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TECHNICAL REPORT
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Project Title: **PRODUCTION AND USE OF ACTIVATED CHAR FOR
COMBINED SO₂/NO_x REMOVAL**

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ABSTRACT

Carbon adsorbents have been shown to remove sulfur oxides from flue gas, and also serve as a catalyst for reduction of nitrogen oxides at temperatures between 80 and 150°C. The overall objective of this project is to determine whether Illinois coal is a suitable feed stock for the production of activated char which could be used as a catalyst for removal of SO₂/NO_x from combustion flue gas, and to evaluate the potential application of the products in flue gas cleanup. Key production variables will be identified to help design and engineer activated char with the proper pore structure and surface chemistry which will enable the development of an effective SO₂/NO_x removal catalyst.

During this reporting period, a series of chars was prepared from an Illinois coal (IBC-102). A 48x100 mesh size fraction of IBC-102 coal was physically cleaned to reduce its ash content from 5.5 to 3.6%. The clean coal was pyrolyzed in a fluidized-bed reactor at 500, 700 and 900°C. The surface area and oxygen content of the char was varied either by oxidation in 10% O₂ or by nitric acid treatment. Steam activation or chemical activation using potassium hydroxide was employed to enhance surface area development. Nitrogen BET surface areas of the chars ranged from 1 to 800 m²/g. Future work will involve the use of a quadrupole mass spectrometer to measure SO₂/NO_x adsorption capacities of the chars. The overall performance of the prepared chars in removing SO₂/NO_x from combustion flue gas will be assessed and compared to that of a commercial activated carbon.

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EXECUTIVE SUMMARY

Worldwide interest in carbon based flue gas desulfurization (FGD) technology is growing and these processes have been proven successful at removing up to 100% SO_2 and over 80% NO_x from combustion flue gas (Tsuji and Shiraishi, 1991). Carbon adsorbents remove sulfur oxides from coal combustion flue gas at temperatures below 120°C, and also serve as a catalyst for reduction of nitrogen oxides at temperatures between 80 and 150°C (Richter et al., 1985). The type of carbon used is probably the most important process consideration, with respect to both adsorption efficiency and maintenance of efficiency during extended operation. One of the unique advantages of the activated carbon FGD process is that it removes nearly every impurity found in combustion flue gas, including SO_2/NO_x , particulates, heavy metals and other air toxics. No other existing FGD process has that capability. German and Japanese researchers have developed this technology to the point of commercialization, however, there remains the need for development of sorbents having higher adsorption capacity and mechanical strength. A high quality carbon adsorbent for SO_2/NO_x removal should have the following properties: high adsorption capacity for SO_2 , rapid SO_2 adsorption kinetics, high catalytic activity for ammonia based NO_x reduction, low reactivity with oxygen, minimal activation losses due to regeneration and high mechanical strength.

No data is available on the production or use of activated carbon derived from Illinois coal for simultaneous removal of SO_2 and NO_x from coal combustion flue gas. This relatively unexplored research area, however, shows considerable promise. A recent ICCI sponsored economic evaluation of mild gasification char as a possible feed stock for activated carbon, and as a sorbent for removing pollutants from electric utility flue gas, concluded that "a flue gas de NO_x process using activated mild gasification char is competitive with selective catalytic reduction" and "the activated char scrubber has the potential to create a significant increase in the market for activated carbon." The proposed research, if successful, could affect markets for Illinois coal in three important ways, 1) the development of low cost FGD processes, using Illinois coal-based activated char, would enable electric utilities to continue burning high-sulfur Illinois coal while complying with the 1990 Clean Air Act, 2) the newly developed FGD process would consume activated char made from Illinois coal, thereby increasing utilization of this resource, and 3) if mild gasification char is deemed a suitable feed stock, a market for this char is identified.

The overall objective of this project is to determine whether Illinois Basin coals are a suitable feed stock for the production of activated char which could be used as a catalyst for removal of SO_2/NO_x from combustion flue gas, and to evaluate the potential application of the products in flue gas

cleanup. Key production variables will be identified to help design and engineer activated char with the proper pore structure and surface chemistry which will enable the development of an effective SO_2/NO_x removal catalyst.

The project has four tasks.

In Task 1, activated chars are prepared from an Illinois coal (IBC-102) and an existing mild gasification char (MGC), prepared previously in an industrial pilot plant under carefully controlled pyrolysis and activation conditions. Chars are prepared at pyrolysis temperatures ranging from 600-900°C. To increase surface area and SO_2/NO_x adsorption capacity, the IBC-102 char and MGC are further activated in steam or CO_2 or chemically activated using potassium hydroxide as the chemical activant. To enhance catalytic activity of the char for SO_2/NO_x removal, selected chars will be oxidized in air or by nitric acid treatment. Another way will be to add to the char a metal, e.g., copper, which is known to be an active catalyst for SO_2 and NO_x removal.

In Task 2, activated char samples are tested for their ability to remove SO_2 and NO_x from a simulated coal combustion flue gas. Carbon type, flow rate and adsorption temperature are the principal process variables to be studied. The adsorption capacity and kinetics of SO_2/NO_x adsorption are obtained for selected chars. A laboratory scale adsorption column/mass spectrometry (AC/MS) system is used to evaluate multi-component gas adsorption. Breakthrough curves for individual gases are determined by passing a known concentration of gas through the AC. When the carbon bed becomes saturated, e.g., inlet $[\text{SO}_2] = \text{outlet } [\text{SO}_2]$, the sorbent is regenerated with heat and/or vacuum. Temperature programmed desorption (5°C/min in helium) of SO_2 and NO_x from the spent char will provide further insight into the kinetics and mechanism of combined SO_2/NO_x removal.

In Task 3, chemical, physical and morphological studies are performed on activated char samples, before and after SO_2/NO_x adsorption, to discern the effects of combined SO_2/NO_x removal on the adsorption behavior of activated char. The tests to be performed include: proximate and ultimate analyses, N_2 -BET (77 K) and CO_2 -DR (273 K) surface areas, pore size distribution, helium and bulk density, particle size and electron scanning microscopy. Attrition resistance (mechanical strength) of the spent char is also evaluated. The overall performance of the char in removing SO_2/NO_x from combustion flue gas mixtures is assessed, and compared to that of representative commercial carbons. The acquired data base will serve as a foundation upon which the physical/chemical properties of activated chars will be optimized for use in a carbon based FGD process.

In Task 4, based on the results obtained in Tasks 1-3, a process flow sheet for the production of activated char from

Illinois coal will be developed to aid in future process and economic analyses. In addition, a preliminary market assessment for activated char with optimal properties for SO_2/NO_x adsorption will be undertaken.

During this reporting period, ten chars were prepared to study the effect of surface area, oxygen content and type of oxygen on the SO_2/NO_x adsorption properties of the chars. A 48x100 mesh size fraction of Illinois Basin Coal No. 2 (IBC-102) was prepared using a staged grinding and sieving technique. The 48x100 mesh fraction was physically cleaned by froth flotation to remove mineral matter prior to char preparation. The mineral matter content of the parent coal was reduced from 5.5 to 3.6% by cleaning.

Chars were prepared in nitrogen in a 2-in. ID fluidized-bed reactor (FBR) at 500, 700 and 900°C. These chars were oxidized in 10% $\text{O}_2/90\%$ N_2 at 390-500°C to increase their surface area and oxygen content. In addition, selected samples were subjected to a nitric acid oxidation treatment (80°C) to increase oxygen content. Steam activation at 860°C was performed to increase surface area of char samples while minimizing further addition of oxygen. Nitrogen surface areas of the prepared chars ranged from < 5 to 315 m^2/g . A chemical activation method was employed to enhance surface area development of the chars. Potassium hydroxide (KOH) was loaded onto the coal by impregnation to incipient wetness. The coal/KOH (1:1 by weight) sample, pyrolyzed at 800°C in the FBR, achieved the highest surface area (800 m^2/g).

During the next reporting period, the surface properties of the prepared chars will be further characterized. An estimate of the micropore size distribution of selected chars will be obtained by analyses of adsorption/desorption isotherms of different sized molecules. Experimental methods are currently being developed to determine by temperature programmed desorption (TPD) the type and amount of oxygen on the surface of the char. The gases evolved during TPD are monitored by nondispersive CO/CO_2 analyzers. The prepared chars will also be tested for their ability to remove SO_2 and NO_x from a simulated flue gas mixture. The type of char, flow rate and adsorption temperature will be the principal process variables studied. A quadrupole mass spectrometer has been ordered and will be used to allow detection of SO_2/NO_x species during multi component adsorption studies. The overall performance of the prepared chars in removing SO_2/NO_x from combustion flue gas will be assessed and compared to that of a commercial activated carbon.

OBJECTIVES

The overall objective of this project is determine whether Illinois Basin coals are a suitable feed stock for the production of activated char, and to evaluate the potential application of the products in a carbon-based system for simultaneous removal of SO_2/NO_x from coal combustion flue gas. Key production variables will be identified to help design and engineer an activated char with properties which will enable the development of an effective SO_2/NO_x removal catalyst.

The project has four tasks:

Task 1. Chars are prepared from an Illinois coal (IBC-102) under carefully controlled pyrolysis and activation conditions. Chars are prepared in 1 and 2-in. ID fluidized-bed reactors (FBR) at pyrolysis temperatures ranging from 600-900°C. To increase surface area and SO_2/NO_x adsorption capacity, selected chars are further activated in steam or CO_2 at 850-900°C to 50-60% carbon conversion. IBC-102 coal is also chemically activated using potassium hydroxide as the chemical activant. Potassium is loaded onto the coal or char by an incipient wetness technique and various coal or char/KOH mixtures (1:1, 1:2, 2:1) are prepared. The potassium loaded coal or char is pyrolyzed in the 2-in. FBR at 600 and 800°C, 0.5 h residence time. To enhance catalytic activity of the char for SO_2/NO_x removal, selected chars and activated chars are oxidized in air at 450°C in the 2-in. FBR to increase the oxygen content of the char. Another way will be to add to the char a metal which is known to be an active catalyst for SO_2/NO_x removal.

Task 2. Activated char samples are tested for their ability to remove SO_2 and NO_x from combustion flue gas. Carbon type, flow rate and adsorption temperature are the principal process variables to be studied. The adsorption capacity and kinetics of SO_2/NO_x (SO_2 , NO , or NO_2 in helium) adsorption on selected chars at various temperatures (25-200°C) and pressures (200-800 torr) are determined using a volumetric adsorption apparatus and/or thermogravimetric analyzer (TGA). A laboratory scale adsorption column/mass spectrometry (AC/MS) system is used to evaluate multi component gas adsorption. A mixture of SO_2 (2500 ppm) and NO_x (500 ppm) in a simulated flue gas mixture (2% H_2O , 5% O_2 , 15% CO_2 , 78% N_2) is passed through the AC at a specified and controlled flow rate (20 cm^3/min). Ammonia is introduced into the feed gas in some runs to observe the effects of

selective catalytic reduction. Breakthrough curves for individual gases are determined. When the carbon bed becomes saturated, e.g., inlet $[\text{SO}_2] = \text{outlet } [\text{SO}_2]$, the sorbent is regenerated with heat (200-400°C) and/or vacuum (1×10^{-5} torr). It will be of additional interest to examine the temperature programmed desorption (5°C/min in helium) of SO_2 and NO_x from the spent char in order to gain new insight into the kinetics and mechanism of SO_2/NO_x adsorption/desorption.

Task 3. Chemical, physical and morphological studies are performed on activated char samples, before and after SO_2/NO_x adsorption, to gain additional insight into the effects of SO_2/NO_x removal on the adsorption behavior of activated char. The tests to be performed include: proximate (moisture, volatile matter, fixed carbon, ash content) and ultimate (carbon, hydrogen, nitrogen, sulfur, oxygen) analyses, N_2 -BET (77 K) and CO_2 -DR (273 K) surface areas, pore size distribution, helium and bulk density, particle size and electron scanning microscopy. Attrition resistance (mechanical strength) of the spent char is also evaluated. The overall performance of the char in removing SO_2/NO_x from combustion flue gas mixtures is assessed, and compared to that of a commercial activated carbon. The acquired data base will serve as a foundation upon which the physical/chemical properties of activated chars will be optimized for use in a carbon based flue gas desulfurization process.

Task 4. Based on the results obtained in Tasks 1-3, a process flow sheet for the production of activated char from Illinois coal will be developed for future process and economic analyses. In addition, a preliminary market assessment of the products developed will be undertaken.

INTRODUCTION

Commercial interest in carbon based flue gas desulfurization technology is growing and these processes have been proven successful at removing up to 100% SO_2 and over 80% NO_x from combustion flue gas. One of the unique advantages of the activated carbon FGD process is that it removes nearly every impurity found in combustion flue gas, including SO_2/NO_x , particulates, heavy metals and other air toxics. No other existing FGD process has that capability. Much of the work performed in the area of activated carbon FGD technology has been centered around understanding the mechanism of SO_2/NO_x removal by carbon. The experimental work to date has, for the

most part, neglected the possibility of improving the physical properties and surface chemistry of the carbon to enhance catalytic activity. A limited number of studies are currently underway in the U.S. on the simultaneous removal of SO_2/NO_x from combustion flue gas using activated carbon. Japanese researchers have developed this technology to the point of commercialization, however, there remains the need for development of sorbents having higher adsorption capacity and mechanical strength.

No data is available on the production or use of activated carbon derived from Illinois coal for simultaneous removal of SO_2 and NO_x from coal combustion flue gas. This relatively unexplored research area, however, shows considerable promise. A recent ICCI sponsored economic evaluation of mild gasification char as a possible feed stock for activated carbon, and as a sorbent for removing pollutants from electric utility flue gas, concluded that "a flue gas deNO_x process using activated mild gasification char is competitive with selective catalytic reduction" and "the activated char scrubber has the potential to create a significant increase in the market for activated carbon." The proposed research, if successful, could affect markets for Illinois coal in three important ways, 1) the development of low cost FGD processes, using Illinois coal-based activated char, would enable electric utilities to continue burning high-sulfur Illinois coal while complying with the 1990 Clean Air Act, 2) the newly developed FGD process would consume activated char made from Illinois coal, thereby increasing utilization of this resource, and 3) if mild gasification char is deemed a suitable feed stock, a market for this char is identified.

Carbon adsorbents may be used to remove sulfur oxides from coal combustion flue gas at temperatures below 120°C , and also as a catalyst for reduction of nitrogen oxides at temperatures between 80 and 150°C (Richter et al., 1985). The type of carbon used is probably the most important process consideration, with respect to both adsorption efficiency and maintenance of efficiency during extended operation. A high quality carbon adsorbent for SO_2/NO_x removal should have the following properties: high adsorption capacity for SO_2 , rapid SO_2 adsorption kinetics, high catalytic activity for ammonia-based NO_x reduction, low reactivity with oxygen, minimal activation losses due to regeneration and high mechanical strength.

Lu and Do (1991) have suggested that there is an optimal micropore structure in the activated char which allows for maximum adsorption of SO_2 and NO_x . Wang (1992) reported a reasonable correlation between surface area and SO_2 adsorption capacity of chars derived from three bituminous coals. However, Ahmed et al. (1992) observed no correlation between NO conversion and surface area or pore volume of four commer-

cial activated carbons; rather NO reduction activity showed an inverse correlation with pH and ash content.

Sorption of SO_2 by activated carbon can be both chemical and physical, and both occur over a relatively wide temperature range, 25-200°C. The degree of each is affected by the presence of oxygen in the flue gas. Various studies have shown that an oxygen-free carbon surface has limited SO_2 adsorption capacity. The presence of water vapor is also important because it reacts with the SO_3 formed by reaction of SO_2 with O_2 to form H_2SO_4 . Physisorption of SO_2 on activated carbon decreases with increasing temperature, e.g., from 8% at 60°C to 0 wt% SO_2 at 250°C (Slack, 1971). Typical SO_2 capacities for activated carbon range from 2 to 7 wt%.

Activated carbon can remove nitrogen oxides as well as gaseous chlorides from combustion flue gas. When ammonia is added to the flue gas in the presence of carbon, the NO is reduced to nitrogen and steam (selective catalytic reduction). The selective catalytic reduction (SCR) of NO with NH_3 is an example of a reaction which can be catalyzed by both carbon supported catalysts and carbon itself. The various factors affecting this catalytic activity of carbon include: the carbon precursor, pyrolysis temperature, degree of activation (burnoff), heteroatoms in the carbon structure and functional surface groups present (Boehm et al., 1984; Ahmed et al., 1992; Singoredjo et al., 1993). Most recently, Singoredjo et al. (1993) concluded that overall SCR activity is the result of a combination of factors; namely, the interaction of oxygen with carbon, the presence of stable carbon-oxygen groups on the surface, nitrogen content and accessibility of the pores.

An activated carbon FGD process could be used alone to remove SO_2/NO_x from the flue gas of coal firing utilities, or in conjunction with other methods of FGD. An activated carbon FGD process is typically placed after the precipitator and just before the stack. This technology has been used to a limited extent in Europe and Japan for removal of SO_2 and NO_x from combustion flue gas. Activated carbon based FGD processes can be integrated into both new and existing power plants. Retrofitting an existing utility boiler with such a FGD process should, in addition to improving SO_2/NO_x emissions, lower overall operating costs. Richter et al. (1985) contend that it is easier to integrate a carbon-based NO_x reduction process into a power plant FGD scheme than to use a catalyst-based NO_x reduction unit, which needs to be operated at relatively high temperatures (> 250°C).

A Japanese company (Mitsui Mining Company, Limited) have taken the Bergbau Forschung (BF) process and modified it to meet their SO_2/NO_x removal requirements (Tsuji and Shiraishi, 1991). Their Mitsui-BF dry $\text{DeSO}_x/\text{DeNO}_x$ process achieves 100% removal

of SO_2 and over 80% removal of NO_x by contacting the flue gas with activated coke and injecting ammonia for nitric oxides reduction over a temperature range of 100-200°C. Halogen compounds and trace elements such as mercury vapor and dioxins contained in the flue gas are also removed by chemical or physical adsorption onto the carbon.

Mitsui has developed technology to produce the activated coke used in their dry $\text{DeSO}_x/\text{DeNO}_x$ process. A comparison of the physical properties and operating performance of their coke and a standard commercial activated carbon revealed that the surface area and SO_2 capacity of their coke was about a factor of three lower than that of the commercial carbon. However, after regeneration a significant decrease in the SO_2 capacity of the commercial activated carbon was observed, whereas the SO_2 capacity of the Mitsui-BF coke was maintained.

The latest process for cleaning sulfur oxides and nitrogen oxides from combustion flue gas, still only in the development stage, involves the use of activated char in conjunction with high frequency electromagnetic radiation (microwaves) (Cha et al., 1992). Sulfur dioxide is adsorbed on activated char and decomposed under microwave energy to sulfur; the nitrogen oxides are decomposed directly under the microwaves to nitrogen. Laboratory tests indicate that up to 98% of the SO_2/NO_x is decomposed to S and N_2 .

Due to recent legislation in European communities, the use of activated carbon for cleaning flue gases from waste incinerators has seen increased interest. A German company (STEAG Aktiengesellschaft) has licensed technology for carbon based systems which have been installed on commercial medical, hazardous and municipal waste incinerators (Brueggendick and Pohl, 1993). In each case the activated carbon technology was given preference over other alternatives because of its removal efficiency for particulates, heavy metals, organic compounds (e.g., dioxins, furans) halogenated hydrogens and SO_2/NO_x . The carbon used is a lignite activated coke with pore surface area of about 300 m^2/g (Thielen and Seipenbusch, 1992). Operating results show that current European emission requirements were met with the activated carbon systems.

EXPERIMENTAL

Char Preparation

The chars used in this work were prepared from an Illinois No. 2, hvC bituminous coal, sample IBC-102 of the Illinois Basin Coal Sample Program (Harvey and Kruse, 1988). This coal was obtained from a western Illinois preparation plant and is relatively low in organic and high in pyritic sulfur. A 48x100 mesh sample was prepared from the parent coal. The IBC-102 coal (-1/8") was sieved prior to grinding to remove

any material smaller in diameter than the desired size fraction. The oversized sample was subjected to a step-wise grinding and sieving size reduction technique which involved grinding the sample in a rod mill for 15-120 s intervals, separating the oversized and undersized material from the desired size fraction by sieving on a Ro-Tap sieve shaker, and grinding the oversized material. The cycle was repeated until there was less than 5% of oversized material remaining.

Prior to char preparation, the coal was physically cleaned to remove mineral matter. In a typical run, 400 g 48x100 mesh IBC-102 coal was combined with 4 L H₂O in a Denver model D-2 batch flotation system. A flotation agent (MIBC) was added at an equivalence of 5 lbs/ton. The mixture was stirred by an impeller at a rate of 1400 rpm. After sufficient mixing, air was introduced into the cell and the clean coal particles were collected from the overflow. Additional mineral matter was removed by repeating the procedure using the clean coal as starting material. The clean coal was vacuum filtered and dried in a convection oven at 105°C. The proximate and ultimate analyses (moisture-free basis) of the coal and clean coal are given in Table 1.

Table 1. Analyses of Coal and Clean Coal Samples.

	IBC-102	Clean IBC-102
Moisture	12.51	2.31
Volatile Matter	39.02	41.26
Fixed Carbon	55.51	55.15
H-T Ash	5.47	3.59
Carbon	73.50	77.35
Hydrogen	5.09	5.43
Nitrogen	1.42	1.49
Oxygen	11.49	9.96
Sulfatic Sulfur	1.11	0.35
Pyritic Sulfur	0.63	0.50
Organic Sulfur	1.28	1.32
Total Sulfur	3.02	2.18
BTU/lb	13146	13876

Chars were prepared at 500, 700 and 900°C, 0.5 h in a 2-in. ID batch fluidized-bed reactor (FBR). In each run, 200 g IBC-102 coal was fluidized in flowing N₂ (6 L/min) and heated to the

desired pyrolysis temperature. A multi-step heating procedure was used to minimize agglomeration of coal particles in the FBR (DeBarr et al., 1991). The physical and chemical properties of the chars were further modified to determine the effect of surface area, oxygen content and type of oxygen on the resulting SO_2/NO_x adsorption capacity of the char. Selected samples were subjected to oxidation in 10% O_2 to increase both surface area and oxygen content. The chars prepared at different heat treatment temperatures exhibited different reactivities. Preliminary TGA studies were performed to obtain oxidation temperatures which would maintain a relatively constant rate of reaction for each of the samples. In a typical run, 50 g char was placed in the 1 in. ID FBR and heated to 390-500°C under flowing N_2 . The sample was oxidized in 10% $\text{O}_2/90\%$ N_2 for 0.5-0.75 h to obtain a 30% weight loss (conversion), then cooled to room temperature in N_2 .

Selected chars were subjected to a nitric acid oxidation treatment. Typically, 10g char was added to 0.2 L 45% HNO_3 solution, heated to 80°C and stirred for 2.5 h. The HNO_3 treated char was washed repeatedly with distilled water to remove excess acid and air dried overnight at 105°C.

Steam activation of selected chars was performed to further develop microporosity and surface area while minimizing oxygen added to the char. Typically, 50 g char was placed in the 1 in. ID FBR and heated to 860°C in flowing N_2 . The N_2 flow was replaced by 50% $\text{H}_2\text{O}/50\%$ N_2 for 0.75 h to achieve 30% carbon conversion. The activated char was cooled to room temperature in N_2 .

A chemical activation method was employed to enhance surface area development and increase the adsorption capacity of the char. The method involved addition of an alkali salt to the raw coal and subsequent heat treatment in inert gas. Potassium hydroxide (KOH) was loaded onto the coal by impregnation to incipient wetness. Typically, 200 g KOH was dissolved in 0.2 L distilled water and mixed thoroughly with the raw coal. 200 g coal/KOH mixture was added to the 2 in. FBR and pyrolyzed at 600 and 800°C, 0.5 h. The sample was cooled in N_2 and washed repeatedly with distilled water to remove excess potassium and air dried overnight at 105°C.

Char Characterization

Single-point BET surface areas of the chars were determined from N_2 (77 K) adsorption data obtained with a Monosorb flow apparatus (Quantachrome Corp.).

RESULTS AND DISCUSSION

A series of chars was prepared to determine the effects of surface area, oxygen content and type of oxygen on the SO_2/NO_x capacity of the char. The surface areas of prepared chars are shown in Table 2 (oxygen contents have yet to be determined). For the three heat treatment temperatures studied, the maximum surface area ($10 \text{ m}^2/\text{g}$) is achieved at 700°C . These results are in agreement with those found previously for chars prepared from bituminous coal (Kruse and Shimp, 1981). At 500°C , a considerable amount of volatile matter remains in the sample, plugging the pores accessible to N_2 , and thereby decreasing accessible surface area. At 900°C , the char begins to become more graphitic in nature, also reducing the accessible surface area. Oxidation in 10% O_2 significantly increases the surface area of the three chars (e.g., from 10 to $315 \text{ m}^2/\text{g}$). The 700°C char exhibits slightly higher surface area after oxidation than the other two chars. It is interesting to note that steam activation (860°C) and oxidation (500°C) of the 900°C char results in a similar increase in surface area and that the nitric acid treatment decreases the surface area of the steam activated char.

Table 2. Nitrogen BET Surface Areas of Selected Chars.

Sample	Surface Area (m^2/g)
IBC-102, 500°C , 0.5 h	1.2
IBC-102, 700°C , 0.5 h	10.0
IBC-102, 900°C , 0.5 h	1.2
IBC-102 + KOH, 800°C , 0.5 h	800
IBC-102, 500°C , 0.5 h; 10% O_2 , 390°C	215
IBC-102, 700°C ; 10% O_2 , 440°C	315
IBC-102, 900°C ; 10% O_2 , 500°C	231
IBC-102, 900°C ; H_2O , 860°C	222
IBC-102, 900°C ; H_2O , 860°C ; 45% HNO_3 , 2.5 h	182

Maximum char surface area ($800 \text{ m}^2/\text{g}$) was achieved by heat treatment of the coal/KOH mixture. Previous studies have shown that surface areas approaching $1500 \text{ m}^2/\text{g}$ can be obtained by pyrolyzing physical mixtures of IBC-102 coal and KOH in a fixed-bed reactor (Lizzio and Rostam-Abadi, 1992). It is believed that physical contact of the coal and KOH is impor-

tant to develop maximum surface area. The use of a fluidized-bed reactor in the present study may have caused separation of the coal and KOH by a thin film of gas, resulting in a char with a lower than expected surface area.

It remains to be determined how surface area and oxygen content affects the SO_2/NO_x adsorption capacity of IBC-102 char. During the next reporting period, the prepared chars will be tested for their ability to remove SO_2 and NO_x from a simulated flue gas mixture. Carbon type, flow rate and adsorption temperature are the principal process variables to be studied. The adsorption capacity and kinetics of SO_2/NO_x (SO_2 , NO , or NO_2 in helium) adsorption on selected chars at various temperatures (25-200°C) and pressures (200-800 torr) will be determined using either a volumetric adsorption apparatus or a thermogravimetric analyzer (TGA). A laboratory scale adsorption column/mass spectrometry (AC/MS) system will be used to evaluate multi-component gas adsorption. A quadrupole mass spectrometer was ordered and will be used to assist in evolved gas analysis during the SO_2/NO_x adsorption/desorption studies. Typically, a mixture of SO_2 (2500 ppm) and NO_x (500 ppm) in a simulated flue gas mixture (2% H_2O , 5% O_2 , 15% CO_2 , 78% N_2) will be passed through the AC at a specified and controlled flow rate (20 cm^3/min). Ammonia will be introduced into the feed gas in some runs to observe the effects of selective catalytic reduction. Breakthrough curves for individual gases will be determined. When the carbon bed becomes saturated, e.g., inlet $[\text{SO}_2] = \text{outlet } [\text{SO}_2]$, the sorbent is regenerated with heat (200-400°C) and/or vacuum (1×10^{-5} torr). It will be of interest to examine the temperature programmed desorption (5°C/min in helium) of SO_2 and NO_x from the spent char to gain further insight into the kinetics and mechanism of combined SO_2/NO_x removal.

CONCLUSIONS AND RECOMMENDATIONS

During this reporting period, ten chars were prepared in order to study the effect of surface area, oxygen content and type of oxygen on the SO_2/NO_x adsorption properties of the chars. A 48x100 mesh size fraction of Illinois Basin Coal No. 2 (IBC-102) was prepared using a staged grinding and sieving technique. The 48x100 mesh fraction was physically cleaned by froth flotation to remove mineral matter prior to char preparation. The mineral matter content of the parent coal was reduced from 5.5 to 3.6% by physical cleaning.

Chars were prepared in nitrogen in a 2-in. ID fluidized-bed reactor (FBR) at 500, 700 and 900°C. These chars were oxidized in 10% $\text{O}_2/90\%$ N_2 at 390-500°C to increase both surface area and oxygen content. In addition, selected samples were subjected to a nitric acid oxidation treatment (80°C) to increase oxygen content. Steam activation at 860°C was

performed to increase surface area of char samples while minimizing further addition of oxygen. Nitrogen surface areas of the prepared chars ranged from < 5 to $315 \text{ m}^2/\text{g}$. A chemical activation method was employed to enhance surface area development of the chars. Potassium hydroxide (KOH) was loaded onto the coal by impregnation to incipient wetness. The coal/KOH (1:1 by weight) sample, pyrolyzed at 800°C in the FBR, achieved the highest surface area ($800 \text{ m}^2/\text{g}$).

During the next reporting period, the surface properties of the prepared chars will be further characterized. An estimate of the micropore size distribution of selected chars will be obtained by analyses of adsorption/desorption isotherms of different sized molecules. Experimental methods are currently being developed to determine by temperature programmed desorption (TPD) the type and amount of oxygen on the surface of the char. The gases evolved during TPD are monitored by nondispersive CO/CO_2 analyzers. The prepared chars will also be tested for their ability to remove SO_2 and NO_x from a simulated flue gas mixture. The type of char, flow rate and adsorption temperature will be the principal process variables studied. A quadrupole mass spectrometer has been ordered and will be used to allow detection of SO_2/NO_x species during multi-component adsorption studies. The overall performance of the prepared chars in removing SO_2/NO_x from combustion flue gas will be assessed and compared to that of a commercial activated carbon.

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PROJECT MANAGEMENT REPORT
September 1 through November 30, 1993

Project Title: **PRODUCTION AND USE OF ACTIVATED CHAR FOR
COMBINED SO₂/NO_x REMOVAL**

DOE Grant Number:	DE-FC22-92PC92521 (Year 2)
ICCI Project Number:	93-1/3.1A-5P
Principal Investigator:	Anthony A. Lizzio, ISGS
Other Investigators:	Joseph A. DeBarr, ISGS Massoud Rostam-Abadi, ISGS
Project Manager:	Frank I. Honea, ICCI

COMMENTS

EXPENDITURES - EXHIBIT B

Cumulative Projected and Estimated Expenditures by Quarter

Quarter*	Types of Cost	Direct Labor	Fringe Benefits	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sep. 1, 1993 to Nov. 30, 1993	Projected	10,780	2,415	1,500	0	0	3,720	1,816	20,231
	Estimated	7,150	1,600	710	0	0	1,975	1,144	12,579
Sep. 1, 1993 to Feb. 28, 1994	Projected	21,560	4,830	3,000	0	0	7,450	3,633	40,473
	Estimated								
Sep. 1, 1993 to May 31, 1994	Projected	32,340	7,245	4,000	0	0	11,160	5,448	60,193
	Estimated								
Sep. 1, 1993 to Aug. 31, 1994	Projected	43,120	9,660	5,000	0	0	14,885	7,266	79,931
	Estimated								

*Cumulative by Quarter

COSTS BY QUARTER - EXHIBIT C

**PRODUCTION AND USE OF ACTIVATED CHAR
FOR COMBINED SO₂/NO_x REMOVAL**

Total CRSC Award \$79,931

SCHEDULE OF PROJECT MILESTONES

Milestones:

- A. Literature Review
- B. Preparation of Activated Char
- C. SO₂/NO_x Adsorption/Desorption Tests
- D. Physical/Chemical Characterization
- E. Process Flowsheet/Market Analysis
- F. Technical/Project Management Reports Prepared/Submitted

DATE

FILMED

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