ABSTRACT

The goal of this project is to develop a technology for producing microengineered adsorbents carbon from Illinois coal and evaluate the potential application of these materials for storing natural gas for use in emerging low pressure, natural gas vehicles (NGV). The focus of the project is to design and engineer adsorbents that meet or exceed the performance and cost targets established for low-pressure natural gas storage materials.

During the first year of this project, granular activated carbons (-20+100 mesh; 0.149-0.84 mm) were produced by physical activation and chemical activation with KOH from an Illinois bituminous coal (IBC-106). The products were characterized for their BET surface area, micropore volume, bulk density, gravimetric and volumetric methane adsorption capacities. The volumetric methane capacities (Vm/Vs) of some of the granular carbons produced by physical activation were about 70 cm³/cm³ which is comparable to that of BPL, a commercial activated carbon. The Vm/Vs values above 100 cm³/cm³ could be obtained by grinding the granular products to -325 mesh (<0.044 mm). The increase in Vm/Vs was due to the increase in the bulk density of the carbons. Methane volumetric adsorption capacity was found to be related to the pore surface area and micropore volume on the unit volume basis (per unit volume).

Future work will focus on investigating: 1) other chemical activation methods such as phosphoric acid and zinc chloride treatment, 2) pelletization of products to increase carbon’s bulk density, and 3) metal oxide dispersion (CaO, MgO) into activated carbon. The later has been shown to increase supercritical adsorption capacity of activated carbon by 50%.
EXECUTIVE SUMMARY

Background

An adsorbed natural gas (ANG) storage system is being considered as an on-board storage technology for natural gas vehicles (NGV) because it is less expensive, lighter, occupies less space, costs less to refuel, and has much greater storage density at low pressure (< 35 atm) than that of compressed natural gas (CNG) storage (Golovoy, 1983; Wegrzyn et al., 1992; Nelson, 1993). Carbon-based adsorbents have been found to have the most favorable gas storage density compared to other adsorbents, e.g., zeolites (Golovoy, 1983). A key issue in commercial development of an ANG storage technology is the availability of low cost carbon adsorbents (< $2/lb) with high capacity for methane storage (Nelson, 1993). In addition, advanced cost-effective carbon adsorbents with sieving properties are needed to preferentially remove impurities (CO, CO₂, N₂, C3-C4 hydrocarbons) from natural gas. Illinois coal is a low-cost starting material that has the potential of being an ideal precursor for synthesis of carbon-based adsorbents with desirable properties for ANG technology.

NGV are presently being developed by numerous organizations throughout the world in hopes of capitalizing upon their inherent advantages over gasoline and other alternative fuels. To date, NGV have been implemented mainly in the form of high-pressure compressed natural gas retrofit. However, with the development of adsorbed natural gas storage, advancements are now possible in dedicated vehicle technology as opposed to current compressed natural gas technology, which limits market opportunities available to NGV due mainly to safety concerns. Adsorbed NGV (ANGV) operate at 15-30% of the pressure of compressed NGV. In the U.S., the utilization of ANGV in fleet applications will likely be their initial entry point into the marketplace. Fleet vehicles (taxis and buses) usually accommodate high mileage and often refuel at a central location. This allows usage of dedicated natural gas refueling facilities and maximizes the cost savings between gasoline and natural gas. The U.S. DOE recently compiled statistics which showed the potential market for fleet NGV to be tremendous (Biederman et al., 1989). The current number of total fleet automobiles and private and commercial light trucks is 48 million. This is expected to rise to 60 million vehicles by the year 2000. These statistics reflect a growing market potential for ANGV of up to 12 million units. This study also showed that Chicago, Illinois would be the ideal market for fleet vehicles, and deemed the city the prime U.S. location to begin marketing ANGV.

The potential benefit of the development of adsorbed natural gas technology to the Illinois coal industry is significant just taking into account the expected increase in fleet vehicles. If by the year 2000, twelve million fleet ANGV are added and were to carry an average of 300 pounds carbon adsorbent for low pressure natural gas storage, it would necessitate a demand for 3.6 billion pounds of low-cost carbon. If this carbon were to be made of coal, the demand for a suitable coal would be 12 billion pounds assuming that 30% of the coal is utilized in the final product. Thus,
6 million tons of additional coal would be needed. These calculations do not account for additional demand due to ANGV entering the main marketplace, where over 250 million units are now in operation. If ANGV find entry into this market, it could mean an even greater demand for coal. The results of research directed towards the development of suitable adsorbent carbons from Illinois coal for natural gas storage should be of great interest to the Illinois coal industry. Based on past history of the auto industry, it is reasonable to assume that if a suitable feedstock for a NGV carbon adsorbent is identified, cost conscious auto makers will rush to adopt use of this material for their adsorbed natural gas vehicles.

Goals and Objectives

The overall goal of this project is to develop a technology for producing microengineered adsorbent carbons from Illinois coal and evaluate the potential application of these novel materials for use in the emerging low pressure ANGV. The focus of the project is to design and engineer adsorbents from Illinois coal that meet or exceed the performance and cost targets established for low-pressure natural gas storage materials.

The project consisted of six tasks. In Task 1, activated carbon samples were prepared from IBC-106 coal in a fixed-bed or a fluidized bed under a wide range of heat treatments and soak times. In Task 2, the physical and chemical properties of the products were evaluated to gain additional insight into the fundamentals of preparation and properties of CMS. In Task 3, the methane adsorption capacity (energy storage density) of products were measured at pressures ranging from 1 to 35 atm with a pressurized thermogravimetric analyzer and with a high pressure volumetric apparatus which was designed and constructed for screening adsorbents. In Task 5, a process flowsheet is proposed to be developed to help determine the technical/economic feasibility of producing activated carbon from Illinois coal for ANG system. In Task 6, technical and management quarterly reports were prepared and submitted to the ICCI.

Results and Discussion

The adsorbent carbons were produced using IBC-106 coal (bituminous) from the Illinois Basin Sample Program bituminous coal, IBC-106. The parent coal (-8 mesh) was grind and sieved from -8 mesh (2.38 mm) to -20+100 and -100 mesh. The Free Swelling Index of IBC-106 coal is 4.5.

Activated carbons were prepared by a physical (from the -20+100 mesh coal) and a chemical activation (from the -100 mesh coal) process in a bench-scale tubular reactor. In the physical activation method, a three-step process was applied: coal oxidation in air at 225°C for 0.5-9 h; devolatilization of oxidized coal in nitrogen at 400-500°C for 1 h; and char activation in 50% steam in nitrogen at 800-850°C for 0.5-5.5 h. In the chemical activation method, coal was mixed with granular KOH
solid (coal/KOH ratio 1:1) and ground into a gel-like solid and the mixture was activated at 800°C in nitrogen for 0.5 and 1.25 h.

The activated carbon products were characterized for their BET surface areas and micropore volumes. Methane adsorption capacities, on the mass basis, were measured with pressurized thermogravimetric analyzer at pressures up to 500 psig (0.35 Mpa). A 4.92 cc pressurized vessel was to measure the Vm/Vs methane adsorption capacity (cm³/cm³), Vm is defined as the adsorbed methane at standard temperature and pressure (cm³) and Vs is the volume of adsorbent packing bed (cm³).

At ambient temperature, methane adsorbs mainly in activated carbon’s micropore because the adsorption temperature is hundreds of degrees above the methane’s critical temperature. Therefore, an activated carbon with a large micropore volume will adsorb more methane than one with a lesser micropore volume. The surface area and micropore volume (cm³/g) of the activated carbon products increased with carbon burn-off. However when the data were presented on the unit volume of the activated carbon (micropore volume x bulk density), the surface area initially increased and reached a maximum point at about 65-70% total coal weight loss (extent of reaction) and then dropped off due to the decrease in the carbon bulk density. Carbon micropore volume showed a similar trend. The bulk density of the activated carbon decreased with the extent of reaction as a result of porosity development. At weight losses above 65% macropore and mesopore volumes were generated at the expense of micropore widening.

The Vm/Vs methane adsorption capacities of carbons (at 500 psig) from Illinois coal ranged from 54 to 76 cm³/cm³. These values are comparable to that of a commercial carbon (BPL, Calgon Carbon) widely researched for natural gas storage.

The Vm/Vs increased to 70 cm³/cm³ at about 65% coal burn off. Further activation beyond 65% weight loss did not promote carbon’s Vm/Vs. Vm/Vs was linearly proportional to the surface area and micropore volume on the unit volume basis (surface area x bulk density, micropore volume x bulk density).

There are several options to maximize the methane storage capacity of activated carbon produced from Illinois coal: 1) maximizing the micropore volume while minimizing the mesopore and macropore volume, 2) controlling the pore size distribution so that the majority of micropores are about 11.4 Å, the optimum pore size for methane storage, 3) minimizing the inter-particle space.

Options (1) and (2) are related to activated carbon production conditions. Recently it has been reported that steam activation creates less micropores than does carbon dioxide activation. In the study presented here, no clear evidence was found to support the idea that the pore size distribution of an activated carbon could be controlled by either activation temperature or the extent of burn off.
Option 3 can be implemented by grinding and pelletization of the activated carbon product. The bulk densities of selected activated carbons prepared in this study increased by 35% by grinding the -20+100 mesh granular samples to -325 mesh. Using this revised bulk density, Vm/Vs values of about 103 cm³/cm³ can be obtained, provide that grinding does not affect the Vm/Vs results.

A limited number of activated carbons were prepared using chemical activation with KOH. The BET surface area and micropore volume of the resultant carbons were 1478 m²/g and 0.62 cm³/g, respectively. These values are significantly higher than those of the physically activated carbons. The Vm/Vs of KOH carbon, however, was lower than that of the most steam-activated carbons. This is attributed to the lower bulk density of KOH carbon. KOH activation of Illinois coal appears to be an effective method to produce carbon adsorbent for gas storage provided that the carbon’s bulk density can be increased.

Future work will focus on investigating: 1) other chemical activation methods such as phosphoric acid and zinc chloride treatment, 2) pelletization of products to increase carbon’s bulk density, and 3) metal oxide dispersion (CaO, MgO) into activated carbon. The later has been shown to increase supercritical adsorption capacity of activated carbon by 50%.
OBJECTIVE

The overall goal of this two-year project is to develop a technology for producing microengineered carbon adsorbents from Illinois coal and to evaluate the potential application of these materials for use in the emerging low pressure natural gas vehicle (NGV). The main objective of the proposed research is to synthesize microengineered adsorbents, from Illinois coal, suitable for use in ANGV which meet the following criteria: a) natural gas storage density of > 150 V/V compared to current 100-120 V/V; b) lower adsorbent cost (< $2/lb). Another important objective is to develop an adsorbent carbon with sieving properties to be used in a guard bed system for controlling the adsorbable contaminants present in natural gas (C2-C4 hydrocarbons, N2, CO2, odorant, water). The tasks of the project are:

Task 1. Adsorbents are prepared from IBC-106 coal in a fixed-bed or a fluidized-bed reactor under a wide range of heat treatment and activation conditions. The pore structure of the chars is tailored for optimum methane storage capacity (about 10-12 Å) via chemical activation with KOH or activation in CO2/H2O. The pore structure may be further modified by carbon deposition with CH4 to achieve proper molecular sieving properties.

Task 2. Adsorbents are characterized for their physical and chemical properties, including N2-BET and CO2 surface area, porosity and pore size distribution and bulk density, to gain insight into the fundamentals of preparation and the properties of products.

Task 3. Molecular sieve properties of selected products are determined by measuring the kinetics of adsorption of O2, N2, CO2, CH4 and C2H6 on chars at 25°C. The ability of the chars to separate impurities from natural gas is tested in an adsorption column/mass spectrometry system.

Task 4. Methane adsorption capacity (energy storage density) of products and the heat of adsorption are measured at pressures ranging from 1 to 35 atm. High-pressure methane capacities of products is determined with a high-pressure volumetric adsorption apparatus at Amoco Corporation and results are compared with commercial products tested for ANG.

Task 5. A process flowsheet for production of microengineered adsorbents from Illinois coal is developed. A technical and economic study as well as a market analysis will be initiated.

Task 6. Technical and management quarterly reports are prepared and submitted to ICCI.
INTRODUCTION

Carbon-based adsorbents have been found to have the most favorable gas storage density compared to other adsorbents, e.g., zeolites (Golovoy, 1983). In ANGV applications, the storage volume is often limited (gas tank). Thus for adsorbents with the same capacity per unit mass, the one having the greater packing density in the storage vessel will result in a greater storage capacity. However, adsorbents with lower packing density, but greater capacity per unit mass, may have greater storage capacities. Matranga et al. (1992) performed Monte Carlo calculations to simulate the adsorption of natural gas on carbon. Adsorption isotherms, storage capacity, and isothermic heats of adsorption were determined from model simulations and compared with experimental data. Their model simulations predicted a maximum storage capacity at 35 atm of 244 V/V for monolithic carbon and 169 V/V for pelletized carbon. (The standard terminology for natural gas storage capacity is V/V or volume of stored material at STP per volume of storage container.) Generally, two approaches are taken to optimize storage capacity using carbon adsorbents. An adsorbent with a high mass uptake but low density, such as the Amoco KOH type carbons, can be treated with binder and compacted to improve packing density and thus increase volumetric storage capacity. On the other hand, a high density but low microporosity carbon can be activated in an attempt to increase the microporosity, and thus storage capacity. However, this will be at the expense of decreasing density. For natural gas storage, macroporosity in carbons is undesirable. Amoco type carbons have large macropore volumes which still exist after compaction. This results in reduced volumetric storage capacity. Conventional activation of coal-derived carbons by air, carbon dioxide or steam, also results in macropore formation. Therefore, to minimize macropore formation and increase gas storage capacity, new or modified methods for the preparation of both types of carbons must be found.

EXPERIMENTAL

Coal Preparation

The adsorbent carbons were produced from an Illinois bituminous coal, IBC-106. The raw coal (20 lb) was provided by the Illinois Basin Coal Sample Program (Harvey and Kruse, 1988). The parent coal was subjected to a step-wise grinding and sieving technique in order to reduce its particle size from -8 mesh (2.38 mm) to -20+100 and -100 mesh. The -20+100 mesh portion was used as feedstock for physical activation and the -100 mesh portion was used as feedstock for chemical activation. Table 1 shows the coal's proximate and ultimate analysis results. The Free Swelling Index of IBC-106 coal is 4.5 (Harvey and Kruse, 1988).

Carbon production

Carbon production by both physical and chemical activation techniques was carried
out in a bench-scale tubular reactor with a horizontal furnace (Lindberg; Type 54232). Figure 1 shows the processing steps involved in the production of the activated carbon samples. In the physical activation method, a three-step process was applied: coal oxidation in air at 225°C for 0.5-9 h; devolatilization of oxidized coal in nitrogen at 400-500°C for 1 h; and char activation in 50% steam in nitrogen at 800-850°C for 0.5-5.5 h. The air oxidation step was performed in an ashing furnace (Fisher Scientific; Model 495A). In each experiment about 12 grams of coal was used. The gas flow rate in the preoxidation, devolatilization, and activation steps was 1 L/min (STP).

In the chemical activation method, about 2 grams of the coal (-100 mesh) was mixed with 2 g of granular KOH solid (coal/KOH ratio 1:1) and ground into a gel-like solid using mortar and pastel. This gel-like solid mixture was activated at 800°C in nitrogen for 0.5 and 1.25 h. After the activation reaction, product was immediately immersed in water to prevent it from oxidation by air.

Carbon characterization

Single-point BET surface areas of the carbons were determined from nitrogen (77 K) adsorption data obtained with a Monosorb flow apparatus (Quantachrome Corp.). BET surface area and t-plot micropore volumes were calculated based on the nitrogen adsorption isotherm (p/p0: 0.001-1) measured with a volumetric adsorption apparatus (Micromeritics). Screening tests were performed with a pressurized thermogravimetric analyzer (Spectrum Research and Engineering) to measure the relatively methane adsorption capacity of products on the mass basis (methane adsorption isotherm) at pressures up to 500 psig (0.35 MPa).

A 4.92 cc pressurized vessel, illustrated in Figure 2, was designed and constructed (100% aluminum) to measure the Vm/Vs methane adsorption capacity (cm³/cm³). The Vm/Vs adsorption capacity is the standard terminology used in industry to evaluate natural gas storage capacity of adsorbents; Vm is defined as the adsorbed methane at standard temperature and pressure (cm³) and Vs is the volume of adsorbent packing bed (cm³).

The operation procedure employed to measure Vm/Vs was:

1. Weigh the vessel with sample in, W₀
2. Purge the vessel with methane for 10 min
3. Weigh again, W₁
4. Pressurize vessel to 500 psig
5. Weigh again, W₂
6. Open the vessel's cap in the hood and weigh again, W₁'

In Figure 2, the equation which was used to calculate Vm/Vs is presented.
RESULTS AND DISCUSSION

Fundamental study of physical activation

It has been recognized that pre-oxidation and devolatilization at an intermediate temperature prior to steam/CO$_2$ activation are necessary steps in production of activated carbon from a caking coal by a physical activation process. The purpose of the preoxidation is to minimize the caking property of the coal. Activated Carbons produced without pre-oxidation generally have low surface area and adsorption capacity because the partial melting of the coal during the devolatilization step destroys microporosity by structural realignment (Sun, 1993). The purpose of the devolatilization step is to create new cross links within coal’s network, hence preserving its inherent microporosity.

A series of activated carbon samples was produced by physical activation method: coal oxidation in air at 225°C for 2 h; devolatilization of oxidized coal in nitrogen at 400°C for 1 h; and char activation in 50% steam in nitrogen at 800°C for 0.5-5.5 h. Figure 3 shows the total coal weight loss (extent of reaction) on the dry ash free (daf) basis as a function of activation time. A constant rate of weight loss was observed for reaction times above 3 h of activation when the coal was completely devolatilized and most of the reactive compounds (functionalities) were burnt off. The surface area and micropore volume of the activated carbon products increased (Figure 4) with carbon burn-off (the micropore volume is defined as the total volume of pores smaller than 17 Å). Surface area and micropore volume data are not reported up to 3 h of activation since this induction period is a combined stage of delayed devolatilization and early gasification. The maximum surface area and micropore volume are generally developed at the later stage of the activation.

Bulk density, pore volume, and surface area of activated carbons

At ambient temperature, methane adsorbs mainly in activated carbon’s micropore because the adsorption temperature is hundreds of degrees above the methane’s critical temperature. Therefore, an activated carbon with a large micropore volume will adsorb more methane than one with a lesser micropore volume. Traditionally, adsorption capacity is measured per unit mass. However, for gas storage application adsorption capacity must be evaluated per unit volume because the adsorbent is stored in a vessel with a limited volume (Quinn, 1992). Therefore, the micropore volumes of activated carbon (or adsorption capacity) must be related to a unit volume or a storage container volume and not simply to a unit mass of carbon. Consequently, the bulk or packing density of the activated carbon becomes very important.

The bulk density of the activated carbon decreased with the extent of reaction (total weight loss during preoxidation, devolatilization, and activation steps) as a result of porosity development. Figure 5 and 6 show the surface area and micropore data
presented in Figure 4 when calculated on the unit volume basis (surface area x bulk density). The surface area initially increased and reached a maximum point at about 70% weight loss, and then dropped off due to the decrease in the carbon bulk density, Figure 5. Carbon micropore volume showed a similar trend, Figure 6.

Macro and meso pore volume data are shown in Figure 7. During steam activation of char a large volume of macropores and mesopores (>17 Å) as well as micropores were generated. A sharp increase in macropore and mesopore volume, and decrease in micropore volume, was observed around 65% weight loss. One possible explanation for the observed phenomenon is that all of the closed pores (mostly micropores) initially present in raw coal were opened as coal weight loss approached 65%. Further weight loss, due to the carbon burn off during steam activation, resulted in the development of macropore and mesopore volumes at the expense of micropore widening.

Methane adsorption capacity

Activated carbon products were evaluated for their volumetric methane adsorption capacities (Vm/Vs) at 500 psig. Table 2 summarizes the properties of selected carbons produced from Illinois coal under different reaction conditions. A commercial activated carbon, BPL manufactured by Calgon Carbon Corp., was used as a reference adsorbent. BPL is a well characterized and widely used commercial product. The Vm/Vs methane adsorption capacities of carbons from Illinois coal ranged from 54 to 76 cm³/cm³. These values are comparable to that of BPL. The measured Vm/Vs of BPL is comparable to those reported in the literature (Innes, 1984 and Parkyns, 1195).

Figure 8 shows the Vm/Vs adsorption capacity of activated carbons as a function of coal weight loss. The Vm/Vs increased to 70 cm³/cm³ at about 65% coal burn off. Further activation beyond 65% weight loss did not promote carbon’s Vm/Vs.

Figures 9 and 10 show the variation in Vm/Vs with surface area and micropore volume. In both cases, the Vm/Vs leveled off at about 65% coal weight loss. The corresponding surface area and micropore volume were 900 m²/g and 0.32 cm³/cm³, respectively. Figures 11 and 12 show that Vm/Vs is linearly proportional to the surface area and micropore volume on the unit volume basis (surface area x bulk density, micropore volume x bulk density).

As mentioned earlier, methane storage is mainly a micropore phenomenon. Methane adsorbs in mesopores, macropores, and inter-particle space has the density of the compressed gas at the storage pressure. There are several options to maximize the methane storage capacity of activated carbon: 1) maximizing the micropore volume while minimizing the mesopore and macropore volume, 2) controlling the pore size distribution so that the majority of micropores are about 11.4 Å, the optimum pore size for methane storage (Matranga, 1992), 3) minimizing the inter-particle space.
Options (1) and (2) are related to activated carbon production conditions. It has been recently reported that steam activation creates less micropores than does carbon dioxide activation (Rodriguez-Reinoso, 1995). In the study presented here, no clear evidence was found to support the idea that the pore size distribution of an activated carbon could be controlled by either activation temperature or the extent of burn off.

Option 3 can be implemented by grinding and pelletization of the activated carbon product. The bulk densities of selected activated carbons prepared in this study increased by 35% by grinding the -20+100 mesh granular samples to -325 mesh. Using this revised bulk density, the highest Vm/Vs value presented in Table 2 would be 103 cm³/cm³, as long as the grinding does not affect the Vm/Vs results. No pelletization tests were performed to date.

Chemical activation with KOH

A limited number of activated carbons were prepared using chemical activation with KOH. The coal was treated with KOH (see experimental section) and heated in nitrogen at 800°C for 0.5 and 1.25 h. The BET surface area and micropore volume of the resultant carbon (0.5 h activation) were 1478 m²/g and 0.62 cm³/g, respectively. These values are significantly higher than those of the physically activated carbons. The Vm/Vs of KOH carbon, however, is lower than that of the most steam-activated carbons. This is attributed to the lower bulk density of KOH carbon. KOH activation of Illinois coal appears to be an effective method to produce carbon adsorbent for gas storage provided that the carbon's bulk density can be increased.

Figure 13 shows the methane adsorption capacity (g/g) of KOH activated carbons along with steam-activated carbons and BPL activated carbon. The methane adsorption capacity (g/g) for KOH carbon is significantly higher than that of BPL. Carbon 1 (Table 2) was prepared from IBC-106 coal without pre-oxidation. It has a surface area comparable to that of the BPL, but its methane adsorption capacity is significantly lower because of its lower micropore volume. Carbon 2 was prepared by preoxidizing the coal for 4 h and had a surface area over 1000 m²/g. As shown in Figure 13, the methane adsorption capacity of Carbon 2 at 500 psig was higher than that of the BPL.

CONCLUSIONS AND FUTURE WORK

Granular activated carbons (-20+100 mesh; 0.149-0.84 mm) were produced by physical activation and KOH chemical activation from an Illinois bituminous coal. Methane adsorption capacities of these activated carbons were measures at pressures up to 500 psig. Some of the activated carbons produced by physical activation had volumetric methane storage capacities (Vm/Vs) of about 70 cm³/cm³. This value is
comparable to that of BPL, a commercial granular activated carbon. \( V_m/V_s \) values exceeding 100 cm\(^3\)/cm\(^3\) could be obtained by grinding the granular products into powder carbons (-325 mesh; <0.044 mm). This increase in \( V_m/V_s \) is mainly due to the increase in bulk density of the activated carbon. It was concluded that macropores and mesopores are generated during steam activation by micropore widening. Maximum volumetric adsorption capacity was observed at about 65% total coal weight loss. Methane volumetric adsorption capacity was found to be proportional to the surface area and micropore volume on the unit volume basis.

A few activated carbons were prepared by chemical activation of coal with KOH. KOH activated carbons had higher surface area, micropore volume, methane adsorption capacity (g/g) and lower \( V_m/V_s \) methane capacity than those of the activated carbons prepared by physical activation.

Future work will focus on investigating: 1) other chemical activation methods such as phosphoric acid and zinc chloride treatment, 2) pelletization of products to increase carbon's bulk density, and 3) metal oxide dispersion (CaO, MgO) into activated carbon. The later has been shown to increase supercritical adsorption capacity of activated carbon by 50%.

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REFERENCES


Innes, R.A., Lutinski, F.E., Occelli, M.L. and Kennedy, J.V. Report AC 01-84CE50071


Table 1. Proximate and ultimate analysis of IBC-106 (-20+100 mesh)

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<thead>
<tr>
<th>Proximate analysis, wt% (as received)</th>
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<tr>
<td>Moisture</td>
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<td>Volatile matter</td>
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<td>Fixed carbon</td>
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<td>Ash</td>
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<table>
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<tr>
<th>Ultimate analysis, wt% (dry)</th>
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<td>Carbon</td>
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<td>Sulfur</td>
<td>3.73</td>
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<td>Oxygen</td>
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Table 2. Selected activated carbons produced from Illinois coal

<table>
<thead>
<tr>
<th>Carbon #</th>
<th>Oxidation °C, h</th>
<th>Activation °C, h</th>
<th>BET (dry), m²/g</th>
<th>Micropore volume cm³/g</th>
<th>CH₄ adsorption at 500 psig g/g</th>
<th>Bulk density g/cm³</th>
<th>Vm/Vs cm³/cm³</th>
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<td>1</td>
<td>-</td>
<td>850, 1.5</td>
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<td>54</td>
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<td>0.0643</td>
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<td>73</td>
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<tr>
<td>3</td>
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<td>825, 3</td>
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<td>0.0610</td>
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<td>76</td>
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<td>KOH</td>
<td>-</td>
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Figure 1. Production of activated carbon from IBC-106 coal.
\[
\frac{V_m}{V_s} = \frac{RT\left[\frac{W_2 - W_1}{M} - \frac{P}{RT}\left(V_i - \frac{W_0 - W_t}{D}\right)\right]}{\frac{W_0 - W_t}{D}}
\]

- \(V_m, \text{cm}^3\): Volume of stored CH\(_4\) @ STP
- \(V_s, \text{cm}^3\): Adsorbent packing volume
- \(W_t, \text{g}\): Empty tube weight
- \(V_t, \text{cm}^3\): Empty tube volume
- \(M, \text{g/mole}\): CH\(_4\) molecular weight
- \(D, \text{cm}^3/\text{g}\): Adsorbent bulk density
- \(P, \text{atm}\): Storage pressure
- \(P_0, \text{atm}\): Ambient pressure
- \(T, \text{K}\): Ambient temperature
- \(R, \text{atm-cm}^3/\text{mole-K}\): Gas constant

Figure 2. Experimental apparatus for methane \(V_m/V_s\) adsorption measurement

Figure 3. Coal weight loss vs. activation time.
Figure 4. Carbon BET surface area and micropore volume vs. coal weight loss.

Figure 5. Carbon bulk density vs. coal weight loss.

Figure 6. Surface area and micropore volume per unit volume vs. coal weight loss.
Figure 7. Carbon macropore and mesopore volume and micropore volume fraction vs. coal weight loss.

Figure 8. Methane volumetric adsorption capacity vs. coal weight loss.

Figure 9. Surface area vs. Vm/Vs methane adsorption.
Figure 10. Micropore volume vs. Vm/Vs methane adsorption.

Figure 11. Vm/Vs methane adsorption vs. surface area on the unit volume basis.

Figure 12. Vm/Vs methane adsorption vs. micropore volume on the unit volume basis.
Figure 13. Methane adsorption isotherms of selected activated carbons.

Figure 14. Cost estimation in terms of surface area.

Figure 15. Cost estimation in terms of methane storage.
PROJECT MANAGEMENT REPORT
June 1, 1995 through August 31, 1995

Project Title: NOVEL CARBONS FROM ILLINOIS COAL FOR NATURAL GAS STORAGE

DOE Grant Number: DE-FC22-92PC92521 (Year 3)
ICCI Project Number: 94-1/4.2B-6M
Principal Investigator: Massoud Rostam-Abadi, ISGS
Other Investigators: Jian Sun and Mark Rood, University of Illinois
                      Anthony A. Lizzio, ISGS

Project Manager: Daniel Banerjee

COMMENTS

A budget revision was approved by the ICCI on July 5, 1995.

BUDGET SUMMARY

<table>
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<th>COST ELEMENT</th>
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<th>REVISED</th>
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<td>Salary</td>
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<td>Material and Supplies</td>
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<td>Travel</td>
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<td>Other Direct Costs</td>
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<td>Quarter*</td>
<td>Types of Cost</td>
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<td>Aug. 31, 1995</td>
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*Cumulative by Quarter
COST BY QUARTER - EXHIBIT C

NOVEL CARBONS FROM ILLINOIS COAL FOR NATURAL GAS STORAGE

Projected Expenditures Actual Expenditures

Total ICCI Award $49,376
Milestones:

A. Preparation of carbon adsorbents (Task 1)
B. Physical and chemical characterization (Task 2)
C. Methane working capacity/heat of adsorption (Task 3)
D. Molecular sieve properties (Task 4)
E. Technical/economic/market studies (Task 5) [Will be completed in year 2]
F. Reports (Task 6)
Project Title: NOVEL CARBONS FROM ILLINOIS COAL FOR NATURAL GAS STORAGE

DOE Cooperative Agreement Number: DE-FC22-92PC92521 (Year 3)
ICCI Project Number: 94-1/4.2B-6M
Principal Investigator: Massoud Rostam-Abadi, ISGS
Other Investigators: Jian Sun and Mark Rood, University of Illinois, Anthony A. Lizzio, ISGS
Project Manager: Daniel Banerjee, ICCI


EQUIPMENT LIST
September 1, 1994 through August 31, 1995

Project Title: NOVEL CARBONS FROM ILLINOIS COAL FOR NATURAL GAS STORAGE

DOE Cooperative Agreement Number: DE-FC22-92PC92521 (Year 3)
ICCI Project Number: 94-1/4.2B-6M
Principal Investigator: Massoud Rostam-Abadi, ISGS
Other Investigators: Jian Sun and Mark Rood, University of Illinois, Anthony A. Lizzio, ISGS
Project Manager: Daniel Banerjee, ICCI

No equipment was purchased.
HAZARDOUS WASTE REPORT
September 1, 1994 through August 31, 1995

Project Title: NOVEL CARBONS FROM ILLINOIS COAL FOR NATURAL GAS STORAGE

DOE Cooperative Agreement Number: DE-FC22-92PC92521 (Year 3)
ICCI Project Number: 94-1/4.2B-6M
Principal Investigator: Massoud Rostam-Abadi, ISGS
Other Investigators: Jian Sun and Mark Rood, University of Illinois, Anthony A. Lizzio, ISGS
Project Manager: Daniel Banerjee, ICCI

No hazardous waste resulted from this project.