ABSTRACT

The objective of this project was to produce adsorbent carbons from Illinois coal suitable for use in commercial gas separation/purification processes. An attempt was made to develop three types of carbon products: a carbon molecular sieve (CMS) for separation of oxygen from air suitable for use in pressure swing adsorption (PSA) systems that generate high purity O₂ for IGCC processes; a high surface area, high density activated carbon for recovery of hydrogen from petroleum and coal-derived gas streams; and an activated carbon with optimal pore structure and density for use in automobile gasoline vapor emissions control systems.

A rotating quartz tube reactor with baffles was designed and constructed to produce gram quantities of CMS and activated carbon from IBC-102 coal. This reactor, which simulates the rotary tube kilns (RTK) typically used by industry to manufacture activated carbon, replaced our fixed-bed reactor and resulted in better gas-solid contact and a more uniform activation of the char. A series of chars were produced from IBC-102 coal in the RTK. Five levels of carbon conversion (Xc) were attained, Xc = 0, 0.22, 0.46, 0.71 and 0.94. CO₂/CH₄/H₂, O₂/N₂ and C₄H₁₀ adsorption tests were performed using a volumetric adsorption apparatus. The CO₂/H₂ adsorption properties of these chars compared favorably with those of a commercial activated carbon (Calgon BPL). Chars prepared by pyrolysis alone (no activation) performed better than the activated chars in separating CO₂ from H₂ and CH₄. The CO₂ activated chars were not able to separate O₂ from N₂ as is. Carbon deposition using benzene as the cracking gas was used to narrow their pore size and increase O₂/N₂ selectivity. The best CMS produced by CO₂ activation followed by carbon deposition had an O₂ capacity and O₂/N₂ selectivity comparable to that of a char made by pyrolysis alone (without activation and carbon deposition). A KOH activated char had an O₂/N₂ selectivity less than one indicating that it could be used to recover oxygen instead of nitrogen from air.

The butane working capacities (BWCs) of carbons prepared from IBC-102 coal were determined at 25 and 68°C by thermogravimetric analysis (TGA). The BWCs of the CO₂ activated chars were considerably less than that of an automotive carbon. To increase butane capacity, a chemical activation method was employed to produce high surface area char from IBC-102 coal. The BWC of this char was more than twice that of the CO₂ activated chars, but still less than half that of the automotive carbon. More importantly, at 68°C, the BWC of the KOH activated char was only 10% less than that of the commercial carbon. The pore size distributions (PSDs) of selected IBC-102 chars and the automotive carbon were determined and used to explain differences in their BWCs.

Pages 16 through 28 contain proprietary information
EXECUTIVE SUMMARY

Commercial interest in carbon molecular sieves is growing and these materials are currently being used to replace less efficient adsorbents (e.g., zeolites) in industrial gas separation processes. Gas separations are a major production cost in the chemical industry today. Production of industrial gases (20-200 ton/day) by noncryogenic methods, e.g., pressure swing adsorption (PSA), is expected to grow faster than the conventional method, cryogenic distillation. It is 10-20% cheaper to produce oxygen and nitrogen in these amounts by PSA than cryogenically (Kirschner, 1994). Although there is still some 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 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 activated carbons. Commercial applications of CMS at the present time include those that separate gas molecules based on size, e.g., the separation of air into oxygen and nitrogen. Other separations that have been achieved on a smaller scale include: oxygen and argon, carbon dioxide and methane, benzene and cyclohexane, ethane and ethylene, and n-butane and isobutane. In all these cases, separations are based on differences in the molecular size of the gaseous species, as opposed to zeolites, which have separation efficiencies based primarily on their chemical affinity for a specific component in the gas mixture. Gas molecules with slightly different critical dimensions, e.g., 0.2 Å, may be adsorbed by CMS at rates that vary by several orders of magnitude. Thus, a small change in the average pore size of a porous carbon substrate will significantly affect the rate of diffusion of a gas molecule in the pore system. Under controlled conditions of heat treatment and activation, it is possible to prepare carbonaceous adsorbents from coal that have a relatively narrow pore size distribution, and which exhibit molecular sieving behavior. Pore structure modification may also be achieved by carbon deposition, i.e., cracking of a suitable hydrocarbon gas within the pores of a carbon substrate.

Air Products, Inc., a world leader in the development and use of industrial gas separations technology, currently employs CMS in tonnage quantities for the separation of air, and production of nitrogen. Two companies produce CMS on a commercial scale. A process for manufacturing two types of CMS from bituminous coal was first developed at Bergbau-Forschung (Carbo Tech is the subsidiary that produces CMS), Germany (Jüngten et al., 1981). Coal is ground to 90% < 40 µm and preoxidized in air at temperatures below the onset of ignition using a fluidized bed. The so-called oxicoal is then mixed with a binder and shaped to granules with diameters between 2 and 3 mm. The granules are carbonized in a special rotary drum. Using these process steps a starting material with uniform properties was made ready for two types of gas separation processes. A CMS for hydrogen recovery having "wide pores" is produced by steam activation of this material. A CMS for air separation having "narrow pores" is produced by depositing carbon in the pores of the steam activated carbon. Takeda Chemicals in Japan produces CMS for air separation from coconut shell.

Today several hundred hydrogen PSA plants, with capacities of up to 10,000 m³/h hydrogen and purities of up to 99.999%, are operating worldwide. Air Products operates PSA processes for dual production of high purity H₂ and CO₂. Typical adsorbents used for PSA systems include activated carbon, zeolites, alumina and silica gels. Air Products typically uses a dual sorbent bed with zeolite followed by activated carbon. The ratio of carbon to zeolite ranges from 5 to 10 depending on the feed gas composition and pressure. The activated carbon is used to remove the CO₂ and light hydrocarbons, while the zeolite is used to remove CO and N₂. Increases in the adsorption capacity as well as the bulk density of the carbon are needed. As the bulk density increases, the mesoporosity and macroporosity of the carbon decreases. This reduces the void volume in the bed and minimizes hydrogen loss. Hydrogen productivity is increased by enhancing the working capacity of the carbon for impurity removal, i.e., the
difference in impurity loading between the feed and that remaining on the carbon after regeneration. A carbon adsorbent needs to adsorb a large amount of impurities and then release them during regeneration. Other carbon properties of importance include mechanical strength and particle size.

A leading carbon manufacturer currently produces a chemically activated wood-based carbon that is used in over 90% of the cars driven in the U.S. This is by far the single largest application for activated carbon in the U.S. today. Due to more stringent environmental regulations on the horizon and less and less available space in engine compartments, carbons with higher butane working capacity and lower cost are needed. Having the proper mix of micropores and mesopores is essential for carbons used in automotive gasoline vapor emissions control systems. The same high surface area carbon used in H₂ purification could also work well in this application, or slight refinements in the activation process could be used to optimize pore structure and performance.

The overall objective of this project was to develop Illinois coal-based CMS and activated carbon for selected gas separation and purification processes. An integrated approach was implemented to produce and test adsorbent carbons in each of the following applications: O₂ and N₂ separation from air, recovery of H₂ from coal-derived gases, and control of gasoline vapor emissions from automobiles. Commercial grade carbons for all three applications should have a high adsorption capacity for the targeted gas molecule(s), have the proper particle size and density, be fully regenerable and be of sufficiently low cost to produce. The project consisted of five tasks. In Task 1, adsorbent carbons were prepared from IBC-102 coal by pyrolysis, physical (CO₂, H₂O) or chemical activation (KOH, H₃PO₄, ZnCl₂), carbon deposition (C₆H₆ or C₄H₁₀) and selected chemical treatments (NH₃, H₂, Cl₂). In Task 2, the O₂/N₂/H₂/CO₂/CH₄ adsorption capacities and selectivities, and the butane adsorption capacity of the prepared carbons were determined and compared to that of commercial CMS and activated carbons. In Task 3, the surface area, pore size distribution, bulk density and attrition resistance of the chars were determined. In Task 4, if a carbon showed commercial potential, a technical/economic evaluation would be conducted. In Task 5, monthly, mid-year and annual technical and management progress reports were prepared and submitted to the ICCI.

To begin the project, a new rotating quartz tube reactor with baffles was designed and constructed to produce gram quantities of CMS and activated carbon from IBC-102 coal. This new reactor replaced the fixed bed we were using and resulted in better gas-solid contact and a more uniform activation and carbon deposition of the char. It also better simulates the rotary tube kilns being used by industry to manufacture adsorbent carbons. A series of carbons was produced from IBC-102 coal in the new RTK. Five levels of carbon conversion (Xₖ) were achieved, Xₖ = 0, 0.22, 0.46, 0.71 and 0.94. The coal was first preoxidized in the RTK at 225°C for 2 h. The preoxidized coal was then pyrolyzed at 900°C in a 2 in. fluidized bed reactor to avoid the build up of tar on the quartz tube. The char was then physically activated in the RTK in 1 atm CO₂ at 860°C for 0, 1, 2.5, 4.5 and 5.5 h, respectively. CO₂/CH₄/H₂, O₂/N₂ and C₄H₁₀ adsorption tests were performed on this series of chars using a volumetric adsorption apparatus. The CO₂/H₂ adsorption properties of this series of chars compared favorably with those of a commercial activated carbon (Calgon BPL). To further increase adsorption capacity, a chemical activation method was used to produce high surface area char from IBC-102 coal. The chemically activated char also adsorbed more CO₂ and had a higher CO₂/CH₄ selectivity than any of the physically activated chars. A two step carbon deposition method was used to increase the O₂/N₂ selectivity of a physically activated char. This CMS could be used to recover nitrogen from air. A chemically activated carbon had an O₂/N₂ selectivity less than one meaning that it had potential to recover oxygen from air. Further work would be needed to optimize the adsorption properties of these carbons for use in commercial air separation PSA
processes.

The butane working capacities (BWC) of physically and chemically activated IBC-102 chars were measured by TGA either in 100% butane at 25°C or in 10% butane at 68°C. Chemically activated char had higher BACs than those made by physical activation. At 25°C, one KOH activated char having a surface area of 1300 m²/g had a BWC 50% less than that of a carbon currently used in automobiles. At 68°C, our best chemically activated coal char had a BWC comparable to that of the automotive carbon. The pore size distributions (PSD) of selected IBC-102 chars and the automotive carbon were determined using a new PSD model. The N₂ BET surface area of the carbons as well as their PSDs determined by this model were used to explain differences in their BWCs.

The remainder of this report contains proprietary information and is not available for distribution except to the sponsor(s) of this project.

OBJECTIVES

The overall objective of this project was to develop carbon-based sorbents from Illinois coal for use in commercial gas separation/purification/recovery processes. The goal was to utilize an integrated approach (Figure 1) to produce novel, low cost adsorbent carbons from Illinois coal that perform as well as or better than commercial CMS, activated carbons and zeolites used by industry to separate and purify gases. Three gas separation/purification applications were the focus of this study: 1) separation of high purity oxygen from air for use in oxygen enriched coal gasification and combustion processes, 2) separation and recovery of high purity hydrogen from refinery offgases and the products of coal gasification, and 3) control of gasoline vapor emissions from automobile engines and gas tanks. The third application is of particular interest since it could involve relatively large amounts of carbon made from Illinois coal. Every car sold in the U.S. after 1971 is required to use a cannister containing 3-5 pounds of activated carbon to capture fuel vapors vented from the fuel tank, engine block and/or carburetor that would otherwise escape into the atmosphere. Assuming there are more than 200,000,000 automobiles in the U.S. alone, the existing market for this carbon is quite large.