performed exceptionally well and was capable of producing a desorption gas stream containing 83% O<sub>2</sub> and 17% N<sub>2</sub> from an air stream<sup>5</sup>. This CMS was a specially pelletized coal that used benzene as the cracking hydrocarbon during the carbon deposition step. Other research also used benzene as the cracking hydrocarbon in producing an oxygen purity of up to 75%. Their starting activated carbon was Pittsburgh Activated Carbon MSC-V, with a narrow pore size distribution around the diameter 0.5-0.55 nm. Moore and Trimm maintain that a successful CMS strongly depends on the porosity of the starting material<sup>6</sup>.

Two commercial activated carbon pellets with no selectivity and average pore size around 4.2 Å and 4-5 Å were evaluated. Using a two-step hydrocarbon deposition process, they were able to increase O<sub>2</sub>/N<sub>2</sub> selectivity from 1 to 21 while maintaining an O<sub>2</sub> capacity of about 8 cc/g. Higher selectivity produces higher product purity, while higher capacity results in higher product recovery. The research of Cabrera concluded that starting material is very important in producing a successful CMS using carbon deposition techniques<sup>7</sup>.

Carbon molecular sieves are microporous materials having pore size dimensions similar to the critical dimensions of the gas molecules to be separated. The pore surface area of CMS is usually less, and the pore size distribution narrower than that of typical activated carbons. In this study, it is desirable to have a CMS with a narrow pore size distribution in the 3-4 Å range. This is based on the Leonard-Jones kinetic diameters of 3.46 Å and 3.68 Å for oxygen and nitrogen respectively. These diameters are of importance because CMS separates gases based on kinetic adsorption as compared to zeolites which rely on equilibrium adsorption. This prior research shows promise for producing Illinois coal-based CMS for oxygen recovery.

Low grade oxygen streams (less than 95%) have many applications, including: feed to a gasifier in an IGCC process, biological treatment of wastewater, feed to ozonator for wastewater treatment, basic oxygen furnace for steel making, nonferrous metals smelting, paper and pulp industry, medical applications, various partial oxidation processes, and any process which involves combustion by increasing combustion efficiency. A CMS-based PSA process is an economic alternative to current methods (zeolites and membranes). The development of a suitable CMS from Illinois coal could lead to a wide range of new process applications for this material. Research directed toward the development of manufacturing processes for the production of high value products from Illinois coal should help to broaden existing markets for this resource. In addition, a CMS production process could utilize char derived from a mild gasification process tailored for Illinois coals. In this case, the molecular sieve market would improve the economic viability of the mild gasification process. The current selling price of CMS is about \$10,000/ton.

The use of Illinois coal-based CMS to enrich oxygen for IGCC plants and other commercial



processes would provide economic benefits for the users and provide a new market for Illinois coal. Commercial CMS currently produced by Carbo Tech (Germany) starts with coal which costs about \$200/ton. Compare this with Illinois coal which currently sells for about \$30/ton. The positive economic benefits to Illinois is obvious. Normally, zeolites or membranes would be used to produce gas streams highly enriched in oxygen, but the use of CMS may provide a significant materials cost savings. Zeolites preferentially adsorb nitrogen instead of oxygen, while CMS tend to do the reverse. Due to carbon's natural affinity for oxygen, the challenge is to produce a CMS for oxygen enrichment above about 40%.

## EXPERIMENTAL PROCEDURES

Our initial CMS research used IBC-102 coal pellets, since commercial CMS is pelletized for use in PSA processes. However, to increase experimental productivity, it was decided to switch to granular coal as the starting raw material. Figure 1 presents an overview of the experimental plan to produce an O<sub>2</sub> or N<sub>2</sub> selective CMS from IBC-102 coal pellets binded with 5% corn starch and granular CMS. The three major steps involved in CMS production are 1) pyrolysis, 2) activation, and 3) carbon deposition or surface treatment. The fixed bed reactor was used exclusively to make CMS using pellets as the starting material, while the fluidized bed reactor (FBR) was used to make large amounts of activated char for carbon deposition and surface treatment experiments. Using granular material instead of pellets increased productivity by 150%.

### Char Preparation

About 2 g of IBC-102 coal pellets (pre-oxidized under atmospheric conditions for two years) were placed in a ceramic boat inside a tube furnace (Lindberg) and heated under flowing N<sub>2</sub> (3 L/min) to 700-1000°C and held for 0.5h. The char was then cooled under flowing N<sub>2</sub> to room temperature. For granular CMS, the starting coal was ground to -24 to +48 mesh and pre-oxidized for two hours in oxygen at 225°C. 150 grams of the pre-oxidized, granular coal was placed in a 2 inch ID FBR and heated under flowing N<sub>2</sub> at 800°C and held for 0.5h. To enhance surface area development and increase adsorption capacity of the heat treated chars, physical and chemical activation methods were employed.

Since it is desirable to have a high micropore volume, physical activation in scientific grade carbon dioxide was carried out. Recent research showed that CO<sub>2</sub> activation increased micropore volume, while steam activation decreased micropore volume<sup>8</sup>. It is further possible to produce a more narrow micropore distribution with CO<sub>2</sub> activation, which is also desirable. After pyrolysis at 800°C in nitrogen, the temperature was increased to 850-900°C in 1 atm CO<sub>2</sub> and held for 1h. After the specified time, the resulting char was then cooled, under flowing N<sub>2</sub> to room temperature. The activation procedure described was the same for both pellets and granular char. The pellets were activated in the tube furnace while the granular char was activated in the FBR.

Chemical activation involved the addition of an alkali salt to the raw coal and subsequent heat treatment in an inert gas. Raw coal was physically mixed with potassium hydroxide (KOH) in a 1:1 ratio by weight and blended together. The blended sample was placed in a ceramic boat inside a tube furnace (Lindberg), heated to 800°C in flowing N<sub>2</sub> and held for 0.5h. It was then cooled to room temperature in N<sub>2</sub>, grinded to -100 mesh and washed several times with deionized water until the pH was about 5.6. This produced a high surface area (HSA) char.

To further modify the pore structure of the activated char to obtain a narrow pore size distribution in the 3-4 Å range, carbon deposition was employed. The chemically or physically activated char (pellets and granular) was placed in a ceramic boat in a tube furnace. The tube and sample were flushed with N<sub>2</sub> (400 cc/min) at room temperature for 15 minutes. The sample was heated under N<sub>2</sub> to temperatures of 650-850°C, and then concentrations of 12% by volume benzene (balance N<sub>2</sub>), 3% by volume benzene, or a combination of both were introduced. Total reaction times ranged from 5 min to 2h. Benzene was used because other researchers had reported favorable results for CD with benzene<sup>5,6</sup>. After the specified time, nitrogen was reintroduced to flush out any residual hydrocarbon before cooling to room temperature under nitrogen. Figure 2 shows the experimental apparatus used to crack benzene and deposit carbon. The resulting char was characterized for O<sub>2</sub>/N<sub>2</sub> selectivity and adsorption capacity.

Traditional CMS production, as described above, results in a CMS which is more oxygen selective. To create a CMS which is more nitrogen selective, the surface chemistry of the activated char must be altered. In preparing a more nitrogen selective CMS, CO<sub>2</sub> activated char was oxidized to add surface oxygen groups to the prospective CMS. This was accomplished adding 45% HNO<sub>3</sub> by weight (balance deionized H<sub>2</sub>O) to a given amount of granulated CO<sub>2</sub> activated carbon in a reflux reactor. The reflux reactor was heated to 80°C and the sample held for 2.5 hours. Afterwards, the char was cooled, washed in deionized water to a pH of about 5.6, and then oven dried. This char was characterized for O<sub>2</sub>/N<sub>2</sub> selectivity. Another CMS involved depositing nitrogen on the surface of a KOH activated char by heat treating with ammonia. A KOH activated char sample was placed in a ceramic boat in the tube furnace and heated to 800°C in flowing N<sub>2</sub>. At 800°C, pure ammonia was introduced for 2 to 6 hours and then cooled under flowing N<sub>2</sub> to room temperature. The resulting char was washed several times to remove residual ammonia. The same ammonia procedure was used on an HNO<sub>3</sub>-oxidized sample. Another surface treatment technique used involved impregnating the HNO<sub>3</sub>-oxidized char with calcium by ion exchange. 1.5 moles of Ca<sup>2+</sup> (in the form of calcium acetate [CaAc]) per mole of oxygen on the char were added to a beaker containing the oxidized char. 500 ml of deionized water was then added, and the mixture was heated to 60°C and stirred on a magnetic stirring plate for 1 hr. The resulting char was washed several times in deionized water to remove residual CaAc and then oven dried.

### Adsorption Kinetics

To evaluate the kinetic adsorption of nitrogen and oxygen, a volumetric adsorption instrument (Quantachrome Autosorb-1) was used to calculate volume adsorbed versus time at 25°C for each gas. A typical kinetic adsorption run proceeded as follows: about 1.0 g of char was placed in a sample cell and outgassed at 120°C for 8h (at 5 millitorr). Helium was used to determine the dead volume of the sample cell. After outgassing again for several minutes, a known volume of O<sub>2</sub> or N<sub>2</sub> was introduced into the sample cell (initial pressure of 300-400 torr) and the decrease in pressure was monitored by a pressure transducer accurate to within about 0.1 torr. The drop in gas pressure was recorded at 10 sec intervals for the first minute and 30 sec intervals for minutes 2-5. Experiments were repeated to check reproducibility. Volumes adsorbed were calculated using the ideal gas law.

### Breakthrough Experiments

Possible interactions between gases in a binary or multi-component mixture must be accounted for when adsorbing a gas mixture onto a carbon substrate. To account for competitive adsorption between different gases, a laboratory scale adsorption column/gas chromatography (AC/GC) system (Figure 3) was used to evaluate adsorption of binary gas components. The adsorption column was 3/8 in. ID x 8 in. length. Approximately 10 grams of sample was placed in the AC yielding a space velocity of approximately 1.8 min<sup>-1</sup>. The sample was desorbed either using heat (120-140°C) or vacuum in flowing He. After complete desorption, medical air was passed through the AC at a specified and controlled flow rate (~15 cm<sup>3</sup>/min) under approximately 1 atm pressure. The AC was maintained at a constant temperature (20-30°C) during the run. For air separation, the [O<sub>2</sub>] and [N<sub>2</sub>] in the effluent was monitored by GC, and a breakthrough time for each component was determined. The shape of the breakthrough curves ([O<sub>2</sub>] vs. time) can be analyzed to obtain information on the kinetics of the competitive adsorption process. When the carbon bed became saturated, e.g., inlet [O<sub>2</sub>] = outlet [O<sub>2</sub>], the sorbent was regenerated with heat (120-140°C) and/or vacuum (1 atm). It will be of additional interest to examine the products of desorption (i.e., O<sub>2</sub> and N<sub>2</sub>) from the spent char in flowing helium. This is another possibility of achieving high purity oxygen. After a series of runs, e.g., at different flow rates, the char was removed from the AC and subjected to physical/chemical characterization tests. The overall performance of the char to recover oxygen from air was assessed and compared to that of other Illinois coal chars and commercial zeolites.

## RESULTS AND DISCUSSION

Commercial CMS for nitrogen generation have an O<sub>2</sub>/N<sub>2</sub> selectivity >9 and O<sub>2</sub> capacity >4 cc/g after carbon deposition. To use CMS for oxygen generation from the low pressure product gas, it is our belief that a O<sub>2</sub>/N<sub>2</sub> selectivity > 20 and O<sub>2</sub> capacity > 6 cc/g is needed. The higher the selectivity, the purer the product. The higher the capacity, the higher the product recovery and the higher the CMS efficiency. Since alteration of surface chemistry is not well known in the scientific community, it hard to say what selectivity requirements are needed for surface treated carbons. However, based on commercial zeolite data, an O<sub>2</sub>/N<sub>2</sub> selectivity of 0.2 seems to be a good candidate. Capacity requirements are unknown,

but are probably on the same order as traditional CMS.

### Pyrolysis and Activation

Table 1 shows the effect of differing heat treatment temperatures (HTT) and activation on the starting pellets. While no selectivity was exhibited after pyrolysis, capacity varied for the samples tested. As mentioned, one of the project goals is to develop a high capacity CMS. The maximum capacity was attained for the char heat treated at 800°C (Table 1). Lowering the pyrolysis temperature, slightly decreased capacity, while increasing pyrolysis temperature significantly decreased capacity. As a result, the 800°C heat treated char was chosen for further activation. Activating the char with CO<sub>2</sub> at 875°C for 1 hour further increased capacity with no molecular sieving effects.

### Carbon Deposition on CO<sub>2</sub> Activated Char

Benzene was cracked at two different concentrations at various temperatures and treatment times for both pellets and granular char. The starting char was pyrolyzed at 800°C and activated with CO<sub>2</sub> at 875°C. Table 2 shows the effect of a single-step hydrocarbon deposition using 12% by volume benzene (balance N<sub>2</sub>) and also at 3% by volume benzene (balance N<sub>2</sub>). From Table 2, one can compare the sieving effects after CD with a more concentrated hydrocarbon stream as opposed to a more dilute hydrocarbon stream. The best pelletized CMS (Table 2) had an O<sub>2</sub> capacity greater than 6 cc/g; however, selectivity was only 2.96. The best granular CMS had an O<sub>2</sub> capacity greater than 4 cc/g; however, selectivity was only 2.01.

Prior research demonstrated that a two-step hydrocarbon deposition process could significantly increase selectivity while maintaining capacity. The process treats the activated char with a high concentration of hydrocarbon for a short period of time, then decrease the hydrocarbon concentration and continue to treat for a longer period of time. The high hydrocarbon concentration quickly and uniformly narrows the pore openings. Then the lower hydrocarbon concentration carefully narrows the pore openings uniformly to 3-4 Å by depositing carbon at the mouth of the pores, preserving most of the activated char capacity. Generally, there is a tradeoff between selectivity and capacity. Tables 3 and 4 show results of some preliminary two-step hydrocarbon depositions while varying temperature and time. The final char has a capacity of 6.88 cc/g, which is acceptable, and selectivity increased is 13.5% (Table 3). However, selectivity is still well below the goal of 20. While the two step process seemed to work well to maintain capacity and slightly improve O<sub>2</sub>/N<sub>2</sub> selectivity, the process did the opposite for the granular samples. While there was significant increase in selectivity, capacity was very low. One CMS sample had an O<sub>2</sub>/N<sub>2</sub> selectivity of 29.5 (Table 4). During the five minute adsorption experiment, this same CMS demonstrated a selectivity as high as 58; however, capacity was extremely small. This CMS would perhaps have potential for nitrogen generation, but not for oxygen generation. The reason(s) for the difference between granular and pelletized samples is unknown at this time.

### Carbon Deposition on KOH Activated Char

Table 5 shows the effect of chemical activation with KOH and CD with benzene. The KOH activated char has very high adsorption capacities for O<sub>2</sub> and N<sub>2</sub> (Table 5) and it is slightly nitrogen selective. Benzene was cracked at two different temperatures in an attempt to deposit carbon at the mouth of the pores. Past research results showed a two-step hydrocarbon deposition is superior in attaining high selectivity while maintaining high capacity. However, as one can see in Table 5, O<sub>2</sub> capacities are greatly reduced with low selectivity after the first carbon deposition step. Further CD at lower concentrations would not have improved results. This is presumably due to carbon filling the pores instead of depositing at the pore openings, which is the intent of CD. The wide pore size of the KOH activated char is hypothesized as the reason for this behavior.

### Surface Treated CMS

Surface treating activated carbon and studying the rate of N<sub>2</sub> and O<sub>2</sub> uptake has not been extensively studied in the scientific community. The only literature on this specific study found to date is over 20 years old, thus surface modification of carbons for oxygen and nitrogen generation is not well understood. The goal is to make a CMS that selectively adsorbs nitrogen over oxygen. This is different from the traditional CMS as described, which selectively adsorbs oxygen. The surface treated CMS may behave like zeolite. Zeolites are polar and since nitrogen has a higher quadrupole moment than oxygen, the nitrogen tends to adsorb to the zeolite more readily than oxygen. The intent of surface treating is to take advantage of nitrogen's higher quadrupole moment by treating the carbon with another polar molecule or some other compound which will form some type of surface functional group that will have an affinity for nitrogen. Table 6 shows the results of a few surface treatment techniques. One can easily see that efforts thus far have produced marginal results, with three of the four sample exhibiting nearly no significant selectivity. However, one can see from Tables 1 and 6, that the HNO<sub>3</sub> oxidized char became slightly more nitrogen selective (O<sub>2</sub>/N<sub>2</sub> = 0.94) from its parent CO<sub>2</sub> activated char (O<sub>2</sub>/N<sub>2</sub> = 0.99). Treating the surface further by ion exchange with Ca<sup>2+</sup> made the oxidized char even more N<sub>2</sub> selective (O<sub>2</sub>/N<sub>2</sub> = 0.91). This selectivity is still well above an O<sub>2</sub>/N<sub>2</sub> selectivity of 0.2. This is the selectivity characteristic of Type 5A Zeolite, which is the commercial adsorbent currently used for generating oxygen. A more thorough discussion and understanding of surface treatment cannot be offered at this time. A more thorough study of surface treatment was not possible because of mechanical problems with our volumetric adsorption instrument (Quantachrome Autosorb-1).

### Breakthrough

To obtain a more accurate assessment of the performance of a CMS, it is necessary to perform breakthrough experiments. Since making larger quantities of char is time consuming, it was decided to only perform breakthrough tests of the best chars produced at ISGS thus far. Recall that breakthrough tests were run using medical air passed through the

AC at a specified and controlled flow rate ( $\sim 15 \text{ cm}^3/\text{min}$ ) under approximately 1 atm pressure. The AC was maintained at a constant temperature (20-30°C) during the run. For air separation, the  $[\text{O}_2]$  and  $[\text{N}_2]$  in the effluent was monitored by GC, and a breakthrough time for each component was determined. Figure 4 shows nitrogen breakthrough tests of a promising char made a few years ago at ISGS. This char was only heat treated at 900°C in nitrogen for 0.5h.  $\text{N}_2$  capacity was 1.29 cc/g and  $\text{O}_2$  capacity was 4.46 cc/g yielding an  $\text{O}_2/\text{N}_2$  selectivity of 4.46. As one can see, the ISGS CMS does produce high purity nitrogen (96%); however, it is still a little short of commercial CMS. Figure 5 shows oxygen breakthrough tests for the char produced with calcium by ion exchange (Table 6). As one can see, an  $\text{O}_2/\text{N}_2$  selectivity of 0.91 only yields a  $\text{O}_2$  of just over 36%.

## CONCLUSIONS AND RECOMMENDATIONS

### Pore Size Characterization

The importance of pore size distribution (PSD) has been stressed in literature and it is stressed here. It is desirable to start with a char that has a narrow PSD and high micropore volume, especially for making traditional CMS by carbon deposition. This is true since CD is a uniform treatment of the activated char. It is obvious that an activated char with a uniform PSD will be narrowed down uniformly and still have a narrow PSD except that the pores will be smaller. A good  $\text{O}_2/\text{N}_2$  CMS has a narrow PSD in the 3-4 Å range. If the PSD is wide, CD treatment will narrow the pores; however, the PSD will still be wide which does not produce a good CMS. The narrow PSD for an activated char can potentially be obtained by activating under the right conditions and with the right gas. The starting coal may also have an impact, but that is currently not known. We were unable to characterize our chars' PSD since our adsorption instrument (Quantachrome Autosorb-1) had mechanical problems for seven of the 12 project months. It is recommended that pore size distributions be characterized for starting chars to gain more insight on the effect of PSD on making an effective CMS.

### Pyrolysis and Activation

Activation of our chars resulted in approximately a 23% weight loss or burn-off. Past research shows that maximum micropore volume occurred at approximately 35% burn-off. Burn-off in the 8-10% range also showed molecular sieve properties around the 5-6 Å range. For future work, it is recommended that activating char to 8-10% and 35% burn-off be examined. If a char activated to 8-10% burn-off results in a narrow micropore distribution, this could be a very good candidate for carbon deposition, particularly using the two-step hydrocarbon deposition process. 35% burn-off should produce the maximum micropore capacity attainable with IBC-102 coal pellets; however, the pore size distribution will need to be characterized to determine how effective carbon deposition will be.

### Carbon Deposition of $\text{CO}_2$ Activated Char

Tables 2, 3, and 4 show the results of carbon deposition. Our best results were obtained using the two-step hydrocarbon deposition process. The first step involved depositing carbon using a concentrated stream of a hydrocarbon for a short period of time, which closes the pore openings on the CMS. The second step involved using a dilute hydrocarbon stream to carefully reduce the pore opening to suitable dimensions to separate oxygen. It is desirable to characterize the porosity of the activated char and resulting CMS after CD. This can give information on what type of process to use for carbon deposition and determine the affect of that deposition. Since our adsorption instrument had mechanical problems, it is hard to give a completely accurate explanation of what is happening to the pore structure during CD. It is recommended that the two-step hydrocarbon deposition process be further explored since it has good potential. However, it is still emphasized that a starting char with a narrow micropore size distribution will have the best results after CD.

#### Carbon Deposition of KOH Activated Char

Table 5 shows the effect of CD with KOH activated char. Based on these results, it seems that KOH activated char is not a good candidate for an O<sub>2</sub> selective CMS produced by carbon deposition.

#### Surface Treatment

As mentioned and as can be seen in Table 6, results of surface treating carbons have been marginal at best. Ammonia treatment seems to have no effect on O<sub>2</sub>/N<sub>2</sub> selectivity and decreases capacity at longer treatment times. Calcium treatment by ion exchange does seem to have only a slight positive effect on selectivity. Past research indicates O<sub>2</sub>/N<sub>2</sub> selectivity can be decreased by outgassing the sample at higher temperatures. However, this may not be feasible for commercial PSA processes. It is recommended that calcium treatment be further studied by increasing treatment time and/or the amount of calcium used. To take advantage of nitrogen's higher quadrupole moment, it is recommended for future work that hydrogenation to remove surface oxygen groups and chlorine (a polar molecule) be used to treat the carbon surface.

#### Breakthrough Analysis

Upon producing a suitable O<sub>2</sub> or N<sub>2</sub> selective CMS, the laboratory scale PSA process designed for this project should be used to evaluate product purity. Currently, our laboratory scale PSA process adsorbs at 1 atm and desorbs by pulling a vacuum and heating the CMS. It is recommended that the process be modified slightly to adsorb under 5 to 10 atm and desorb at 1 atm by acquiring a very fine metering valve. This slight modification will allow our laboratory scale PSA process to operate under conditions more similar to a commercial scale PSA process.

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Table 1. Effect of HTT and activation on the molecular sieve properties of IBC-102 pellets (fixed bed) and granular (fluidized bed).

Sample	2 min		
	O <sub>2</sub> (cm <sup>3</sup> /g)	N <sub>2</sub> (cm <sup>3</sup> /g)	O <sub>2</sub> /N <sub>2</sub>
IBC-102 pellets, 700°C	6.37	6.15	1.04
IBC-102 pellets, 800°C	7.01	6.98	1.00
IBC-102 pellets, 900°C	3.83	3.66	1.05
IBC-102 pellets, 1000°C	3.39	3.19	1.06
IBC-102 granular, 700°C	6.89	6.33	1.09
IBC-102 granular, 800°C	7.25	6.90	1.05
IBC-102 granular, 900°C	7.15	6.77	1.06
IBC-102 pellets, 800°C, CO <sub>2</sub> , 875°C, 1h	10.02	10.55	0.95
IBC-102 granular, 800°C, CO <sub>2</sub> , 875°C, 1h	8.69	8.61	0.99

Table 2. Effect of single step hydrocarbon deposition on molecular sieve properties for IBC-102 pellets and granular.

Sample	2 min		
	O <sub>2</sub> (cm <sup>3</sup> /g)	N <sub>2</sub> (cm <sup>3</sup> /g)	O <sub>2</sub> /N <sub>2</sub>
Pellets CD, 800°C, 12% C <sub>6</sub> H <sub>6</sub> , 20 min	8.05	2.72	2.96
Pellets CD, 650°C, 3% C <sub>6</sub> H <sub>6</sub> , 1h	9.26	9.27	1.00
Pellets CD, 650°C, 3% C <sub>6</sub> H <sub>6</sub> , 2h	8.79	9.19	0.96
Granular CD, 800°C, 12% C <sub>6</sub> H <sub>6</sub> , 10 min	4.28	2.13	2.01
Granular CD, 800°C, 12% C <sub>6</sub> H <sub>6</sub> , 5 min	7.67	6.82	1.13

Table 3. Effect of two step hydrocarbon deposition on molecular sieve properties of IBC-102 pellets.

Sample	2 min			5 min		
	O <sub>2</sub> (cm <sup>3</sup> /g)	N <sub>2</sub> (cm <sup>3</sup> /g)	O <sub>2</sub> /N <sub>2</sub>	O <sub>2</sub> (cm <sup>3</sup> /g)	N <sub>2</sub> (cm <sup>3</sup> /g)	O <sub>2</sub> /N <sub>2</sub>
Pellets CD, 800°C, 12% C <sub>6</sub> H <sub>6</sub> , 20 min, 650°C, 3% C <sub>6</sub> H <sub>6</sub> , 1h	7.65	2.65	2.89	8.43	3.61	2.34
Pellets CD, 800°C, 12% C <sub>6</sub> H <sub>6</sub> , 20 min, 750°C, 3% C <sub>6</sub> H <sub>6</sub> , 1h	6.03	1.94	3.11	7.53	2.66	2.83
Pellets CD, 850°C, 12% C <sub>6</sub> H <sub>6</sub> , 20 min, 850°C, 3% C <sub>6</sub> H <sub>6</sub> , 1h	1.67	0.65	2.58	2.48	1.03	2.42
Pellets CD, 800°C, 12% C <sub>6</sub> H <sub>6</sub> , 10 min, 3% C <sub>6</sub> H <sub>6</sub> , 1h	6.88	2.05	3.36	8.00	2.91	2.75

Table 4 Effect of two step hydrocarbon deposition on molecular sieve properties of IBC-102 granular

Sample	2 min			5 min		
	O <sub>2</sub> (cm <sup>3</sup> /g)	N <sub>2</sub> (cm <sup>3</sup> /g)	O <sub>2</sub> /N <sub>2</sub>	O <sub>2</sub> (cm <sup>3</sup> /g)	N <sub>2</sub> (cm <sup>3</sup> /g)	O <sub>2</sub> /N <sub>2</sub>
Granular CD, 800°C, 12% C <sub>6</sub> H <sub>6</sub> , 10 min, 3% C <sub>6</sub> H <sub>6</sub> , 1h	0.52	0.17	3.03	1.11	0.34	3.25
Granular CD, 800°C, 12% C <sub>6</sub> H <sub>6</sub> , 5 min, 3% C <sub>6</sub> H <sub>6</sub> , 1h	0.70	0.21	3.40	1.37	0.47	2.89
Granular CD, 800°C, 12% C <sub>6</sub> H <sub>6</sub> , 5 min, 3% C <sub>6</sub> H <sub>6</sub> , 1.25h	0.93	0.19	4.87	1.98	0.56	3.57
	5.5 min			10 min		
Pellets CD, 800°C, 12% C <sub>6</sub> H <sub>6</sub> , 5 min, 3% C <sub>6</sub> H <sub>6</sub> , 1.5h	0.50	0.02	29.5	0.90	0.11	8.4

Table 5. Effect of KOH activation and carbon deposition on the molecular sieve properties of IBC-102 coal

	2 min	5 min
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Sample	O <sub>2</sub> (cm <sup>3</sup> /g)	N <sub>2</sub> (cm <sup>3</sup> /g)	O <sub>2</sub> /N <sub>2</sub>	O <sub>2</sub> (cm <sup>3</sup> /g)	N <sub>2</sub> (cm <sup>3</sup> /g)	O <sub>2</sub> /N <sub>2</sub>
KOH Activated	15.31	13.91	0.91	15.31	14.32	0.94
KOH, CD, 9% C <sub>6</sub> H <sub>6</sub> , 800°C, 20 min	1.54	3.27	2.12	1.85	4.42	2.40
KOH, CD, 9% C <sub>6</sub> H <sub>6</sub> , 850°C, 20 min	1.10	1.05	0.97	1.10	1.22	1.10

Table 6. Effect of various surface treatment techniques on O<sub>2</sub> and N<sub>2</sub> adsorption.

Sample	2 min			5 min		
	O <sub>2</sub> (cm <sup>3</sup> /g)	N <sub>2</sub> (cm <sup>3</sup> /g)	O <sub>2</sub> /N <sub>2</sub>	O <sub>2</sub> (cm <sup>3</sup> /g)	N <sub>2</sub> (cm <sup>3</sup> /g)	O <sub>2</sub> /N <sub>2</sub>
CO <sub>2</sub> , HNO <sub>3</sub> , 80°C, 2.5h	6.53	6.98	0.94	6.64	7.10	0.94
KOH, NH <sub>3</sub> , 900°C, 2h	11.41	11.31	1.01	11.41	11.44	1.00
KOH, NH <sub>3</sub> , 800°C, 6h	7.31	7.81	0.94	7.39	7.84	0.94
CO <sub>2</sub> , HNO <sub>3</sub> , NH <sub>3</sub> , 800°C, 6h	5.96	5.54	1.07	6.06	5.73	1.06
CO <sub>2</sub> , HNO <sub>3</sub> , Ca <sup>2+</sup>	6.80	7.40	0.92	6.93	7.61	0.91



Figure 1. Experimental plan for production of CMS from IBC-102 coal.

Figure 2. Experimental set-up for carbon deposition using benzene.

Figure 3. Experimental PSA process.



Figure 4. Breakthrough curve for oxygen selective CMS.

Figure 5. Breakthrough curve for nitrogen selective CMS.