

PRODUCTION OF CARBON MOLECULAR SIEVES FROM ILLINOIS COAL

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Keywords: coal, carbon molecular sieve, adsorption, gas separation

INTRODUCTION

Gas separations are a major production cost in the chemical industry today. Production of industrial gases by noncryogenic methods, e.g., pressure swing adsorption (PSA), is expected to grow much faster than by the conventional method, cryogenic distillation [1]. 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 [2,3].

Carbon molecular sieves (CMS) have become an increasingly important class of adsorbents for application in the separation of gas molecules that vary in size and shape [1-6]. CMS are microporous materials with average pore dimensions similar to the critical dimensions of an adsorbate molecule. Selectivity for gas uptake by CMS is controlled by the relative rates of diffusion of the adsorbing gaseous species, as opposed to zeolites, which have separation efficiencies based primarily on their chemical affinity for a specific component in the gas mixture [6]. Gas molecules with only slightly varying critical dimensions, e.g., 0.2 Å, may be adsorbed by CMS at rates that vary by several orders of magnitude [7]. Thus, a small change in the average pore size can significantly affect the rate of diffusion of a gas molecule through the pore structure. Under controlled conditions of heat treatment [8-13] and activation [11-13], it has been possible to prepare carbonaceous adsorbents (chars) from coal which exhibit molecular sieve behavior. Pore structure modification can also be achieved by carbon deposition, i.e., the cracking of a suitable hydrocarbon gas within the pores of a carbon substrate [13-17].

The coal research program at the Illinois State Geological Survey has recently initiated a project to determine whether Illinois Basin coals are suitable feedstocks for the production of CMS and to evaluate the potential application of these products in gas separation processes. Data generated in this study will be used to design and engineer CMS with a proper pore size which will resolve a specific gas separation problem. This paper reports data on the kinetics of adsorption of oxygen, nitrogen, carbon dioxide, methane and hydrogen at 25°C on a series of chars prepared from an Illinois Basin coal under various pyrolysis and activation conditions. The effects of coal and char pretreatments such as preoxidation, demineralization, addition of potassium salt and carbon deposition on the molecular sieve properties of the char are also being investigated.

EXPERIMENTAL

Char Preparation: Chars were prepared from a Colchester (Illinois No. 2) hvC bituminous coal (sample IBC-102 of the Illinois Basin Coal Sample Program [18]). The coal is from a western Illinois preparation plant and is relatively low in organic and high in pyritic sulfur. The proximate and ultimate analyses for the coal and for the size fraction (12x40 mesh) used in this study are given in Table 1.

A microbalance reactor (Cahn RG) was used initially to prepare chars. Typically, 500 mg of coal was placed in a wire mesh basket and heated at 20°C/min in flowing N₂ (500 cm³/min) to a temperature between 600 and 1000°C and held for 0.5 h. The char was cooled in N₂, ground to -200 mesh and stored under N₂ for future characterization. A horizontal fixed-bed reactor was used to prepare larger quantities of char (up to 15 g) under similar conditions.

To enhance surface area development and increase the adsorption capacity of the char, both "physical" and "chemical" activation methods [19] were employed. Physical activation of the char was done in 1 atm CO₂ at 850°C. Upon reaching the desired conversion level, the reactant gas was switched to N₂ and the char sample cooled to 25°C. Chemical activation involved the addition of an alkali salt to the raw coal and subsequent heat treatment in inert gas. More specifically, the coal was physically mixed with potassium hydroxide (KOH) in a 1:1 ratio (by weight), ground with a mortar and pestle to -200 mesh, and pyrolyzed in N₂ at 800°C for 0.5 h. The char was cooled in N₂ to room temperature and washed with distilled water to remove the residual potassium. Since this char became noticeably warm upon removal from the furnace following pyrolysis, the char was submerged in water (quenched) to prevent any further oxidation.

Some chars were prepared by preoxidizing the coal at various O_2 partial pressures (0.2-1.0) and temperatures (130-220°C) prior to pyrolysis. In order to study the influence of mineral matter present in the coal on the molecular sieve properties of the char, a portion of the coal was acid-washed with 5 N HCl (60°C, 3 h); the ash yield was reduced from 3.2 to 1.2%.

The adsorption properties of the char were also modified by carbon deposition (CD). The char sample (1-3 g), placed in the horizontal tube furnace, was heated in flowing N_2 to 800 or 1000°C and held at this temperature for 0.5 h before switching to either 10% (balance N_2) or 100% CH_4 (300 cm^3/min). After a given CD time, N_2 was reintroduced to flush out any residual CH_4 before cooling to 25°C.

Char Characterization: Total surface areas of selected chars were determined from the amount of N_2 and CO_2 adsorbed at 77 and 195 K using a dynamic sorption method in conjunction with a single-point BET adsorption equation [20]. For comparison, a volumetric adsorption apparatus (Autosorb-1, Quantachrome Corp.) was used to obtain equilibrium adsorption data over the entire range of relative pressure. The N_2 (77 K) and CO_2 (273 K) surface areas, in this case, were determined using the multi-point BET and Dubinin-Radushkevich (DR) equations, respectively.

An experimental procedure was developed using the volumetric adsorption apparatus to determine the kinetics of adsorption (volume adsorbed vs. time) of a single gas, e.g., O_2 , N_2 , CO_2 , CH_4 , or H_2 , at 25°C. A typical run proceeded as follows: 0.3-1.5 g char was placed in a sample cell and outgassed (1×10^{-5} torr) at 180°C for 8 h. Helium was used to determine the dead volume of the sample cell. After outgassing again for several minutes, a known volume of gas was introduced into the sample cell (initial pressure of 350-500 torr) and the subsequent decrease in pressure monitored at 6 s intervals by a pressure transducer accurate to within ± 1 torr. After 10-30 min adsorption time, the sample was outgassed under vacuum at 25°C for 10 min and the same experiment repeated to ensure experimental reproducibility. Volumes adsorbed were calculated using the ideal gas law.

RESULTS AND DISCUSSION

Previously in this study [21], only values of N_2 and CO_2 equilibrium adsorption capacities were reported for our prepared chars. Differences in the N_2 and CO_2 surface area of each were attributed to the molecular sieving nature of the char; however, questions concerning how these materials would behave in an actual gas separation process remained. A knowledge of the kinetics of adsorption of select gases should allow us to better assess the potential usefulness of these materials in specific gas separation processes. In this section, three gas separation processes of commercial importance, N_2/O_2 , CO_2/CH_4 and CH_4/H_2 , are examined. Kinetic data obtained at 25°C for adsorption of these gases on selected chars are presented and discussed.

Oxygen/Nitrogen Separation: The demand for the two major industrial gases, oxygen and nitrogen, is on the rise due to their increased use in the combustion and gasification of coal [22] and in the steel and electronics manufacturing industries [23]. High purity N_2 can be produced using CMS in a PSA process. Nitrogen is the high pressure product and oxygen (35-50%) is produced as the low pressure product [2,3]. Air separation using microporous carbons relies on the fact that O_2 (kinetic diameter, 3.46 Å) diffuses into the carbon more rapidly than N_2 (3.68 Å) [24]. The kinetics of O_2 and N_2 adsorption at 25°C on the IBC-102 chars prepared at 600, 800, 900 and 950°C are shown in Figure 1. All chars adsorb more O_2 than N_2 and, thus, have some molecular sieving capability for air separation. Table 2 presents the O_2 and N_2 adsorption capacities of each char measured after 5 min and the ratio of both, or O_2/N_2 selectivity. Analysis of Figure 1 reveals that the O_2/N_2 selectivity decreases with time of adsorption, e.g., for the 800 and 900°C chars, the O_2/N_2 selectivities after only 30 s were 2.98 and 4.81, respectively, compared to 1.34 and 3.46 after 5 min. To be effective as a molecular sieve, the product should have a high selectivity ratio as well as a high adsorption capacity. A high selectivity indicates that the sieve readily discriminates between components in the gas mixture. A high adsorption capacity, of course, indicates that the molecular sieve will adsorb a large volume of gas. Table 2 shows that both the O_2 and N_2 adsorption capacities of the 800-1000°C chars decrease with increasing heat treatment temperature (HTT) while the O_2/N_2 selectivity increases from 1.34 to 4.10. Nandi and Walker [9] reported O_2/N_2 adsorption data (measured at 0.8 atm and 25°C) for several chars derived from lower rank coals. The extent of O_2 and N_2 adsorption showed a similar trend with HTT; however, their O_2/N_2 selectivities were substantially lower than those of the IBC-102 chars at any given HTT.

The IBC-102 char produced at 900°C seems to possess optimum molecular sieve properties for O_2/N_2 separation. A comparison of the the O_2/N_2 adsorption properties of this char with those of a coal-based carbon molecular sieve (CMS-A) used in air separation [12,17], a commercial CMS manufactured by Takeda Chem. Ind., Co. (measured at 1 atm and 25°C) [25] and a standard Linde type 4A zeolite is shown in Figure 1. The ability of each material to separate O_2 from N_2 is remarkably similar (except, of course, for the zeolite), suggesting that IBC-102 coal may, indeed, be a suitable feedstock for the production of CMS. No U.S. company currently manufactures CMS for commercial gas separation processes. Air

Products uses a coconut char-based CMS imported from overseas in its recently developed PSA process for production of N_2 from air [26,27]. A European patent [28] describes a process developed to manufacture CMS from coconut char. Typical values of O_2 adsorption capacity and O_2/N_2 selectivity obtained for a series of coconut char-based CMS were 4-6 cm^3/g and 6.5-8.5, respectively. In order to be competitive with currently available coconut char-based CMS, chars derived from coal should have comparable molecular sieve properties. Table 2 shows that our best product (900°C char) has an O_2 adsorption capacity of 4.46 cm^3/g and a selectivity of 3.46.

Table 2 presents O_2/N_2 adsorption capacities for two chars prepared from demineralized IBC-102 coal. For the 800°C char, acid-washing leads to a 1 cm^3/g decrease in the O_2 adsorption capacity, but a 40% increase in O_2/N_2 selectivity. For the 900°C char, there is a slight increase in the O_2 adsorption capacity, but the O_2/N_2 selectivity decreases by 18%. It seems there is no clear advantage in acid-washing this coal before pyrolysis. Table 2 presents O_2/N_2 adsorption data for two chars prepared from preoxidized IBC-102 coal. (Particle agglomeration, an eventual consideration in process scale-up, was not observed with these two chars, unlike the chars that were prepared from non-oxidized coal.) In both cases, the O_2 and N_2 adsorption capacities increase and O_2/N_2 selectivity decreases compared to the chars prepared from non-oxidized coal. The char yield from coal preoxidized at 220°C was about 35% compared to about 45% from coal preoxidized at 180°C. The more severely oxidized coal produces a char with less favorable O_2/N_2 molecular sieve properties. Table 2 also presents O_2/N_2 adsorption data for the 900 and 950°C chars activated to 14 and 10% conversion (X_2), respectively, in 1 atm CO_2 at 850°C. The O_2 adsorption capacity of both chars increases; however, this is offset by a substantial decrease in O_2/N_2 selectivity. Further work is needed to optimize coal preoxidation and char activation process conditions.

Table 2 presents O_2/N_2 adsorption data and Figure 2 shows the kinetics of O_2/N_2 adsorption for Carbonsieve, a CMS used in chromatographic applications. This material adsorbs slightly more N_2 than O_2 . Although Carbonsieve's (CO_2 -DR) surface area is about four times greater than that of the 800°C char, its O_2 adsorption capacity is only 40% greater, suggesting that total surface areas are not a good indicator of char adsorption capacity at room temperature. The closeness in value of the N_2 and CO_2 surface areas for Carbonsieve, however, does suggest their utility as a preliminary indicator of molecular sieving behavior. That is, carbons which do not exhibit large differences in CO_2 and N_2 surface areas do not make good sieves for the separation of N_2 and O_2 [9,24].

In another attempt to improve the molecular sieve properties of char made from IBC-102 coal, the coal was mixed with an alkali salt (KOH) prior to pyrolysis. Table 2 shows that there is a five-fold increase in the CO_2 -DR surface area of this char as compared to chars prepared without addition of KOH. The mesopore and total pore volumes of this "high-surface-area" (HSA) material were determined to be 0.20 and 0.80 cm^3/g , respectively. (Commercial CMS having 5-10 Å pores typically have total pore volumes no greater than 0.25 cm^3/g and surface areas which do not exceed 500 m^2/g [29].) Wennerberg and O'Grady [30] produced HSA carbons by mixing KOH with various carbon substrates, including petroleum coke and coal, and heat treating in inert gas. The physical and chemical properties of these materials have since been extensively studied by those investigators and others (see, for example, refs. 31-33). Whether these materials exhibit molecular sieving behavior, however, remains to be determined. Figure 2 shows that the HSA char adsorbs more N_2 than O_2 and its O_2/N_2 selectivity is quite low (0.40) compared to the chars prepared from untreated coal. Note that, although the CO_2 -DR surface area of the HSA char is five times greater than that of the char prepared at 800°C from untreated coal, its O_2 adsorption capacity is about the same. Figure 2 shows the kinetics of O_2 and N_2 adsorption to be very similar for Carbonsieve and the HSA char; neither appear to be a suitable adsorbent for air separation. It is interesting to note that the N_2 adsorption capacity (14.87) and N_2/O_2 selectivity (2.51) of the HSA char compare quite favorably with those of the commercial zeolite (8.26, 3.84).

In an attempt to improve the molecular sieve properties of the HSA char, carbon deposition was used to narrow the pores. Figure 2 shows the kinetics of O_2 and N_2 adsorption on the HSA char exposed to 10% CH_4 at 1000°C for 6 min. Depositing carbon in the pores of the HSA char is seen to have a significant effect on the kinetics and extent of O_2 and N_2 adsorption. The O_2 adsorption capacity nearly doubles while that of N_2 decreases by about one third. Table 2 lists the value of O_2/N_2 selectivity after 5 min adsorption time as 1.12, which is still lower than that of any of the chars prepared at 600-1000°C. Figure 2 shows the kinetics of O_2 and N_2 adsorption on the HSA char exposed to 10% CH_4 at 1000°C for 15 min. The rate of both O_2 and N_2 adsorption is considerably slower and the adsorption capacities less than those of the HSA char exposed to 10% CH_4 at 1000°C for 6 min. The O_2/N_2 selectivity, however, increases to 1.85 which is comparable to that of the untreated 800°C char. It is interesting to note that the O_2 and N_2 adsorption capacity of the 800°C char is about twice that of the HSA char (10% CH_4 , 1000°C, 0.25 h) even though they have similar surface areas. Further work is needed to optimize the carbon deposition conditions, most notably, the CD temperature, time and methane concentration (see, for example, ref. 34).

Figure 2 is also interesting in that it may help explain the unexpectedly low value of O_2 adsorption capacity obtained for the HSA char (see also Table 2). It shows the kinetics of O_2 and N_2 adsorption for the HSA

char produced by quenching the sample in H₂O upon removal from the furnace following pyrolysis. The quenched HSA char is seen to have adsorbed more than twice the amount of O₂ as the unquenched HSA char; its O₂/N₂ selectivity of 0.93 is similar to that of Carbosieve (see Table 2) and also some highly activated carbons tested by Nandi and Walker [9]. The reason for the higher O₂ uptake could be that the quenched char does not have a chance to chemisorb oxygen after its removal from the furnace since it is immediately quenched in water. The unquenched HSA char, on the other hand, was observed to chemisorb a considerable amount of oxygen upon exposure to air (i.e., it became noticeably warm) and, thus, most of the sites were already occupied by oxygen prior to an O₂ adsorption experiment at 25°C. This results in an apparently lower value of O₂ adsorption capacity being measured for the unquenched char. It is interesting to note that the O₂ adsorption capacity of the HSA char increases after CD (see Table 2) even though some of the pores were undoubtedly blocked by deposits of carbon formed by the cracking of methane at 1000°C. Recall that the HSA char sample was heated in N₂ at 1000°C for 0.5 h prior to a CD experiment, which would have removed most, if not all, of the oxygen present on the char surface as CO and CO₂.

Carbon Dioxide/Methane Separation: The incentive for developing more efficient CO₂/CH₄ separation processes, in particular, PSA using CMS, has increased with the recent advent of several innovative technologies [3]. The adsorption of CH₄ and CO₂ on CMS and activated carbon has been investigated by Schollner [35] for separation of CH₄ from fermentation gas via a PSA process. Methane is also found in combination with CO₂ and N₂ in some natural gas reservoirs (50% CH₄, 50% CO₂), in the effluent gas from oil wells undergoing CO₂ flooding for enhanced oil recovery (20-80% CO₂) and in municipal and industrial landfill gases (40-60% CO₂) [3]. Recovering methane as a medium- or high-BTU gas would be the primary aim of a CO₂/CH₄ PSA process. Significant progress in this area has been realized; both zeolites and CMS have been used as adsorbents [3,36].

The chars produced in this study were tested for their ability to separate CO₂ from CH₄, which have kinetic diameters of 3.3 and 4.0 Å, respectively. Figure 3 shows the kinetics of CO₂ and CH₄ adsorption and Table 3 lists the CO₂ and CH₄ adsorption capacities and CO₂/CH₄ selectivities of the chars prepared at 600-1000°C. The CH₄ adsorption capacity decreases significantly with increasing HTT, while the CO₂ adsorption capacity exhibits a maximum at a HTT of 800°C. Note that the CO₂ adsorption capacities of these chars are about one order of magnitude greater than the corresponding O₂ and N₂ adsorption capacities listed in Table 2. Also, the CO₂/CH₄ selectivity of the char is optimized at a HTT of 900°C and is quite high compared to its corresponding O₂/N₂ selectivity, 66.40 vs. 3.46. The CO₂ adsorption capacity of this char, however, is considerably less than that of the char prepared at 600 or 800°C; so, in effect, there is a tradeoff between high CO₂ adsorption capacity and high CO₂/CH₄ selectivity, i.e., one cannot achieve both by varying just the HTT. Due to the paucity of CO₂/CH₄ separation data in the literature, a comparison with other work is not possible at the present time. However, it is thought that these chars would show good potential for application in a commercial CH₄/CO₂ separation process.

Figure 4 presents the kinetics of CO₂/CH₄ adsorption and Table 3 lists CO₂ and CH₄ adsorption capacities and the CO₂/CH₄ selectivity for Carbosieve and the HSA char. It is interesting to note the similarity in the CO₂/CH₄ (as well as in the O₂/N₂) adsorption properties of these two materials. Both materials adsorb about the same amount of CO₂ at 25°C as the 800°C char even though their CO₂-DR surface areas (measured at 0°C) are greater by a factor of four. The CO₂/CH₄ selectivities of Carbosieve and the HSA char are only 2.86 and 2.57 compared to 13.50 and 66.40 for the 800 and 900°C chars. Apparently, the former two are not nearly as efficient as the latter two chars in separating CO₂ from CH₄. The high CO₂ adsorption capacity of the HSA char is desirable; however, its relatively low CO₂/CH₄ selectivity does not lend itself to being used in a commercial CO₂/CH₄ separation process.

Table 3 lists the CO₂ and CH₄ adsorption capacities and CO₂/CH₄ selectivity and Figure 4 also shows the kinetics of CO₂/CH₄ adsorption for the HSA char exposed to 10% CH₄ at 1000°C for 6 and 15 min. There is a slight increase in the CO₂/CH₄ selectivity (2.57 to 2.98) of the 6 min char while there is considerably more improvement in the CO₂/CH₄ selectivity of the 15 min char (2.57 to 7.09), but its CO₂ adsorption capacity decreases to one sixth its original value. The CO₂/CH₄ molecular sieve properties of these two chars still do not match those of the 600-950°C chars prepared from coal without added KOH.

Methane/Hydrogen Separation: Hydrogen is utilized in a variety of chemical and petrochemical processes. The demand for H₂ would be better met if an adsorbent material could be developed to more efficiently recover it from coke oven, steam reforming, or other coal utilization process gases. In general, all the gases produced in these processes have similar compositions, i.e., they contain principally H₂, along with N₂, O₂, CO, CH₄, and CO₂ in various proportions. The efficient removal of H₂ from this mixture is of considerable commercial importance [37].

Figure 5 shows the kinetics of adsorption of H₂ and CH₄ on the chars prepared at 600-1000°C. The diffusion rate of H₂ is quite high for the 600, 800 and 900°C chars and equilibrium is reached after only 20 seconds. Only the 1000°C char restricts, to some extent, entry of H₂ into its pore structure, i.e., equilibrium

is not reached even after 5 min. The H₂ adsorption capacities of the 600-1000°C chars are quite low and are essentially unaffected by HTT, contrary to the behavior previously observed (in most cases) for CH₄, O₂, N₂ and CO₂ adsorption. The CH₄ diffusion rate is highest for the 600°C char and monotonically decreases with HTT. The pore structure of the 900 and 1000°C chars has sufficiently closed to the point where the char now adsorbs more H₂ than CH₄. For adsorbing CH₄ from a CH₄/H₂ mixture, Table 3 shows that the 600°C char would probably be the best choice with both its relatively high CH₄ adsorption capacity and CH₄/H₂ selectivity. Jüntgen et al. [38] observed similar trends in the kinetics of H₂ and CH₄ adsorption on a "wide pore" CMS, "narrow pore" CMS, activated coal and a Type 5A zeolite. Hydrogen uptake by all four materials was essentially the same, i.e., a relatively high H₂ diffusion rate and low H₂ adsorption capacity were measured. Methane adsorption, on the other hand, varied according to the pore structure of the material. Their "narrow pore" CMS showed similar molecular sieving behavior to that of our 900 and 1000°C chars, whereas their "open pore" CMS displayed behavior similar to that of our 600 and 800°C chars.

Figure 6 presents the kinetics of CH₄ and H₂ adsorption on the HSA char at 25°C. Equilibrium for H₂ is reached within seconds. Table 3 shows that the extent of CH₄ and H₂ adsorption on this char is about three times greater than that on the 600°C char. The CH₄/H₂ selectivity of the HSA char was 39.5, highest among all the chars studied. For the HSA chars upon which carbon was deposited, Figure 6 and Table 3 show that the extent of both CH₄ and H₂ adsorption and the CH₄/H₂ selectivity decrease with increasing CD time. It is interesting to note the similarity in the kinetics of CH₄ and H₂ adsorption on the 800°C and the HSA (10% CH₄, 1000°C, 0.25 h) char (see Figures 5 and 6).

CONCLUSIONS

Chars were prepared from IBC-102 coal under various pyrolysis and activation conditions in a horizontal tube fixed-bed reactor. Chars having commercially significant BET surface areas of 1200-1700 m²/g were produced using select additives and heat treatment conditions. These high-surface-area (HSA) chars had more than twice the surface area of commercial molecular sieves. Experimental techniques were developed to study, at ambient temperature, the kinetics of adsorption of selected gases, e.g., N₂, O₂, CO₂, CH₄ and H₂, on these chars. The results were intriguing. A char prepared at 900°C was found to have similar N₂ and O₂ adsorption properties to those of commercial CMS used in air separation processes. On the other hand, the HSA char was found to adsorb more N₂ than O₂ and, therefore, was not considered a viable candidate (as is) for separating N₂ from O₂. Carbon deposition, using methane as the cracking gas, increased the O₂/N₂ selectivity of the HSA char; however, this was somewhat offset by a decrease in its O₂ adsorption capacity. Other gas separations of commercial interest studied included CO₂/CH₄ and CH₄/H₂. A char prepared at 800°C showed excellent molecular sieving properties for separating CO₂ from CH₄, i.e., both a relatively high CO₂ adsorption capacity and CO₂/CH₄ selectivity were achieved. The CO₂/CH₄ sieving ability of the HSA char was questionable. That is, although the CO₂ adsorption capacity of the HSA char was slightly greater than that of the 800°C char, its CO₂/CH₄ selectivity was lower by a factor of ten. With regard to CH₄/H₂ separation, the CH₄ adsorption capacity and CH₄/H₂ selectivity decreased with increasing HTT and CD time; H₂ adsorption was minimal and essentially independent of HTT. Future work will focus on optimizing the molecular sieve properties of the most promising chars for a given gas separation process using the char activation and carbon deposition methods employed in this study. Processing conditions will be sought which optimize molecular sieving behavior and minimize loss of adsorption capacity.

ACKNOWLEDGEMENTS

This work was funded in part by the Illinois Department of Energy and Natural Resources through its Coal Development Board and the Center for Research on Sulfur in Coal.

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Table 1. Proximate and Ultimate Analyses of IBC-102 Coal.

Proximate Analysis (wt%)	As-received	12x40 mesh
Moisture	13.9	10.6
Volatile Matter	35.3	37.8
Fixed Carbon	45.5	48.3
Ash	5.3	3.2
Ultimate Analysis (wt%)	As-received	12x40 mesh
Carbon	65.40	70.54
Hydrogen	6.03	6.05
Nitrogen	1.26	1.36
Oxygen	19.17	16.93
Sulfur	2.84	1.92
Sulfate	0.29	0.16
Pyritic	1.45	0.80
Organic	1.09	0.96

Table 2. O₂ and N₂ Adsorption Capacities, O₂/N₂ Selectivity and N₂-BET and CO₂-DR Surface Areas of Chars Prepared from IBC-102 Coal.

Sample	V _{O₂} (cm ³ /g)	V _{N₂} (cm ³ /g)	V _{O₂} /V _{N₂}	N ₂ -BET (m ² /g)	CO ₂ -DR (m ² /g)
Linde Type 4A Zeolite	2.15	8.26	0.26	35	316
CMS-A [12,17]	4.27	0.98	4.36	1	575
Takeda Type 3A CMS [25]	5.58	3.85	1.45	----	----
IBC-102, 600°C, 0.5 h	6.00	3.71	1.62	12	375
IBC-102, 800°C, 0.5 h	7.02	5.22	1.34	5	290
IBC-102, 900°C, 0.5 h	4.46	1.29	3.46	----	----
IBC-102, 950°C, 0.5 h	2.38	0.58	4.10	----	----
IBC-102, 1000°C, 0.5 h	0.17	0.00	----	2	5
IBC-102 Dem, 800°C, 0.5 h	6.17	3.21	1.92	----	----
IBC-102 Dem, 900°C, 0.5 h	4.67	1.62	2.84	----	----
IBC-102, 800°C, Preox., 220°C, 1 h, 100% O ₂	7.53	6.97	1.08	----	----
IBC-102, 800°C, Preox., 180°C, 2 h, 50% O ₂	10.05	8.27	1.21	----	----
IBC-102, 900°C, CO ₂ , X _c = 0.14	7.84	6.12	1.28	----	----
IBC-102, 950°C, CO ₂ , X _c = 0.10	6.12	3.80	1.61	----	----
Carbosieve	9.76	10.49	0.93	1040	1220
IBC-102 + KOH (1:1), 800°C, 0.5 h (HSA char)	5.93	14.87	0.40	1400	1690
HSA char, 10% CH ₄ , 1000°C, 0.10 h	11.40	10.19	1.12	710	980
HSA char, 10% CH ₄ , 1000°C, 0.25 h	3.39	1.83	1.85	15	240
HSA char, H ₂ O qucnch	13.75	14.74	0.93	1330	1550

Table 3. CO₂, CH₄ and H₂ Adsorption Capacities and CO₂/CH₄ and CH₄/H₂ Selectivities of Chars Prepared from IBC-102 Coal.

Sample	V _{CO2} (cm ³ /g)	V _{CH4} (cm ³ /g)	V _{CO2} /V _{CH4}	V _{H2} (cm ³ /g)	V _{CH4} /V _{H2}
IBC-102, 600°C, 0.5 h	78.42	19.22	4.08	0.56	34.32
IBC-102, 800°C, 0.5 h	93.85	6.95	13.50	0.64	10.86
IBC-102, 900°C, 0.5 h	29.88	0.45	66.40	0.56	0.80
IBC-102, 950°C, 0.5 h	12.68	0.30	42.27	0.62	0.48
IBC-102, 1000°C, 0.5 h	0.96	0.03	32.00	1.04	0.03
IBC-102 Dem, 800°C, 0.5 h	80.53	2.66	30.27	0.52	5.11
IBC-102 Dem, 900°C, 0.5 h	39.21	0.83	47.24	0.55	1.51
IBC-102, 900°C, CO ₂ , X _c = 0.14	111.05	8.64	12.85	0.60	14.40
IBC-102, 950°C, CO ₂ , X _c = 0.10	55.15	4.98	11.07	0.60	8.30
Carbosieve	118.41	41.40	2.86	----	----
IBC-102 + KOH (1:1), 800°C, 0.5 h (HSA char)	147.10	57.27	2.57	1.45	39.50
HSA char, 10% CH ₄ , 1000°C, 0.10 h	96.00	32.20	2.98	1.30	24.77
HSA char, 10% CH ₄ , 1000°C, 0.25 h	24.07	3.40	7.09	0.96	3.54
HSA char, H ₂ O quench	137.06	58.73	2.33	----	----

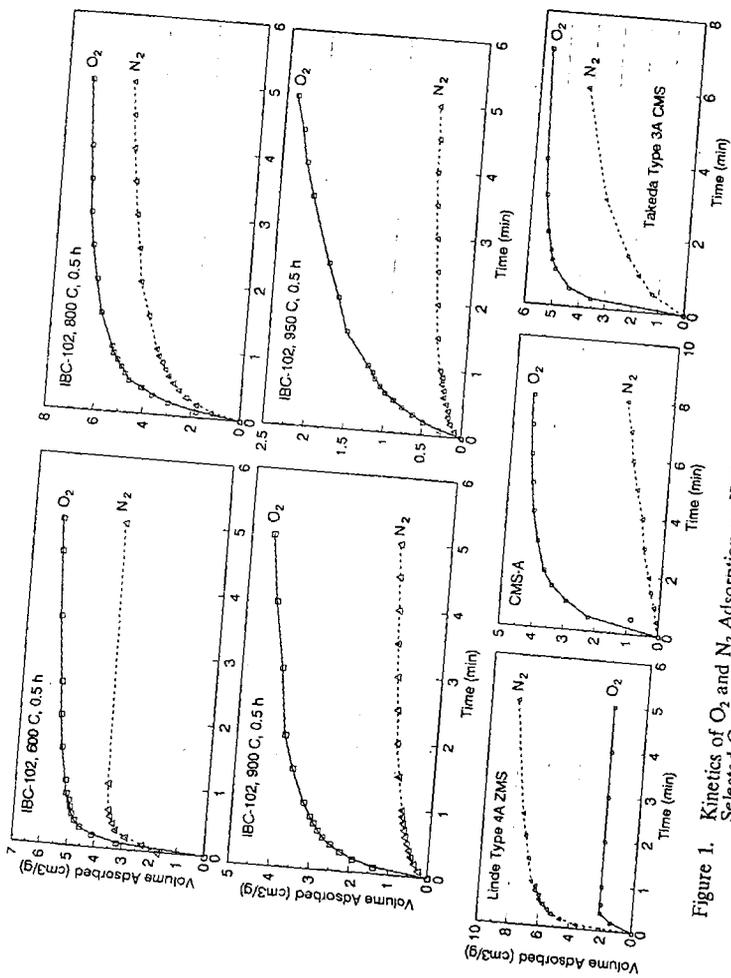


Figure 1. Kinetics of O_2 and N_2 Adsorption on IBC-102 Chars Prepared at 600.95°C and on Selected Commercial Molecular Sieves Used in Air Separation.

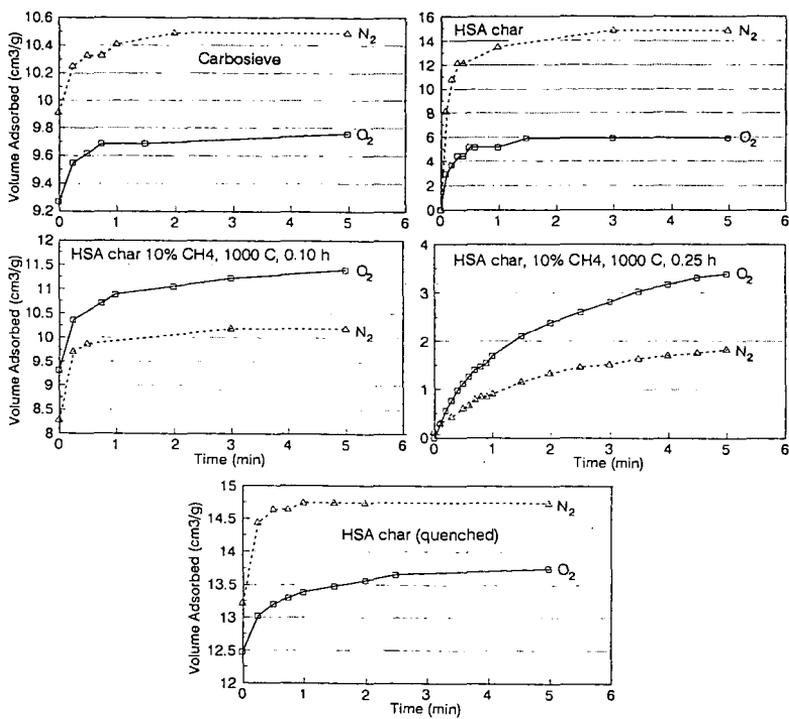


Figure 2. Kinetics of O_2 and N_2 Adsorption on Carbosieve and Selected HSA Chars.

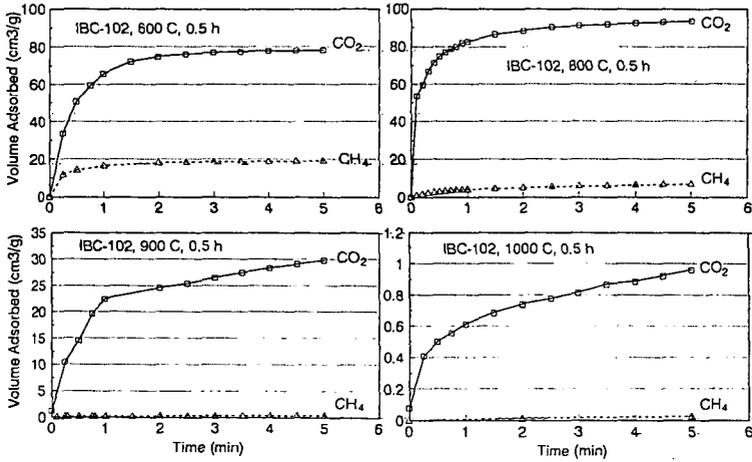


Figure 3. Kinetics of CO₂ and CH₄ Adsorption on IBC-102 Chars Prepared at 600-1000°C.

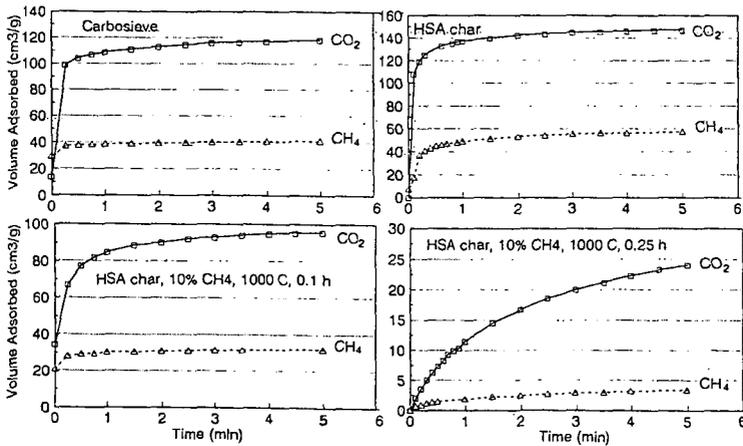


Figure 4. Kinetics of CO₂ and CH₄ Adsorption on Carboisieve and Selected HSA Chars.

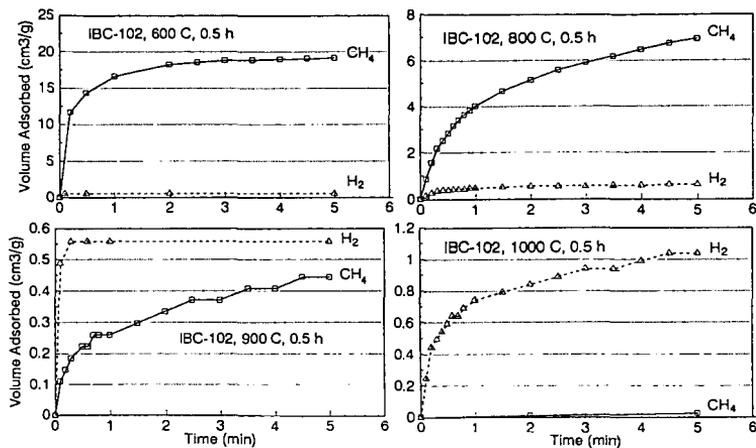


Figure 5. Kinetics of CH₄ and H₂ Adsorption on IBC-102 Chars Prepared at 600-1000°C.

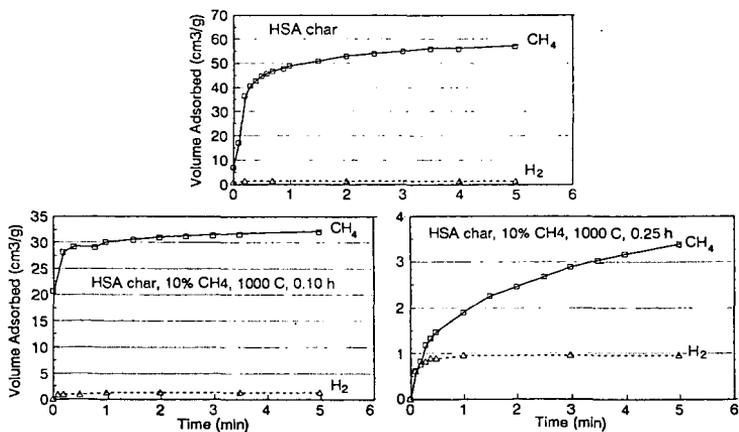


Figure 6. Kinetics of CH₄ and H₂ Adsorption on Selected HSA Chars.